Physical-mechanical characterization of direct restorative dental materials
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To Matilde and Gonçalo,
who always stood by me and dealt with all my absences with a smile.

“By failing to prepare, you are preparing to fail.”
Benjamin Franklin

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Keywords

Dental composites, filler effect, pH and aging effect, mechanical properties, tribological characterization.

Abstract

Direct restorative dental materials possess very special characteristics. These materials operate in a singular environment that is the mouth. The factors at play are numerous and their variation range is important. Humidity, load cycles, pH, temperature, bacteria, external agents, environment, material properties and contact geometry, etc., are some examples. Teeth and restorative materials are, therefore subjected to complex and numerous factors.

During the past decade clinicians and patients have developed an interest in to posterior composite resins. The demand for restorations with a natural appearance in the posterior region and the controversy as to the mercury action of amalgam, although it's excellent mechanical properties, has attracted researchers to focus on the improvement of the resin composites to be applied in posterior teeth.

Resin composites have been by far the most successful in dental applications by meeting several stringent design requirements difficult to achieve with homogeneous materials such as ceramics and metal alloys. When the intention is to repair cavities, the product needs to be aesthetically matched in color and translucence with other teeth and retain its gloss. It must match the hardness of the opposing tooth and be resistant to wear or fatigue fracture. It must be dimensionally stable and withstand the largely varying thermal stresses in the mouth. "Packable" composites have been termed as alternative to amalgam, for usage in posterior restoration.

Criteria to select a composite in detriment of another are very complex and the few existent standards do not allow for establishing a consensus as to which tests must be used to determine and compare composites properties.

Mechanical and tribological properties of direct restorative filling materials are crucial not only to serve and allow similarity with human enamel and dentine but also to compare composites between them and determine objective criteria for their selection.

This work is focused on the mechanical and tribological characterization of posterior direct commercial restorative materials. Due to their characteristics, commercial composites are materials which can not be altered (filler volume fraction, average particle dimension and matrix composition are pre-fixed parameters), thus limiting the objectives of the initial study. With

the introduction of the production of a composite material which allowed variation of its constituents, the initial work was complemented.

The mechanical properties assessment was done with the following tests: Vickers hardness, Impulse excitation of vibration and four point bending tests. The mechanical properties assessed were: hardness, elastic modulus (static and dynamic), flexural resistance and work-of-fracture.

To determine the tribological behavior of composites reciprocating sliding tests was used. Wear and the mechanisms involved were evaluated on the composites as well as on the antagonist (human teeth and glass spheres). A classical and an energetic approach were used to understand the behavior of the composites and their antagonists. The use of glass sphere as antagonist material was subjected to validation, by comparison to the material pair composite natural tooth. Although difference in wear volumes of the distinct pairs does exist, extrapolation of results is possible with similar and acceptable results.

Eight direct restorative commercial composites were tested against glass spheres, to determine wear resistance under different wear mechanisms: abrasion and attrition. The evaluation of environment influence in these tests allows us to understand composites behavior under reciprocating contact through the measuring of wear volumes and coefficients of friction of the contact pair and analyzing the removal mechanisms involved in the wear process. In this analysis, some composite-glass pair some materials showed some discrepancy regarding wear and the coefficient of friction, thus a complementary study involving, only, three commercial composite was done. A load-scanning test was used to understand and explain the wear regime transition of these. This test permitted the perception of the wear/fracture mechanisms induced by the different values of coefficient of friction.

The influence of external factors on the mechanical behavior of composites was also evaluated. Two types of environment in the reciprocating wear tests were introduced: artificial saliva/distillate water and abrasive slurry. The other external parameters introduced in the study were aging time and pH. Two batches of seven commercial composites were aged in 3, 7 and 9 pH buffer solutions during three periods 3, 6 and 22 months. The tribological and mechanical evaluation of these composites was done after each aging period. Generally and from the point of view of application, it was possible to draw conclusions relatively to commercial composite mechanical and tribological behavior. The effect of external factors on the behavior of these commercial materials was also evaluated and the properties variation quantified.

Due to the nature of the study, parameterized evaluation, of produced composites brought further progress, with clear conclusions as to volume content, filler dimension, matrix on the mechanical and tribological properties studied.

The tribological behavior was evaluated and removal mechanisms enclosed in the wear process are discussed, taking into account the systematic SEM observations to evaluate the failure modes.

Palavras-chave

Compósitos dentários, efeito do reforço, efeitos de pH e envelhecimento, propriedades mecânicas, caracterização tribológica.

Resumo

Materials dentários de restauro directo possuem características muito especiais. Estes materiais operam num ambiente singular que é a boca. Os factores em jogo são diversos e a sua gama de variação elevada, destes destacam-se; humidade, ciclos de carga, temperatura, bactérias, agentes externos, meio ambiente, propriedades dos materiais, geometria de contacto, etc., são alguns exemplos. Os dentes e os materiais de restauro estão, portanto, sujeitos a vários e numerosos factores.

Durante as últimas décadas clínicos e pacientes têm desenvolvido grande interesse pelas resinas para restauro de dentes posteriores. As exigências por restauros com uma aparência natural na região posterior da boca além das controvérsias relativamente à amalgama e à acção do mercúrio, apesar das suas excelentes propriedades mecânicas, tem atraído a atenção dos investigadores na melhoria destes compósitos para a aplicação em dentes posteriores.

Estas resinas compósitas têm sido certamente dos mais bem sucedidos materiais em aplicações dentárias cumprindo requisitos rigorosos e difíceis de alcançar com materiais homogéneos tais como materiais cerâmicos e ligas metálicas. Quando a intenção é a reparação de cavidades torna-se necessário combinar esteticamente a cor com a translucidez dos outros dentes e ao mesmo tempo mater o brilho. O material de restauro deve possuir a dureza do dente oposto e ser resistente ao desgaste ou à fractura por fadiga. Deve, também,ser dimensionalmente estável e resistir às tensões, em grande parte devido às variações térmicas existentes na boca. As resinas “compactáveis” foram denominadas por alternativas à amalgama para o restauro de posteriores.

Os critérios de selecção de compósitos bem como as poucas normas existentes não permitem estabelecer consenso relativamente a quais os testes a usar para determinação das propriedades ou para comparação de desepenho dos compósitos. A determinação das propriedades mecânicas e tribológicas de materiais de restauro directo são cruciais verificar a semelhança destes materiais com o esmalte e a dentina, mas também para comparar compósitos entre si e determinar critérios objectivos para a sua correcta selecção.

Este trabalhado é centrado na caracterização mecânica e tribológica de materiais comerciais para restauro posterior. Devido às características, estes materiais não podem ser alterados (fracção em volume das partículas, dimensão da partículas e composição da matriz são

parâmetros fixos) o que limitou os objectivos iniciais do estudo. Através da introdução de um material compósitos produzido em laboratóio este permitiu a variação dos seus constituintes, sendo o trabalho complementado.

A avaliação das propriedades mecânicas foi efectuada com a ajuda dos seguintes testes: dureza Vickers, teste dinâmico do módulo de elasticidade e flexão em quatro pontos. As propriedades mecânicas avaliadas foram: dureza, módulo de elasticidade (dinâmico e estático), resistência à flexão e trabalho de fractura.

Para a determinar o comportamento tribológico dos compósitos foi usado um teste de desgaste alternativo. O volume de desgaste do compósito e do antagonista (dente humano ou esfera de vidro) e os mecanismos envolvidos foram avaliados. Foram usadas abordagens; clássica e energética para perceber o comportamento dos compósitos e seus antagonistas. O uso da esfera de vidro como material antagonista foi submetido a validação, sendo comparado com o desempenho do dente humano.

Embora os volumes de desgaste sejam diferentes é possível extrapolar os resultados dando aproximações similares e aceitáveis.

Oito materiais comerciais de restauro directo foram ensaiados contra esferas de vidro por forma a determinar a sua resistência ao desgaste e os diversos mecanismos envolvidos: abrasão e desgaste. A avaliação da influência do meio ambiente nestes testes permitiu entender o comportamento dos compósitos em contacto de deslizamento alternativos através da medição dos volumes de desgaste e coeficientes de atrito dos pares de materiais em contacto e analisar os mecanismos de desgaste envolvidos no processo. Nesta análise alguns pares de materiais mostraram alguma discrepância em relação ao desgaste e ao coeficiente de atrito, um estudo complementar foi efectuado para três desses compósitos. Testes de “load-scanning” foram usados para perceber e explicar o regime de transição destes materiais. Este teste permitiu perceber os mecanismos de desgaste/fractura provocados por diferentes valores de coeficiente de atrito.

A influência de factores externos no comportamento mecânico dos materiais compósitos também foi avaliada. Dois tipos de ambiente, nos testes de deslizamento alternativo foram introduzidos; saliva artificial/água destilada e solução abrasiva. Os outros parâmetros externos introduzidos no estudo forma o efeito do; envelhecimento e pH. Dois lotes destes sete materiais compósitos foram envelhecidos em soluções de pH 3, 7 e 9, durante: 3, 6 e 22 meses. A avaliação tribológica e mecânica destes compósitos foi realizada após cada período de envelhecimento. Do ponto de vista de aplicação foi possível tirar conclusões relativamente ao comportamento dos compósitos comerciais no que diz respeito ao desempenho mecânico e tribológico. O efeito dos factores externos sobre o comportamento deste materiais comerciais foi avaliada sendo quantificada a variação nas propriedades.

Devido à natureza da avaliação parameterizada dos compósitos produzidos o estudo trouxe progressos com conclusões claras relativamente à influência da: fracção em volume de partículas, dimensão das partículas de enchimento e matriz nas propriedades mecânicas e tribológicas dos compósitos com material de enchimento.

O comportamento tribológico foi avaliado e os mecanismos de remoção envolvidos no processo de desgaste discutidos tendo em conta as observações sistmáticas dos modos de falha.

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- Ramalho A., Antunes P.V., Reciprocating wear test of dental composites: effect on the antagonist, Wear, 259(7-12), (2005): 1005-1011.
- Ramalho A., Antunes P.V., Carvalho M.D.B., Gil H., Rocha J., Mechanical Properties of Particle Reinforced Resin Composites, Materials Science Forum, Vol. 514-516, (2006): 619-623.
- Ramalho A. and Antunes P.V., Reciprocating wear test of dental composites against human teeth and glass, Wear, 263, (7-12), (2007): 1095-1104.
- Antunes P.V. and Ramalho A, Influence of pH values and aging time on the tribological behaviour of posterior restorative materials, Wear, 267 (2009): 718-725

Abbreviations

ϕ	Average particle dimension [mm]
δ	Deflection at break load P [m]
σ_1	Maximum normal stress [GPa]
μm	Micrometer
σ_{m}	Maximum tensile strength [MPa]
σ_{Tresca}	Tresca stress [GPa]
σ_x	Normal stress in OX axis [GPa]
Ag	Silver
a_0	Flaw size [mm]
AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
Bis-EMA	Ethoxylated Bisphenol A Glycol Dimethacrylate
Bis-GMA	2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propane
BSE	Back-scattered electrons
cA	Polyester resin matrix A with 30 Wt %, silica filler with average particle dimension of 6 μm
cB	Polyester resin matrix B with 30 Wt %, silica filler with average particle dimension of 6 μm
cC	Polyester resin matrix C with 30 Wt %, silica filler with average particle dimension of 6 μm
CI	Confidence Interval
Cl	Chlorine
CNC	Computed numerically controlled
COF (μ)	Coefficient of friction
CQ	Camphorquinone
Cu	Copper
d	Specimen width [mm]
DBTDL	Dibutyltin dilaurate

DIN	Deutsches Institut fr Normung
E	Elastic Modulus, or, Young Modulus
E_{C}	Composite Elastic Modulus
EDMA	Ethylene Glycol Dimethacrylate
E_{m}	Matrix Elastic Modulus
FDA	Food and Drug Administration
F_{FORCE}	Friction force [N]
ft	Fundamental frequency [Hz]
h	Height of sphere removed material antagonist [mm]
HEMA	2-Hydroxyethyl Methacrylate
Hg	Mercury
$\mathrm{HV}_{0.2}$	Vickers hardness numbers with 0.2 kg load used in the test
I	moment of inertia of the cross section [kgm^2]
IEV	Impulse Excitation of Vibration
ISO	International Organization for Standardization
k	Wear coefficient
$K_{1\mathrm{C}}$	Fracture toughness factor
KCl	Potassium chloride
K_E	Einstein coefficient
kg	kilogram
L	Four point bending test outer span [mm]
MEKPO	Methyl ethyl ketone peroxide
MMA	Methyl Methacrylate
n	Number of cycles in reciprocating sliding test
NaCl	Sodium chloride (salt)
nm	Nanometer
°C	Celsius degrees
OHSU	Oregon Health Sciences University
P	Break load, maximum load ate the point of fracture [N]
P	Four point bending tests break load [N]
pH	Measure of the acidity or basicity of an aqueous solution
PMMA	Poly(methyl methacrylate) - Poly(methyl 2-methylpropenoate)
PR	Polyester resin without reinforcement particles
PR A/B	Polyester resin matrix with A Wt %, silica filler with average particle dimension of B μm
PR C	Polyester resin matrix with C Wt %, silica filler with average particle dimension of 6 μm
r	Average radius values of scar crater's [mm]
R	Antagonist sphere radius [mm]
R^2 (r^2)	Coefficient of determination

rA	Resin type A - Composition (mol %): 63% mol Bis-GMA; 26% mol TEGDMA; 11% mol MMA and 0% mol UDMA: no filler.
Ra	Arithmetical mean roughness of a surface
rB	Resin type B - Composition (mol %): 5/7% mol Bis-GMA; 23% mol TEGDMA; 10% mol MMA and 10% mol UDMA: no filler.
rC	Resin type C - Composition (mol %): 50% mol Bis-GMA; 21% mol TEGDMA; 9% mol MMA and 20% mol UDMA: no filler.
S	Flexural Strength [GPa]
s	Sliding distance [mm]
SEM	Scanning Electron Microscope
SEN	Single edge notch
SiC	Silicon Carbide paper
Sn	Tin
STD	Standard deviation
t	thickness or height of specimen [m]
T_1	Constant Poisson ratio
TEGDMA	Triethylene Glycol Dimethacrylate
TMPTMA	Trimethylol propane trimethacrylate
UDMA	Urethane dimethacrylate-1.6-bis(methacryloxy-2-ethoxycarbonylamino)-2.4.4-trimethylhexane
USA	United States of America
V	Volume of removed material [mm3]
Vol.%	Volume percentage
VP	Inorganic filler volume percentage
VRE	Volume ratio/energy
WOF	Work-Of-Fracture
Wt %	Weight percentage
Zn	Zinc

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Chapter 1

General introduction and motivation

1.1 Introduction

Human teeth are the hard, resistant structures occurring on the jaws and in or around the mouth area of vertebrates. Teeth are used for masticating food, and for other specialized purposes. A tooth consists of a crown and one or more roots. The crown is the functional part that is visible above the gum. The root is the unseen portion that supports and fastens the tooth in the jawbone. The root is attached to the tooth-bearing bone — the alveolar processes — of the jaws by a fibrous ligament called the periodontal ligament or membrane. The shape of the crown and root vary among different teeth in the human mouth.

All teeth have the same general structure and consist of three layers. An outer layer of enamel, which is wholly inorganic, is the hardest tissue in the body, and covers part or the entire crown of the tooth. Typical values for enamel hardness range from 3.1 GPa to 8 GPa. Regarding enamel elastic modulus, values range from 19.9 GPa to 91 GPa when measured perpendicular to crystal orientation, and from 93 GPa to 113 GPa parallel to crystal orientation (Srivicharnkul *et al.*, 2005). The middle layer of the tooth is composed of dentine, which is less hard than enamel and similar in composition to bone. The dentine forms the main bulk, or core, of each tooth and extends almost the entire length of the tooth, being covered by enamel on the crown portion and by cementum on the roots. Dentine consists of a number of micro-fibers imbedded in a dense homogeneous matrix of collagenous proteins.

In terms of mechanical properties; hardness of fully hydrated peritubular dentine ranges from 2.23 GPa to 2.54 GPa, while the elastic modulus ranges from 17.7 GPa to 21.1 GPa for the intertubular dentine, with the lower values for dentine near the pulp (Kinney *et al.*, 1996).

Dentine is nourished by the pulp, which is the innermost portion of the tooth. The pulp consists of cells, tiny blood vessels, and a nerve that occupies a cavity located in the centre of the tooth. The pulp canal is long and narrow with an enlargement, called the pulp chamber, located coronally. The pulp canal extends almost the whole length of the tooth and communicates with the body's general nutritional and nervous systems through the apical foramina at the tip of the roots (fig. 1.1).

To reduce wear during masticatory function, all teeth include highly mineralized tissues that present physical properties based on their composition and micro morphology (Gwinnett, 1992). The anatomical crowns of teeth are covered by dental enamel, which consists of 92% – 96% inorganic matter, 1% – 2% organic material and 3% – 4% water by weight (Gwinnett, 1992). Hydroxyapatite is the inorganic matter which is contained in the basic structural unit of enamel,

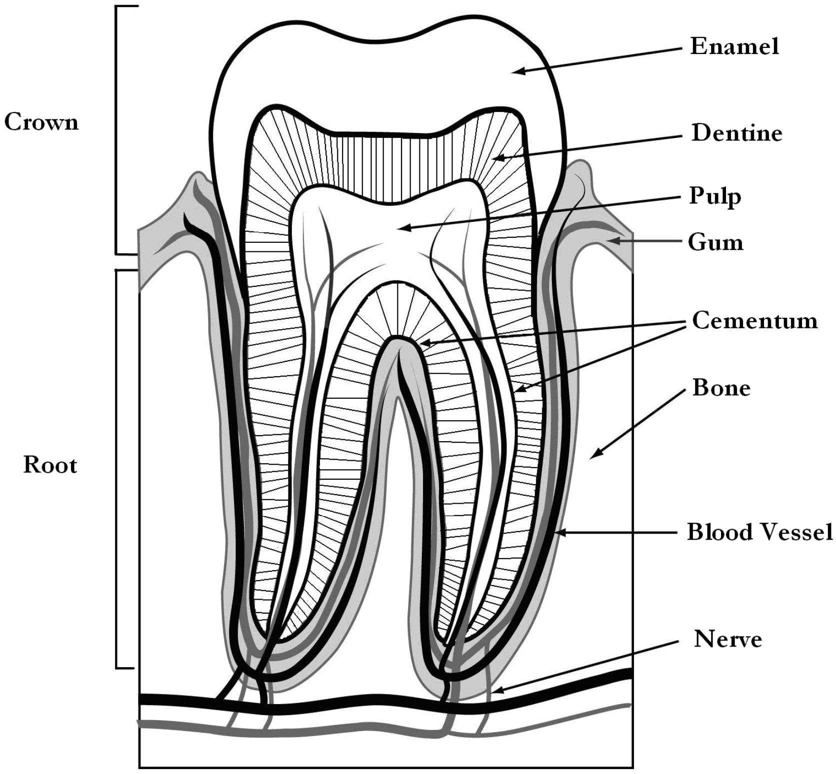


Fig. 1.1: Human tooth.

the rod or prism (Tyldesley, 1950). Enamel hardness is attributed to its high mineral content (Caldwell *et al.*, 1957) and the brittle property is due to its high elastic modulus and low tensile strength (Meckel *et al.*, 1965). Clinically, enamel cracks and fractures can occur despite enamel being a very strong substrate. Studies have shown that enamel is anisotropic and its mechanical properties may be dependent on the type and direction of the stress applied, as well as the prismatic orientation (Urabe *et al.*, 2000; Rasmussen *et al.*, 1976; Hassan *et al.*, 1981; Xu *et al.*, 1998).

The middle layer, dentin, is a hydrated biological composite composed of 70% inorganic material, 18% organic matrix and 12% water (weight percentage), with properties and structural components that vary with location (Mjör, 1972). The collagen phase of intertubular dentin contributes to a lower modulus of elasticity than that of enamel, while the lower mineral content is associated with a decrease in dentin microhardness as compared with enamel (O'Brien, 1997).

The structural composition of dentin includes oriented tubules surrounded by a highly mineralized cuff of peritubular dentin and an intertubular matrix consisting of type I collagen fibrils reinforced with apatite (Mjör, 1966; Tronstad, 1973). The relative contribution of tubules, peritubular and intertubular dentin varies significantly in composition with location (Marshall Jr. *et al.*, 1997).

The thermo-physical properties of a tooth vary from one layer to another, and are anisotropic and inhomogeneous even in the individual layer (Kishen *et al.*, 2000; Kishen and Asundi, 2001). Due to intrinsic mechanical properties, fundamentally elastic moduli, of these two layers, differences in thermal expansion coefficient and deformation between the enamel and dentine layers may induce thermal stresses and subsequent crack initiation and propagation through the enamel-dentine junction (Brown *et al.*, 1972, Jacobs *et al.*, 1973).

The main reasons for placing a dental restoration are; primary caries or noncarious defect such as abrasion/erosion, traumatic tooth fracture, developmental defect, cosmetic reasons, and restoration of an endodontically treated tooth or other unspecified defects or reasons (Giannini *et al.*, 2004). The hierarchical structure of the hard tissues of human teeth guarantees function for decades. Caries, the most frequent disease, is known to damage the enamel, the dentin and the cementum through the production of acidic species that dissolve the ceramic tooth structure. This fenomena is also observed in dental erosion which habitually accompanies excessive citrus fruit consumption (Ganss *et al.*, 1999). Unfortunately, the destroyed tooth structures do not fully regenerate, although re-mineralization of small carious lesions occurs under optimized dental hygiene (Mäkinen, 2010).

The treatment of carious lesions is accomplished via removal of affected hard tissues. The progression of caries is enhanced within the dentin compared to the enamel. The faster spread through the dentin is generally visible in sections or projections as triangles with their basis along the enamel-dentin junction (Ekstrand *et al.*, 1998). Therefore, dentists are regularly forced to amputate not only the massively damaged enamel but also a significant amount of healthy enamel to guarantee the complete substitution of carious dentin by the restorative material (Deyhle *et al.*, 2011; Braga *et al.*, 2007; Traebert *et al.*, 2005; Tyas *et al.*, 2000).

Between enamel and dentin, a biological interface may dissipate stresses inhibiting further crack propagation (Dennison and Hamilton, 2005; Strassler *et al.*, 2005). The dentin-enamel junction has high fracture toughness and, along with the more resilient underlying dentin, supports the integrity of enamel by preventing its fracture during function (Beauchamp *et al.*, 2008).

Such operative procedures may have a significant effect on the removal of patients' dental tissue and the longevity of their tooth structure (Tyas, 2005). Restorative dentistry has progressed to a minimal-intervention approach that encourages preservation of tooth structure (Tyas, 2005; Wolff *et al.*, 2007). Of particular importance is the clinician's decision regarding primary placement of the first restoration on a previously unrestored tooth's surface.

As the current restorative materials do not fully fit the performance of the natural healthy hard tissues, the resulting limited lifespan renders further interventions (Sunnegardh-Gröberg *et al.*, 2009; Van Nieuwenhuysen *et al.*, 2003; Anusavice, 2005; Brantley *et al.*, 1995). Alternatively, establishing vigorous preventive oral health maintenance plans can extend a tooth's life cycle markedly by delaying or minimizing restorative procedures (Bader and Shugars, 2006; Dennison and Hamilton, 2005; Strassler *et al.*, 2005).

The destruction of healthy tissue has always been a big concern, and caries today, still represent the most widespread human disease (Langeland, 1987). The reasons which lead to the appearance of caries are inumerous, but the process normally initiates with wearing of the thin surface protective layer of enamel and the consequent and more rapid dentine wear. The pulp material is then exposed to bacteria leading to infection and degradation of healthy tooth tissue. Thus, if unnoticed, partial or total removal of the tooth may be necessary.

The Etruscans were one of the earliest to report treatment of dental disease (1000 to 660 B.C.) since then many discoveries in materials and techniques were developed (Van Noort, 1994).

Therefore restorative materials are expected to replace and perform as natural tooth materials. The demand of achievement is so great that most of the times restorative filling materials replace enamel and dentin, which have very different mechanical properties, namely hardness and elastic modulus. Thus, the goal of research when developing these restorative materials is to develop the ideal restorative material which would be identical to natural tooth structure, in strength adherence and appearance. The properties of an ideal filling material can be divided into four categories: physical properties, biocompatibility, aesthetics and application.

Dentistry uses three basic materials; ceramics, metals and polymers. The use of these materials is based upon inherent properties and will influence their selection for use in dentistry. For example, metals are inherently strong, in general, and have high stiffness (modulus of elasticity). These properties would tend to recommend them as restorative materials. On the other hand, metals conduct heat rapidly and are opaque (an aesthetic), limiting their usefulness in restorative dentistry. Ceramics and polymers are thermally insulating and tend to be more translucent. Hence, these materials insulate the pulp from extremes of heat and cold and offer the potential of more lifelike aesthetics. Ceramics tend to have lower toughness than metals and polymers have much lower strength (O'Brien, 2002).

Regarding restorative material application there are two groups: direct and indirect filling materials. Direct filling materials are used of teeth for restoration. They differ from indirect restorations, such as crowns, bridges or inlays, because no laboratory stage is involved in the provision of the restoration.

As for direct filling restorative materials there are many choices available on the market. Amalgam alloy has now been used for over 150 years primarily for premolar and molar restorations (Mandel, 1991). These materials have improved theirs properties and performance to very high standards. Amalgam is a very forgiving material which has broad clinical working conditions, is relatively cheap, and allows for a quick rehabilitation of the masticatory function. Despite these advantages, this metallic material has also some disadvantageous properties: corrosion, ease of fracture, large amount of sound tissue to be removed in order to obtain a retentive cavity, the more recent aesthetic demands and the biocompatibility problems due to the release of metallic ions into the oral environment. The presence of amalgam near precious metal restorations can occasionally induce galvanic currents. Because amalgam does not adhere to tooth structure it does not compensate for the loss of strength of the tooth due to caries and the cavity preparation (Willems, 1992). Allergic reactions and hypersensitivity effects on oral mucosa are also discussed in literature (Bergman, 1990).

The primary alternatives to dental amalgam are: resin composite, glass ionomer, ceramic, and gold restorations.

Composite resin filling materials are the most common alternative to dental amalgam. They are sometimes called "tooth-colored" or "white" fillings because of their color. Composite resin fillings are made of plastic acrylic resin reinforced with powdered glass. The color (shade) of composite resins can be customized to closely match surrounding teeth. Like amalgam, resin composites have advantages and disadvantages. Advantages include minimal removal of healthy tooth structure for placement and capacity to mimic surrounding teeth. Disadvantages include, durability, need for more frequent replacement and higher cost when compared with other dental filling materials.

The science of dental materials involves the study of the composition and properties of materials and the way in which they interact with the environment in which they are placed.

This classification of materials embodies an enormous variation in material properties from hard, rigid materials at one extreme to soft, flexible products at the other. Many dental materials are fixed permanently into the patient's mouth or are removed only intermittently for cleaning. Such materials have to withstand the effects of a most hazardous environment. Temperature variations, wide variations in acidity or alkalinity and high stresses all have an effect on the durability of materials.

Besides the innumerous and complex factors involved such as; materials, environment, material properties and contact geometry and load, the human factor still persists. Direct filling materials, are handled entirely by the dentist and conditions for application varies greatly.

During the past decade both clinicians and patients have developed an interest in posterior composite resins. This growth in interest results from a desire for aesthetics restorations, as well as the amalgam metal character and toxicity. The demand for restorations with a natural appearance in the posterior region and the controversy as to the mercury action of amalgam, although be it still has excellent mechanical properties, has attracted researchers to focus on the improvement of the resin composites in order to be applied in posterior teeth. To reach this objective it is essential to understand the mechanisms operating within that special environment that is the mouth.

The more reliable way to validate the behavior of the composite materials is doing *in vivo* studies. These are long term studies, time consuming, and often involve a small number of patients; therefore it is very difficult to extract results likely to apply to the general public. Due to these difficulties, *in vitro* studies seem to be a good alternative. The problem is to validate the results attained via *in vitro* studies with the ones executed *in vivo*. This correlation is very complicated as there are no standards for mechanical characterization of these composites, namely wear tests. There are a large number of variables involved in the *in vitro* studies, and the type of tests used in experimental approach varies greatly within investigating teams.

The question is which properties are relevant to composite behavior and how do they interact with the environment. The primary relevant properties can be divided in two groups; mechanical and tribological. Laboratory tests must be carefully selected in order to characterize and predict the possible clinical behavior and contribute to further development and facilitate proper material selection.

These restorative materials must have properties and characteristics which allow them to replace human natural tooth tissues. These materials should have comparable properties analogous to the major human enamel and dentine which will be replaced. Thus, resin composites must have an optimal combination of physical and mechanical properties in order to meet this criterion.

1.2 Thesis outline

The aim of the present work is to evaluate the most important characteristics/properties of posterior restorative materials regarding physical and tribological properties which allow for a classification. Because the work started with commercial composites and after analyzing the articles review and the first test results it was clear that the usage of commercial composites is not enough. Due to the fact that these materials' components could not be set up at will, the use of produced composites in laboratory was necessary. These composites, using the same evaluation techniques and procedures established for commercial resin composites, permitted the variation of: filler content; weight fraction, particles dimension; and matrix composition. These parameterized studies allow for characterization of the produced composites and therefore understand the influence that each of the composites components had in their mechanical and tribological properties. Another important field of study is the evaluation of some external parameter that really is evaluated for commercial resin composites. A long term study is presented regarding the evaluation of pH values and aging time for seven of the commercial composites presented in the entire study.

Restorative material characterization was based on two sets of properties. First mechanical tests; Vickers microhardness, impulse excitation of vibration and four point bending, regarding the *in vitro* tribological evaluation a reciprocating wear test was conceived. With these tests the material properties evaluated were: mechanical tests: microhardness, Young's modulus (dynamic elastic modulus), flexural resistance, work-of-fracture and Young's modulus (static elastic modulus); concerning tribological behavior the reciprocating wear test allowed for determination of the coefficient of friction (COF). Several material pairs (tested in distilled water and abrasive slurry environment) resulted in wear volumes of composites and theirs antagonists.

In chapter 2, a review of literature on dental materials for posterior restorations is presented. The subjects presented address mainly resin composites and amalgam properties evaluation and characterization. Which properties are important to characterize these materials in mechanical and tribological? Another approach regards the external factors relevant for their performance evaluation.

In chapter 3, materials, testing equipments and experimental procedures are presented and defined. Regarding materials, all evaluated materials are presented; commercial composites, laboratory produced composites, amalgam as well as the antagonist materials used in wear tests, pre-molar human teeth and glass spheres.

Testing equipment is divided in two sections; first; a section where the equipment used to determine mechanical properties is shown, and secondly the description of apparatus associated to the tribological tests which are used to determine the dental materials behavior. Finally the experimental procedures and result analysis are expounded and explained.

In chapter 4, shows the more important preliminary tests done which allow for the establishment of; test apparatus; procedures, mechanical characterization of materials to test and the main parameters to study. After these preliminary studies, the chapter relates to mechanical test results for: Vickers hardness, impulse excitation of vibration (IEV) and four point bending tests. Regarding commercial composites materials the results of aging time and pH effects are also presented along with the reference conditions, *i.e.*, prior to aging. Conclusions concerning these effects are done subsequently. This chapter is divided in terms of results presentation and partial conclusions.

In chapter 5, shows the validation of the main experimental methodology used to assess the wear of dental composite materials. This validation concerns specially the use of glass sphere as antagonist material in the reciprocating wear tests.

After validating reciprocating wear tests, the influence of two types of environment on the contact: artificial saliva/distilled water and abrasive slurry. For this particular study eight commercial restorative composites were tested against glass spheres, with only one normal load condition. The goal of this part of the study was the determination of the wear resistance under different wear mechanisms: abrasion and attrition. The evaluation of environmental influence on these tests allows for understanding composite behavior under reciprocating contact through the measurement of wear volumes of the contact pair followed by analysis of the removal mechanisms involved in the wear process.

Analyzing the previous tests, and as already expected, it was concluded that commercial restorative materials are closed system were nothing can be altered, and therefore very difficult to establish a cause effect concept. Laboratory produced composites was the way to contour this difficulty, and, therefore change composite parameters like; filler volume fraction, average particle dimension and matrix composition.

Due to the analysis of some composite-glass pair that showed slight discrepancy a complementary study involving three commercial composite was done. Load-scanning tests were used to understand and explain the regime transition of these materials using an energetic approach occurred in reciprocating wear tests. This test allowed for understanding the wear/fracture mechanisms induced by the values of coefficient of friction.

The final study regarded an application of the implemented methodology with the intention of evaluating the effect of aging time in baths with different pH values on seven commercial composites evaluating their performance in reciprocating wear test. Commercial restorative composites were evaluated after three aging periods 3, 6 and 22 months in pH 3, pH 7 and pH 9 buffer solutions. All these studies involve directly or indirectly wear process with removal mechanisms and therefore scanning electron microscope (SEM) observations were done on the contacting surfaces.

In chapter 6, conclusions are drawn based on the range of variation of analyzed properties for mechanical and tribological performance. This analysis is done for commercial composites as well as for laboratory produced composites. Suggestions of further directives are presented.

Chapter 2

Literature review

2.1 Introduction

The following paragraphs present a brief introduction to the main research areas of this thesis and vital areas of interest to address the objectives/motivation in this area of subject.

The review starts with the characterization of the most used direct restorative materials, both amalgam and resin composite. Afterwards, the more important material properties, physical and tribological are presented, in order to understand the process of characterization and selection of these materials.

A report regarding the most critical external factors which affect teeth and restorative materials is also presented.

2.2 Direct restorative materials

Amalgam has been the material of choice for posterior tooth restoration for more than 150 years. The past 25 years have witnessed significant advances in restorative materials themselves and in the bonding systems for retaining a restoration in the prepared tooth. As a result, there has been a shift toward resin composite materials during this same period because of concerns about the aesthetics and biocompatibility of dental amalgam. In addition, other materials such as glass ionomer cements, ceramic inlays and onlays, and gold alloys have been used as alternatives to amalgam (Mackert and Wahl, 2004).

More than 50% of all dental restorations today are restorations of old dental fillings. There is therefore a need for a dental filling material that will perform more satisfactorily. The major reason for the failure of existing dental materials is secondary caries that develops due to bacterial ingress at the interface of the filling and the tooth (Kraft, 2002).

The use of restorative polymeric materials in dentistry has been primarily driven by the esthetic features of these materials. However, interest in polymeric materials as replacements for amalgams has been further promoted by suggestions of adverse health effects from the exposure to mercury in dental amalgams not only for patients but also for medical assistants (Hörsted-Bindslev, 2004).

Many hundreds of millions of people worldwide have teeth containing mercury amalgam fillings. Bates (2006) affirms that the use of these fillings has been decreasing. It was estimated that, in 1990, nearly 100 million amalgam fillings were inserted in teeth in the United States (Department of Health and Human Services, 1993). This represents approximately 75-100 tons of mercury placed in people's mouths (Eneström and Hultman, 1995). Clarkson (2002) has characterized dental amalgam as one of "the three modern faces of mercury". The other two are methyl mercury in fish and ethyl mercury (thimerosal) as a preservative in vaccines.

Exposures to mercury from dental amalgams are below mercury exposures conclusively associated with health effects in occupational studies. This is due to the durations of exposure and follow-up are often limited and occupational populations too small to detect uncommon effects (Weiner *et al.*, 1990).

Several studies conducted recently all over the world, focusing on amalgam effect on children did not reveal substantial difference in the evaluated factors. DeRouen *et al.* (2006) conducted in Lisbon, Portugal, 507 children were randomly assigned to receive either amalgam ($n = 254$) or mercury free composite ($n = 253$) and were followed for 7 years (1997-2005). No statistically significant differences in neurobehavioral assessment (memory, attention, motor development, nerve conduction velocities) or intelligence were found between the two groups. A second study (Bellinger *et al.*, 2006; Bellinger *et al.*, 2007) and (Bellinger *et al.*, 2008) conducted in two US cities followed 534 children (267 for amalgam and 267 for resin composite) for 5 years. Likewise, there were no statistically significant differences in full-scale intelligence quotient (IQ) scores, memory, or visuomotor ability between children with and without amalgam.

In a more recent study Ye *et al.*, (2009) conducted with 403 children aged 7-11 years in five schools from Xuhui (China) concluded that although urinary mercury concentration was slightly elevated among children with amalgam fillings, no evidence was found of adverse effects on the outcomes evaluated.

In conclusion, despite the very widespread use of dental amalgam fillings, epidemiologic data to establish their safety are inadequate (Bates, 2006). Despite their extensive use in dental applications around the world and suggestions that amalgams could be totally replaced by polymeric composite materials, there remain problems related to the limited lifetime of the composite materials *in vivo*, as a result of premature degradation (Anusavice and de Rijk, 1990; Bayne, 1992; Øilo, 1992). The restoration durability has perhaps been one of the strongest arguments for the continued use of dental amalgams in many practices, despite adverse public pressure. General use of polymeric materials over the past 20 years has indicated a high benefit to-risk ratio (McHugh, 1992). Systemic reactions to the polymers and related degradation products, however, have not been closely examined (Bayne, 1992).

While the degradation of restorative dental materials which contain polymeric resins has been of interest for some time (Matos *et al.*, 2011; Wei *et al.*, 2011; Ferracane, 2006; Osorio *et al.*, 2005), most of this work has concentrated on the loss of mechanical function and physical structure (Condon and Ferracane, 1997a), rather than on the chemical breakdown and the subsequent effects of this chemical breakdown on the surrounding biological elements, specifically, salivary and tissue components interfacing with the materials (Santerre *et al.*, 2001). A great number of published studies have examined the effects of polymer resin components (Ferracane *et al.*, 1998) on biological function (*i.e.*, bacteria and cells residing in the soft tissue of the oral cavity) have been concerned with leached monomer components and not biodegradation products derived as a result of exposure to cells and biological fluids (Ørstavik and Hensten-Pettersen, 1978; Grieve *et al.*, 1991; Tanaka *et al.*, 1991; Jontell *et al.*, 1995; Hansel *et al.*, 1998; Mohsen *et al.*, 1998). It was only in the early part of the 1990s that serious consideration was given to the possibility that enzymes, associated with saliva and oral tissues, may be involved in catalyzing chemical reactions which could degrade dental resin systems (Munksgaard and Freund, 1990; Larsen and Munksgaard, 1991; Larsen *et al.*, 1992), although others (Øysaed *et al.*, 1988) had previously suggested that composite resins were prone to oxidation and could release formaldehyde as a by-product (Santerre *et al.*, 2001).

Nevertheless, posterior composites are still not as easy to handle as dental amalgam, associated with the problem of technique sensitivity and an incremental placement. Hence, easy to manipulate posterior composites that exhibit a sufficient wear resistance and fracture resistance would be beneficial for *in vivo* clinical applications.

Composites have been introduced with high expectations as an alternative to amalgam. More recently and with the focus on the perceived high-filler load, these materials were expected to exhibit superior physical and mechanical properties as well as improvements in handling. Besides inorganic filler materials, the resin matrix has an important influence on the properties of the composite materials system (Kawaguchi *et al.*, 1989) and (Peutzfeld, 1997). However, in the past 30 years there have been no fundamental changes in the monomer systems since the introduction of dimethacrylates, in form of the monomer of bis phenol A (Bis-GMA) by Bowen in 1962.

2.2.1 Amalgam

Amalgam remains the most important class of material for the restoration of posterior teeth, despite the unaesthetic appearance and its association with toxicity and hygiene problems and galvanic corrosion. Over the years, our understanding of these materials has advanced considerably, but until late 1960s there was little change in this field and the composition was maintained relatively stable for the last 50 years (Van Noort, 1994).

Dental amalgam is a complex substance with a structure, properties and clinical performance that are heavily influenced by manipulation of the material prior to setting.

Controversies exist over which of clinical behavior and amalgam's fundamental material properties arise from direct cause-effect relationships.

Mitchell *et al.* (2007) refers that during the 1990s, anti-amalgam newsletters and Web sites reported that dental amalgam had been banned in Europe, especially in Germany and Sweden. Burke (2004) surveyed regulatory agencies in ten countries, and wrote "there were few restrictions worldwide to the placement of dental amalgam.". Wahl in 2001 had already confirmed the non-existence of restrictions to contest these rumours (Burke, 2004). Currently a United Nations Environment Programme (2002); from Denmark implemented restrictions limiting the use of amalgam to molar teeth restorations. Different recommendations were done by Sweden, Norway, Austria, and Germany asking that amalgam not be placed in pregnant women (Burke 2004). Germany also recommends that amalgam not be placed in patients with renal impairment (Burke, 2004). Most of the other nations surveyed, including the United States, United Kingdom, Australia, Finland, and Ireland, have issued no recommendations for restrictions on amalgam use.

According to Mitchell *et al.* (2007) the percentage of posterior teeth that are restored with resin composite continues to grow. In most of the world, however, dental amalgam remains the most widely used material for load-bearing restorations in posterior teeth. In the United States, amalgam is used for approximately 60% of all direct posterior restorations. Dental schools throughout the world continue to teach amalgam as the material of choice for large and complex posterior restorations. To date, no nation has outlawed the use of amalgam. Several nations have cautioned dentists against placing amalgam restorations in pregnant women, and Denmark limits amalgam to molar teeth. Few amalgam restorations are placed in Japan, Finland, and Sweden. Posterior amalgam restorations are more widely used and taught in the United States, Canada, and the United Kingdom than in Europe, Scandinavia, and Australia. Long-term data from longitudinal studies that have become available over the last 10 years have made possible a reassessment of the durability of amalgam restorations in posterior teeth. The longevity of amalgam restorations depends on the setting in which they are placed. Studies conducted in general practices produced median survival times for posterior amalgam restorations of 7 to 15 years. Survival times for larger, more complex restorations fall within the lower end of this range. Studies conducted in ideal conditions (typically in dental schools, in which a limited number of calibrated dentists working under few time constraints place restorations in motivated patients) revealed median survival times of 55 to 70 years. Comparable studies of posterior resin composites placed in ideal conditions revealed median survival times of 20 to 45 years. These studies suggest that the potential survival time of amalgam and resin composite in posterior teeth is longer than had been thought and that under these conditions, amalgam outlasts composite. Unfortunately, no long term studies of posterior resin composites have been conducted in general practice settings. Relatively short-term studies suggest that the median survival time of posterior resin composite studies may be less than 10 years.

Composition and microstructure An amalgam is formed when mercury is mixed with another metal or metals. Mercury is liquid at room temperature (solidifying at −39°C), and it reacts readily with metals such as silver, tin and copper, to produce solid materials. Dental amalgam alloys, to be mixed with mercury to form amalgam restoration, are manufactured in two basic physical forms. These are irregular shaped particles produced by lathe cutting and the spherical particles produced by atomisation. Irregular particles range from 20 μm to 120 μm in length, 10 μm to 70 μm in width and 10 μm to 35 μm in thickness. Mean average size of spherical particles are inferior to 30 μm in diameter. Amalgam alloys are mainly classified as low-copper and high-copper types. The former have existed since the late 19th century (Black, 1896), the latter since the 1960s.

The alloy used in the traditional dental amalgam consists of a mixture of silver, tin, copper, zinc and sometimes mercury, typically composition is shown in the next table 2.1 (Van Noort, 1994).

Table 2.1: Typical constitution of dental amalgam.

Constituent	**% of total**
Ag	67 – 74
Sn	25 – 28
Cu	0 – 6
Zn	0 – 2
Hg	0 – 3

Silver is the main constituent, present in combination with tin as the inter-metallic compound Ag_3Sn, known commonly as the γ phase. This γ phase reacts readily with mercury to form the dental amalgam. Copper is present to increase strength and hardness of the amalgam. This effect is more noticed if copper content is higher then 6%. Zinc is essential to the initial production of the alloy. Mercury is sometimes added to provide a more rapid reaction in the pre-amalgamation process (Amalgamation — the process of mixing liquid mercury with one or more metals or alloys to form an amalgam).

Dental amalgam will continue to be the restorative material of choice for many clinical situations. By paying careful attention to material selection and handling and by having an appreciation of their limitation, amalgam should provide patients with restorations that will give satisfactory function for many years.

2.2.2 Composites

Composite materials are as much an engineering concept as they are a specific material. The modern term composite arose in the aircraft industry in the early middle part of the last century. Recently there has been renewed interest in such composites since by choice of a suitable matrix resin, based, say on starch, totally biodegradable composite may now be made-with the material showing adequate stability during useful life. By definition composite materials, often referred as composites, are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure.

The hard dental tissues, mainly enamel and dentin, are natural composite materials. Concerning dentistry and regarding restorative dental materials the term composite is commonly used to designate an important sub-group of these restorative materials. The term is an abbreviation or synonym of composite resin or polymer/ceramic composite or, sometimes, resin-bonded ceramic, and the class of materials denoted incorporate a substantial quantity of dispersed phase of particle ceramic within a resin monomer matrix (Watts, 1992).

These resin-based materials used in direct restorative materials have three major components; an organic resin matrix, an inorganic filler and a coupling agent. The resin forms the matrix of the composite material binding the rest of the composites' components, *i.e.*, reinforcement filling material or materials and the coupling agent.

Matrix — a plastic resin material that forms a continuous phase that binds the filler particles.

Filler — Reinforcement particles and/or fibers that are disperse in the matrix.

Coupling agents — Bonding agent that promotes adhesion between filler and resin matrix.

Dental composites

Dental composites are highly cross-linked polymeric materials reinforced by a dispersion of glass, crystalline, or resin filler particles and/or short fibers bound to the matrix by silane coupling agents.

Matrix Resin matrix is the clinically active component of the composite. Initially a fluid monomer that through the application of visible light with certain wavelength and intensity transforms itself into a rigid polymer. This transformation capacity, from fluid to rigid mass allows these materials to be used for direct restorative applications (Van Noort, 1994).

Since it was invented, in the beginning of 1960 the viscous aromatic dimethacrylate monomer 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propane (Bis-GMA) has been present in a great variety of materials. Due to its main characteristics; large molecular size and chemical structure, it is superior to many monomers of lower molecular mass by virtue of; (i) lower volatility; (ii) lower polymerisation shrinkage; (iii) more rapid hardening, and (iv) production of stronger and stiffer resin (Watts, 1992). To solve this stiffness problem, low viscosity monomers known as viscosity controllers are added, such as methyl methacrylate (MMA) ethylene glycol dimethacrylate (EDMA) and triethylene glycol dimethacrylate (TEGDMA) one of the most commonly used (Van Noort, 1994).

Most monomers used in dental resin composites possess either pendant or backbone functional groups apart from the methacrylate double bonds. By means of a cross-linking agent, groups from different polymer chains may react to increase the degree of crosslinking in such a way that the mechanical properties of the polymer matrix are improved.

In order to guaranty the composites long life before application it is important to ensure that premature polymerisation doesn't occur, inhibitors such as hydroquinone, are included in 0.1%

amounts or less. The organic monomer phase also incorporates low concentrations of chemicals required for activation and initiation of polymerisation reaction by either chemical curing or visible-light activated curing (Watts, 1992).

Filler Reinforcement phase materials started as ceramic oxide, such as silica or alumina, or a glass, including some soft polishable glasses (Glenn, 1982). Irregular shaped particles are more utilized due to their better mechanical retention ability in resin. Recent generations of resin composites incorporate high proportions of hard strong particles in order to produce high strength composites and therefore approach some of their mechanical properties to natural tooth substance. High filler content is also responsible for the reduction of polymerization shrinkage in the curing process.

The use of glass fillers has two great advantages, their presence reduce thermal dimensional changes due to zero or negative thermal expansion coefficients and due to their good reflective index they possess, just like the organic monomer, adequate translucence index.

The incorporation of large volume of hard filler particles has been based on the concept of attainment of high compressive strength and stiffness and on evidence that abrasion resistance improves as filler content increases and that fine fillers wear more then large particles (Draughn and Harrison, 1978). However, abrasive wear and other mechanical characteristics depend on the particle size distribution and the way in which they are packed together as well as the largest size particles. The original composites tended to contain particles as large as 50 to 100 μm, but particles larger then 20 μm cause poor finishing and polishing (Watts, 1992). It was postulated that improved wear resistance results from filler particle separation distances of less than 0.1 μm so that the softer resin is protected from abrasion (Smith, 1985).

At the lower limit in size range are particles of pyrolytic silica, used exclusively in the so-called microfilled composites. Diameters are 0.05 μm and surface areas of about 50 m^2/g. These very fine particles act as thickening agents and create technical problems in mixing large amounts into liquid monomers. A few percent of these fillers are incorporated in composites based on larger particle size fillers to minimize settling out problems.

Many microfilled materials are produced by incorporation of pyrolytic silica into monomer which is then polymerized and ground. This ground polymer, containing the disperse filler, is then used to make a paste with more monomer. The presence of this organic filler acts as an aid in reducing polymerization contraction. By appropriate techniques, materials containing 66 – 70 mass % sintered filler agglomerates have been produced.

The combination of macro and microfilled composites advantages led to restorative materials containing significant amounts of microfilled material and a major amount of silica or glass fillers with particle size in the range of 0.5 μm – 5 μm.

Many of the performance improvements in direct restorative composite materials during the last decades are due to developments in inorganic fillers technology.

Coupling agent Besides resin matrix and fillers, the third important element in the system is coupling agent, a bond between reinforcement particles and matrix is attained by the use of an organic silicon compound, or silane coupling agent. This component promotes a good bond between fillers and the resin matrix and is essential in composites formulation; molecules have a reactive group at both its ends and are coated on the filler particle surface before mixing with the oligomer in order for the composite to have the desired mechanical and tribological properties (Chen, 2010). During polymerization, double bonds on the silane molecule also react with the polymer matrix. The formation of a strong covalent bond between inorganic fillers and the organic matrix is essential for obtaining good mechanical properties in dental composites.

Silane coupling agents provide the bond between two components in dental composites, but this bond can be degraded by water absorbed by the composites (Craig, 2002). The idea of increasing the micromechanical retention between fillers and resin in order to reinforce the coupling agent was first described by Bowen and Reed in 1976. Their strategy was to use multi-phase glasses which can be etched and produce porous fillers (Bowen and Reed, 1976).

Ineffective silane coupling between filler and matrix within dental composites is prone to accelerated *in vivo* degradation. During fabrication of resin composites, the silanization process is a critical step that, to a large degree, determines the physico-mechanical properties. If there is a breakdown of the interface, the stresses developed under load will not distribute evenly through the material, as a result, structural defects that may lead to micro-cracks will occur at the filler-matrix interface (Yoshida *et al.*, 2002); these in turn may initiate crack growth along the filler-matrix coupling during cyclic loading.

These coupling agents promote bonding, withholding filler particles during sliding contact at the composite core. As a result hard filler particles are maintained in the soft matrix, and are present to engage in abrasive wear with opposing materials, teeth or restorative materials, greatly improving the wear resistance of the material.

Classification of resin composite

The increase in replacement of amalgam by resin composites due to aesthetical reasons in posterior restorations led to the emergence of a high number of resin composite systems in the market. The alternatives and developments are many, short fibers reinforcement particles, whiskers, nano-fillers, etc., therefore to keep track of recent development materials and to situate others several classifications have been proposed. The majority of resin composite classification is based on the particle size and/or size particles distribution.

The American Dental Association described two categories of direct filling resins in specification number 27 (Council on Dental Materials American Dental Association, 1977). Filler size distribution and filler amount are the most common and more elaborated criteria used to rank resin composites (Van Noort, 1994; McCabe and Walls, 2008; Anusavice, 2003). This classification based on filler size and distribution is done with direct relation to physical and mechanical properties of these materials (Li *et al.*, 1985; Braem *et al.*, 1989; Chung, 1990; Chung and Greener, 1990), of which the dynamic Youngs modulus (Braem, 1985; Braem *et al.*, 1986), hardness (Craig, 1989) and surface roughness (Willems *et al.*, 1991) are the more relevant proof of relation between filler and mechanical properties.

The more common classification of composites (table 2.2) is based on filler particle size and size distribution; six groups can be identified. For hybrid composites there are subgroups overlapping due to particle size, *i.e.*, filler from either the small or the traditional category, with microfillers (submicron, colloidal filler particles). Any direct restorative resin system with fillers from two or more size ranges can, in principle, be considered hybrid. The same may be applied to composites that contain fibre and/or nanoparticles fillers.

Due to adjustment viscosity of the composites paste most of the commercialized composites use fillers in micrometer size range and also contain small amounts (inferior to 5% in weight) of microfillers, therefore a single hybrid classification would not be very meaningful (Anusavice, 2003).

Traditional composites Traditional composites also referred to as conventional or macrofilled composites are constituted by large reinforcement particles, being that the more common materials used are finely ground amorphous silica and quartz. These composites contain glass

Table 2.2: Classification of resin composites regarding filler size and size distribution; clinical application.

Class of composite	**Particle dimension**	**Particle size**	**Clinical use**
Traditional	Large particles	1 – 50 μm glass	High-stress areas
Hybrid	Large particles	1 – 20 μm glass 0.04 μm silica	High-stress areas requiring improvement polishability
	Midifiller	0.1 – 20 μm glass 0.04 μm silica	High-stress areas requiring improvement polishability
	Midifiller/Small particle filled	0.1 – 2 μm glass 0.04 μm silica	Moderate stress areas requiring optimal polishability
Packable hybrid	Midifiller/minifiller	Midifiller/minifiller hybrid, but with lower filler fraction	Situation in which improved condensability is needed
Flowable hybrid	Midifiller	Midifiller hybrid, but with finer particle size distribution	Situation in which improved flow is needed and/or where access is difficult
Homogeneous	Microfill	0.04 μm silica	Low stress and subgingival areas that require a high luster and polish
Heterogeneous	Microfill	0.04 μm silica Pre-polymerized resin particles containing 0.04 μm silica	Low stress and subgingival areas where reduced shrinkage is essential

filler particles with average particle size of 10 μm to 20 μm and the largest particles of 50 μm, and are characterized by a wide distribution in particle size. Inorganic filler loading ranges from: 70% to 80% in weight or 60% to 70% in volume. Due to the inclusion of such large particles surface finishing is poor and in sliding contact, resin could be removed along with these protruding filler particles.

Small particle composites To minimize surface finishing and improve physical and mechanical properties small particle filled composites relatively to traditional composites have reinforcement particles which range from ≈ 0.5 μm to 3 μm. Concerning filler loading these composites contain more inorganic material due to the broad size range distribution of reinforcement particles, typically 80% to 90% weight and 65% to 70% volume than traditional composites. Some small particle composites use amorphous silica as filler, but most incorporate glasses that contain heavy metals for radiopacity. The matrix constitution is similar to traditional and microfilled composites. In order to improve viscosity and help the resin's paste into the cavity, colloidal silica is usually added in percentages inferior to 5%, and primary filler consists of silane coated ground particles. Comparatively to traditional composites small particle composites exhibit superior physical and mechanical properties, due to increasing filler content (Anusavice, 2003). Compressive strength and elastic modulus exceed those of both traditional and microfilled composites. These composites are characterized by tensile strength values of 2 and 1.5 times relatively to microfilled and traditional composites respectively. The coefficient of thermal expansion is less than that of other composites, although it is still approximately twice that of tooth structure. These mechanical improvements due to filler distribution result in better wear resistance and decrease in polymerization shrinkage content (Anusavice, 2003).

Microfilled composites Microfilled composites contain silica particles in the range 0.01 μm – 0.1 μm with a typical average particle dimension of 0.04 μm (40 nm). This value is one-tenth of the wavelength of visible light and 200 to 300 times smaller than the average particles in traditional composites.

Due to average particle sizes these composites exhibit smooth surfaces very similar to that obtained for unfilled acrylic resins. Colloidal silica particles tend to agglomerate during mixing, but not all agglomerates are broken, agglomerates account for particle sizes ranging from 0.04μm to 0.4 μm.

The very small particle size produces a massive increase in available surface area for a given volume of filler (typically 103 – 104 times more surface area). Consequently, it is not possible to incorporate very high filler loadings for small particle size and products which are available contain only 30% – 60% filler by weight. Even at these lower levels, calculations show that many filler particles must be present as agglomerates and not as individual particles surrounded by resin. The method of incorporating the smaller particles varies, direct blending with resin being difficult. The most widely used method is to prepare pre-polymerized blocks of resin containing high filler loading of silica. The block is splintered and ground to give particles of resin up to 100 μm, in diameter each containing silica. These particles are blended with monomer, initiators or activators to form pastes. The final inorganic filler content may be only 50% in weight but if the composites particles, filler particles grinded and added to pre-polymerized composite highly loaded with colloidal silica particles, are counted as filler particles, the filler content is closer to 80% weight ($\approx$ 60 vol.%). Thus microfilled composites, despite having much lower volume fraction of inorganic filler than traditional or small particle composite, will not shrink as much as should be expected. A downside to these composites is the relatively weak bond between particles and matrix, facilitating wear by chipping mechanisms.

Hybrid composites Hybrid composites contain two kinds of filler particles, large filler particles, with an average size of 15μm – 20 μm and also a small percentage in weight of colloidal silica, which has a particle size ranging from 0.01 μm to 0.05 μm. Although almost all composites integrate a small percentage of this colloidal silica their behavior is very much determined by the size of the larger filler particles. This material was developed in order to obtain a better finished surface than small particle composite can provide, meanwhile maintaining the good mechanical properties. This category of composite materials has surface smoothness similar to microfilled composites and can be used in anterior restoration applications.

Most of the hybrid composites consist of colloidal silica, 10 wt% to 20 wt%, and ground particles of glasses containing heavy metals, with an overall particle content of approximately 75 wt% to 80 wt%. Average particle size ranges from 0.4 μm to 1 μm for the glasses, and within the typical size distribution, 75% of the ground particles are smaller then 1.0 μm.

Regarding physical and mechanical properties these systems generally range between those of the traditional and small particles composites and are superior to microfilled composites.

Flowable composites Flowable composite system have a reduced filler content in order to provide adequate consistency to enable the material to flow and spread uniformly and adapt to cavity form and produce the desired dental anatomy. Flowable composites are a result of modification of hybrid and small particle composites. Although the reduction of inorganic material allows for its low viscosity it also makes them more susceptible to wear. Flowable composites are also indicated for applications in which a degree of adaptation is needed.

Packable composites The so-called packable and condensable composites form a special category of hybrid composites. These restorative direct posterior composites are the most adapted for posterior restorations. When compared with amalgam the technique of composite placement is more time consuming and demanding.

These composite systems were introduced in the market in order to respond to certain issues such as shrinkage, wear and handling. They have been mistakenly called "condensable composites," but they do not condense. They offer higher viscosity trying to mimic amalgam placement techniques. They offer the potential to obtain better proximal contact when packing against a matrix band. To obtain such characteristics, manufacturers use a higher percentage of irregular (mixture of different size particles or glass rods) or porous filler (packables are generally loaded in excess of 80 percent in weight, and traditional hybrids are generally loaded less than 80 percent in weight) to reduce the amount of resin, increasing the viscosity and thus, creating this particular handling property. Unlike conventional hybrids, this category of composite-based resins is relatively resistant to displacement during insertion (packing).

In 1983 Lutz and Phillips published their system classification for characterizing dental composites based on particle size. The classification was based upon the types of fillers at the time — that is, macrofillers, microfillers, and three versions of microfiller based complexes. Six composite classes were considered:

- Traditional composites;
- Hybrid composites;
- Homogeneous microfilled composites;
- Heterogeneous microfilled composites;
    - Splintered pre-polymerized particles;
    - Spherical pre-polymerized;
    - Agglomerated microfiller complexes.

More recently, Willems *et al.* (1992) published a similar classification system. The basic difference between the two system classifications reflects the fact that the most popular non-microfilled composites have smaller mean particle sizes and fewer large particles than composites of a decade ago. The term "hybrid" is no longer used, since almost all dental composites have of two size ranges of reinforcement particles, an amorphous silica is present in order to improve handling and reduce stickiness. The first level of distinction between composites is filler content; composites are classified as midway-filled ($<$ 60 vol.%) and compact-filled ($>$ 60 vol.%). Each category is than subdivided regarding average particle size, *i.e.*, ultrafine (average particle size < 3 μm) and fine (average particle > 3 μm). Microfilled composites category remains unchanged, although new materials are included which are predominantly filled with amorphous silica but also contain some macroscopic reinforcing fillers or radiopacifiers. The new system also included is this classification, namely, fiber-reinforced materials. A simpler classification system has been described by Bayne *et al.* (1994). In this system, the three popular types of composites are described by the size of their largest fillers; microfilled (average particle size range 0.01 – 0.1 μm), minifilled (average particle size range 0.1 – 1.0 μm), and midifilled (average particle size range 1.0 – 10.0 μm). Scanning electron micrographs of the polished surfaces of representative composites in each class demonstrate the differences in particle size and surface smoothness. This classification system is less inclusive than previous ones, but provides necessary information about the largest added particles which significantly affect polishability. Therefore, the two most important filler considerations at present are the amount and size of the particles.

In the last years the most recent innovation has been the development of the nanofilled composites, containing only nano-scale particles.

The more noticeable modification of manufacturers regarding composite formulation of their microhybrids was to include more nanoparticles, and possibly pre-polymerized resin fillers, similar to those found in the microfilled composites, and have them name this group “nanohybrids.” Therefore, it is difficult to clearly distinguish nanohybrids from microhybrids (Ferracane, 2011). Their properties, such as flexure strength and modulus, tend to be similar, with the nanohybrids as a group being in the lower range of the microhybrids, and both being greater than microfilled. (Ilie and Hickel, 2009a; ADA, 2010). While some have shown evidence for reduced stability during water storage for nano-hybrid or nano-filled composites *vs.* microhybrids (Ilie and Hickel, 2009b), others have shown an opposite trend (Curtis *et al.*, 2009) or fairly similar susceptibility to aging (Hahnel *et al.*, 2010). It has been suggested that the slightly lower properties of some nanohybrid composites may be due to the incorporation of pre-polymerized resin fillers (Blackham *et al.*, 2009).

The state of the art of the composition of dental composites has been changing rapidly in the past few years. The nanofill and nanohybrid materials represent the state of the art in terms of filler formulation (Chen, 2010; Klapdohr and Moszner, 2005). New options for reinforcing fillers generally have focused on nanosized materials and hybrid organic-inorganic fillers (Chen, 2010).

2.3 Restorative composite materials properties

The development of resin-based materials with inorganic fillers came with great promise as a substitute for dental amalgam. Although resin composites tend to replace amalgam they, still, do not perform as well as the latter. In spite of their fast evolution regarding matrix and filler technology there are problems associated to restorations. These problems were due almost entirely to the properties of the materials and partially to the dentists’ difficulty in material manipulation.

Restorative materials are subject to a very specific environment that varies from patient to patient, and even within the same patient conditions vary along the day. Mastication forces, occlusal habits, abrasive foods, chemically active foods and liquids, temperature fluctuations, humidity variation, pH variation, bacterial by products, and salivary enzymes all contribute to uncontrollable factors that affect composite restoration longevity (Larsen *et al.*, 1992; Gee *et al.*, 1996b; Asmussen, 1984; Ferracane and Marker, 1992; Ferracane and Berge, 1995; Sarrett *et al.*, 2000).

The mechanical properties of resin composites are dependent on the filler component with many studies reporting relationships between fillers and flexural strength (Söderholm, 2010; Atai *et al.*, 2004; Akihiro and Ferracane, 1996), compressive strength (Marghalani and Al-jabab, 2004), diametral tensile strength (Prakki *et al.*, 2009; Duymus *et al.*, 2008), transverse strength (Duarte Jr *et al.*, 2009), shear punch strength (Nomoto *et al.*, 2001), fracture toughness (Watanabe *et al.*, 2008), hardness (Mayworm *et al.*, 2008), wear (Liu *et al.*, 2009; Ramalho and Antunes, 2005, Xu *et al.*, 2004), shrinkage stress (Min *et al.*, 2010) and thermal expansion (Mucci *et al.*, 2009).

To increase the longevity of dental restorations the development of new restorative materials such as resin based composites must consider their tribo-mechanical properties evaluation.

Unfortunately, it is practically impossible to vary one mechanical characteristic and, at the same time, keep others unchanged, and then a design procedure is necessary to select materials, volume ratios and the shape of the particles to develop or characterize the specified or desired material properties.

Current dental composites have adequate mechanical properties for use in all areas of the mouth. But concern still exists when the materials are placed in high stress situations, especially in patients with bruxing or parafunctional habits. The concern here is for fracture of the restoration as well as wear. Wear is considered to be a lesser problem for current materials as compared to those that were the standard of care a decade ago, in large part due to refinement in the size of the reinforcing fillers which significantly reduced the magnitude of abrasive wear.

However, it is important to compare restorative composites in order to allow for the correct selection for each application needed, as this is essential to know the mechanical properties of dental composites relatively to other dental restorative materials. In general, dental composites have similar flexure strength, fracture toughness and tensile strength as porcelain and amalgam, and are superior to glass ionomers. Perhaps the property in which dental composite are most conspicuously deficient in comparison to amalgam is elastic modulus, with resin composite being typically several times lower.

Due to the lack of specific international standards for restorative dental materials, in order to assess the more important properties it is essential to establish which properties are fundamental for direct restorative materials. The desired mechanical and physical properties are difficult to define because there is currently little correlation between the properties of composites and their clinical performance, resulting in difficulty to translate the *in vitro* results to *in vivo* ones. Nevertheless and independently from the specific standards or the use of standards of other areas to characterize, compare and design direct restorative materials the two main properties category are mechanical and tribological properties.

2.3.1 Mechanical properties

Physical properties of materials correspond to the way these materials respond to changes in the environment. Physical properties can be in mechanical, electrical and thermal fields. Material response to environment solicitations characterize the materials, depending on; temperature, applied force and how applied, compression, extension, flexure, etc. These responses correspond to material properties.

Direct restorative materials behavior and durability depend on a series of material properties, such as hardness, strength and stress-strain. All material properties depend on composition, manufacture, storage and technician handling. Direct restorative filling materials obtain their ultimate properties after placement *in situ*, and therefore, are even more susceptible to exterior influences and applicability skills.

Therefore it is vital to evaluate the essential properties of core restorative materials *in vitro* studies through parametric characterization and evaluation. Correct knowledge of restorative materials properties allows for design development and respective selection appropriated to their specific application.

The combination of these properties allows for material characterization as well as to determine which are the meaningful expression for the characterization of dental composites under various conditions.

There are no satisfactory guidelines as to the requirements for the clinical success of composite restoration. It is commonly agreed that the properties should be as good as possible, but there is no agreement on the performance level (Braem, 1985).

All mechanical properties are influenced by resin composites components. The increase of filler content or particle dimensions will alter the mechanical and tribological properties.

Therefore the focus of mechanical properties evaluation should be centered on the variables regarding composites components, type of filler, inorganic filler size, particle size distribution, filler content, coupling agent, matrix, etc.

Many material properties are interrelated. For example, elastic modulus is related to hardness, fracture toughness and fatigue behavior. Understanding the relationships between properties and physical behavior enables a minimal test set to be identified. These tests need to relate to different aspects of material performance in a clinical setting. It is very important to understand mechanisms and relationships between physical behaviors in order to transpose *in vitro* test results to *in vivo* environment situations.

Mechanical properties more often focused on within literature regarding restorative resin composites are: flexural strength, hardness, elastic modulus and fracture toughness.

Although direct filling materials may withstand the complex nature of masticatory forces in aggressive oral environments without significant wear, they fail in a brittle manner. Thus, when a dental practitioner is faced with materials that exhibit non-reproducible mechanical properties, subject to technique sensitivity, it is essential to endeavor for appropriate materials properties with an acceptably low failure rate during service. This is not always easy to achieve on the basis of limited laboratory test results, or to understand how *in vitro* properties translate into *in vivo* results. Mechanical property tests, such as hardness and strength, have been valuable in broadly defining usage boundaries, but have had limited success in predicting clinical outcomes (Kelly, 1999). An exception is fracture toughness, which has recently become of interest in the dental field (Kelly, 1995). This material property measures the ease of crack growth from a pre-determined flaw or specimens without flaw. Dental materials have been found to be particularly susceptible to this kind of failure (Watanabe *et al.*, 2008; Moshaverinia *et al.*, 2010). Flaw distribution, specimen size and shape, environmental effects, and test conditions may play significant roles in the response of a dental restoration. Thus, the issues of material property characterization and reliability prediction are particularly important in view of the different geometries of dental restorations.

Flexural strength

Measurement of flexural strength is essential in selecting polymer based restorative composite. It is considered a clinically relevant test as it measures the collective response of tensile stresses at the lower surface of the specimen and compressive stresses at the upper surface of the specimen (Sideridou *et al.*, 2007).

Flexural strength is commonly measured for the restorative material by either three or four point beam in bending, but other methods such as bi-axial flexural testing have also been reported (Curtis *et al.*, 2008; Cung *et al.*, 2004) in literature. In general, three point bending tests result in higher strength compared to four point bending tests. This is because in the latter case a larger flaw population is exposed to the applied stresses, resulting in lower apparent strength.

In the three point loading test, high compressive bending and transverse stresses cause damage under the support bearings. After this damage, the effective thickness over which the shear stresses are distributed is reduced and therefore the shear stresses in the rest of the specimen are increased. When the maximum shear stress reaches the shear strength, an interlaminar shear crack starts to propagate unstably and the load drops significantly. In the four point bending test, the bending and transverse stresses are not high enough to damage the specimen before interlaminar shear failure. Therefore, the four point short beam bending test is valid for measuring the interlaminar shear strength. The reason for the shear crack not occurring at the maximum shear stress location may be because there is not enough energy to propagate the crack (Cui *et al.*, 1992).

Surface flaws such as inclusions, voids, cracks, and heterogeneous distribution of organic and inorganic phases have shown to be the fracture initiation sites ruling the strength of resin based composites (Rodrigues *et al.*, 2008).

Due to lower filler content microfilled/small particles composites have lower strength compared to hybrid and nanofilled composites (Rodrigues *et al.*, 2007). Although strength degradation is different for different material types when aged in water, no significant difference in strength was reported by Rodrigues *et al.* (2008) for both a microhybrid and nanofilled composite after 24 hours of water storage. Curtis and coworkers (Curtis *et al.*, 2008) reported no change in mechanical strength after 24 hours of water hydration, but they also found a progressive reduction in strength over 12 months of aging for the same composites. In the case of nanofilled composite, the higher surface area to volume ratio and porous nature of the agglomerated nanoparticle filler was suggested to be the reason for hydrolytic strength degradation (Rodrigues *et al.*, 2008). Such results indicate that strength is dependent upon the size and morphology of the reinforcing filler. Kim *et al.* (2002) also observed a significant influence of the filler rate and morphology on the flexural strength and modulus, microhardness and fracture toughness of the composites evaluated. Also, Yap and Teoh (2003), comparing different categories of composites, observed that the microfine composite, with the lowest filler content (40% in volume), presented the lowest flexural properties (strength and modulus).

Besides filler content distribution, the quality of the bond between the matrix-phase and the filler phase, and matrix degradation also considerably influence the strength of resin composites (Manhart *et al.*, 2000b; Sideridou *et al.*, 2007; Curtis *et al.*, 2008). Hydrolytic degradation the cohesive behavior of the two-phase system matrix-filler restricts the effective transfer of the load from the matrix to the filler, thus reducing the strength of the composite. It has been observed that silane treated inorganic fillers demonstrate superior mechanical properties compared to untreated or rubber treated fillers (Debnath *et al.*, 2004) due to enhanced interfacial bonding. High values of strength reduction are also reported when composites age in food simulating solvents such as ethanol/water mixtures (50/50 vol.% or 75/25 vol.%) or artificial saliva, in comparison to water aging. Studies by; Musanje and Davell (2003) and Soderholm *et al.*, (1996) report strength reduction after artificial saliva storage. Corrosive degradation of the filler was suggested to be related to performance diminishing.

A great variety of results have been reported regarding the effect of resin viscosity on strength. Asmussen and Peutzfeldt (1998) showed that substitution of high viscosity Bis-GMA or relatively more flexible TEGDMA with UDMA increased the tensile strength. Consequently varying the relative amount of the resin components alters substantially the mechanical properties of resin composites materials. Other investigators Musanje and Ferracane (2004), reported no significant difference in the flexural strength for high, medium, and low viscosity hybrid composites.

Xu *et al.* (2003a) presented a method for embedding fiber preform insert imparts superior reinforcement to restorations which should improve the performance of direct-filling resin composites in large restorations with high occlusal-loads. The main objectives of introduction of fiber preform reinforcements was to reduce polymerization shrinkage and fiber pull-out during polishing and wear. In that study, a fiber preform with a diameter of 1.3 mm was produced by impregnating the resin in to the fiber bundle which was then cured using visible light and later cut into rods of desired length. Each sample consisted of single fiber preform which was placed longitudinally in the center. Composite samples with a fiber preform rod showed almost 2.5 times higher flexural strength compared to a typical hybrid resin composite.

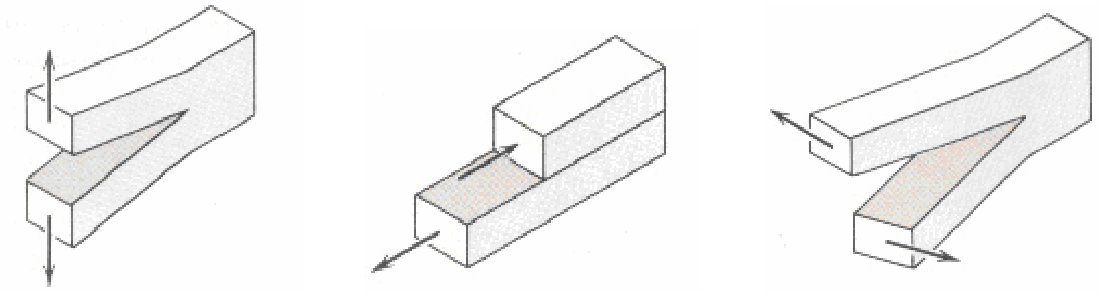
Failure of a dental restoration occurs when its load bearing capacity is diminished due to material degradation in the oral environment. This process is usually assisted by pre-existing voids, imperfect interfaces, and residual stresses. Under the continuous application of mechanical and/or environmental loads, progressive degradation eventually leads to crack initiation and growth that results in failure of a dental restoration. Thus, resistance to crack initiation and growth is an important consideration for a reliable assessment of dental restorations.

Fracture toughness

For brittle materials, a fracture mechanics assessment using fracture toughness as the criterion for failure is the most appropriate method. Fracture toughness is an intrinsic property of materials and is defined as a stress condition (K_C values) at the initiation of the crack propagation.

Plane-strain fracture toughness depend of tensile opening mode, K_IC, K_IIC, and K_IIIC are the fracture toughness of a material under the three different modes of fracture, mode I, mode II, and mode III, respectively, fig. 2.1. Fracture toughness is a very useful indicator of marginal fracture and wear resistance, which are important failure mechanisms for these restorative materials.

Steels and ductile metals have K_IC values in excess of 50 MPam$^{1/2}$. At low temperatures, many metals become brittle, and fracture toughness drops to about 10 MPam$^{1/2}$ (Ashby and Jones, 1980). Resin composites are characterized by fracture toughness that range up to 2 MPam$^{1/2}$; such small values affect clinical performance of these direct filling materials.



(a) Mode I (b) Mode II (c) Mode III

Fig. 2.1: The different modes of fracture I, II, and III.

Higher composite fracture toughness, K_IC, is commonly associated with both improved fracture and wear characteristics of the restorations (Bonilla *et al.*, 2001). Also, by knowing the maximum inherent flaw size, a_0, and minimum K_IC value the clinical performance of a restoration may be predicted under various levels of oral stresses (Tyas, 1990).

Commonly reported sample geometries and associated methods for measuring the fracture toughness of resin composites are noted in table 2.3 (Shah, 2008). Fujishima and Ferracane (1996) showed that among the first four methods, double torsion method was the most conservative while Chevron short rod method gave much higher fracture toughness.

The use of linear elastic fracture mechanics to understand the failure characteristics and properties of dental composite materials has increased in past years. Many researchers have examined the fracture toughness of dental resin composites using a variety of testing methods, including the single-edge notched beam method (Lloyd and Adamson, 1987; Ferracane *et al.*, 1987; Fujishima *et al.*, 1991a; 1991b; Johnson *et al.*, 1993; Uctasli *et al.*, 1993; Kim *et al.*, 1994), the compact tension method (Kovarik *et al.*, 1991; Kovarik and Fairhurst, 1993; Takeshige, 1994), the short rod with chevron notch method (Pilliar *et al.*, 1986; 1987; Mair and Vowles, 1987), the double torsion method (Goldman, 1985; Cook and Johannson, 1987; Montes-G and

Table 2.3: Various sample geometries and associated fracture toughness test methods (Shah, 2008)

Sample geometries	**Methods**
Single edge notch (SEN)	3-point beam bending
Compact tension specimen	Uniaxial tension
Chevron notch	Short rod design
Notched and grooved plate	Double torsion method
Disk shaped specimen	Brazilian disk test (diametral tensile test)

Draughn, 1987; Davis and Water, 1987; Truong and Tyas, 1988), the indentation hardness method (Ferracane, 1989; Higo *et al.*, 1991) and the ring specimen method (Sawa, 1993). The results of these studies are in general agreement that the K_{IC} of composites increases as filler volume fraction is increased. However, a review showed that many of these studies reported widely different values of fracture toughness for the same materials (Kovarik and Fairhurst, 1993). Because fracture toughness is a characteristic property of a material, its value should be independent of the mode of measurement.

It is hypothesized that the reason that different tests for K_{IC} provide different results for the same material lies in the difficulties in producing appropriate specimens and in conducting the test. The fracture toughness of certain materials may be influenced by the sharpness of the initial flaw from which the crack is propagated as well as by the specimen geometry. The test protocol for the single-edge notched test and the compact tension test (ASTM Standard E399, 1983), which was written for metallic materials, requires that the crack be propagated from a pre-crack produced by fatigue. Because it is very difficult to produce a pre-crack in a dental composite specimen of relatively small size, this procedure is rarely followed. However, at least two studies have shown that some materials display a lower value for K_{IC} when the failure crack is propagated from a pre-crack as opposed to a blunter notch created by molding the material around a razor blade (Ferracane *et al.*, 1987; Kovarik and Fairhurst, 1993).

In contrast to the single-edge notched procedure, the double torsion test does not require a preliminary pre-cracking procedure because the first crack produced in the test can be used to propagate subsequent cracks on the same specimen (Evans, 1973). Similarly, the short-rod test produces a region of stable cracking which serves as a pre-crack for the ultimate unstable crack propagation. However, it is questionable whether this stable crack growth region always forms, suggesting that the failure crack may actually be propagated from the relatively blunt chevron notch (ASTM Standard E 1304, 1997).

Elastic modulus

The elastic modulus or Young's modulus of composite resin materials is an important property, which can yield useful data related to the materials behavior. Elastic modulus can be measured by dynamic or quasi-static methods. Quasi-static methods are destructive, the most common are the tensile test or three or four point bending tests. In bending tests the span displacement and load applied are recorded. Plotting the initial straight-line portion of the stress-strain curve is a measure o the elastic modulus. Generally the results of static tests register lower values of dynamic elastic modulus (Anusavice, 2003; Braem *et al.*, 1986; Sabbagh, 2002).

As a property, elastic modulus is very important because it can be used as a material parameter and allows estimating the expected deformation for a material under a certain load. Elastic modulus indicates the relative stiffness of a material and it is measured by the slope of the elastic region of the stress/strain diagram in static tests. Elastic modulus plays an important role in the stress generated during shrinkage which accompanies the polymerization of resin composites.

Stress is a critical parameter for the success or failure of the adhesive interface and may lead to marginal gap formation. Elastic modulus obtained in *in vitro* conditions, at ambient temperature and in dry conditions, do not have the same value when the material is applied in the mouth, hydration and temperature conditions will change and along with aging would affect the visco-elastic behavior of the composite material (Helvatjoglu-Antoniades *et al.*, 2006). Contraction stress build-up occurs since shrinkage is obstructed and the material is rigid enough to resist sufficient plastic flow to compensate for the original volume (Davidson and Feilzer, 1997; Feilzer *et al.*, 1990a).

In the formulation and development of restorative dental composites, it is of ultimate importance to understand the elastic properties of the material in order to achieve the best clinical results. Ideally, the elastic properties of the restorative materials must be closely matched to that of enamel and/or dentin. This would then allow a more uniform masticatory stress distribution across the restorations-enamel/dentin interface. An imperfect match of the elastic values between the materials and the surrounding hard tissues will lead to marginal misadaptation and fracture problems.

When restoring an adhesive cavity, the composite material is bonded to the walls of the rigid tooth structure which restrains shape changing, except at the free surface, and further internal stresses will result. The magnitude of contraction stress was determined to depend, apart from the visco-elastic properties (Davidson and Feilzer, 1997; Dauvillier *et al.*, 2000), on the configuration factor of the restoration (ratio of bonded to un-bonded composite surfaces) (Davidson and Feilzer, 1997; Feilzer *et al.*, 1987; Uno and Asmussen, 1991). The elastic modulus of a composite must also be similar as possible to the material were it will be applied, in order for both materials to have analogous deformation. The tooth itself, however, is a composite of enamel and dentin, which elastically are totally different materials. From these materials the one with the lowest elastic modulus, dentin, with an elastic modulus of 18 MPa could be used as a standard (Willems *et al.*, 1992).

In many restorative materials the assumption of linear elasticity can be applied if they are uniform, homogeneous and isotropic (Chabrier *et al.*, 1999; Darvell, 2002). Inorganic filler reinforced resin-composites are considered isotropic materials; the filler particles are homogeneously embedded in the matrix and linked with the matrix phase through the coupling agent (Braem *et al.*, 1987). The binding between the two phases should be strong enough to allow sufficient stress transfer from the matrix to the filler particles. Different moduli, such as Young's, shear or bulk, arise from different modes of stress application. However, in the case of linear elasticity, these are inter-related via Poisson's ratio, the ratio of lateral to axial strain (Watts, 1994). A full comprehension of elastic behavior requires the values of all the above-mentioned moduli.

Several investigators determined elastic modulus and also Poisson's ratio thought various different experiments. Some of these procedures are static tests (Ikejima *et al.*, 2003; Chung *et al.*, 2004; Watts, 1994; Jager *et al.*, 2004; Chabrier *et al.*, 1999; Warfield *et al.*, 1968; Draughn, 1981; Boyer *et al.*, 1982; Papadogianis *et al.*, 1984; Feilzer *et al.*, 1990a; Van Meerbeek *et al.*, 1993; Kim *et al.*, 1994; Alster *et al.*, 1997; Kim K.H. *et al.*, 2002; Irie *et al.*, 2006; Feilzer *et al.*, 1990; Masouras *et al.*, 2008) and other dynamic tests (Nakayama *et al.*, 1974; Wetton, 1984; Braem *et al.*, 1986; Braem, *et al.*, 1987; Braem, *et al.*, 1989; Willems *et al.*, 1992 ; Labella *et al.*, 1999; Abe *et al.*, 2001; Suansuwan and Swain, 2001; Sakaguchi *et al.*, 2002; Rizkalla and Jones, 2004; Denisova *et al.*, 2004). Some mathematical models based on, but also improving, the older Voigt's and Reuss/Angew's rules of mixtures, have also been developed to predict Young's modulus of composite materials (Braem *et al.*, 1987; Chantler *et al.*, 1999; Sakaguchi *et al.*, 2004). However, data existing in the literature, for bulk and shear moduli of dental polymeric restorative materials are incomplete. In a study by Helvatjoglu-Antoniades *et al.*, (2006) high correlations in both dynamic and static moduli of elasticity were observed, although dynamic moduli were found to be higher than static.

Therefore, dynamic measurement of the Young's modulus is an alternative to quasi-static tensile tests. The strain interval used for the dynamic measurement of Young's modulus is small, which means in turn that stresses are small such that dislocation activity is negligible, as is the build-up of internal damage. A specimen then behaves more truly as a linear elastic solid, (Hauert *et al.*, 2009).

Adding rigid particles to a polymer matrix base improves elastic modulus since the rigidity of inorganic fillers is generally much higher than that of organic polymers. The composite modulus consistently increases with increasing particle content (Fu *et al.*, 2008), in this case for 10% filler weight fraction elastic modulus increased almost fifty percent in relation to the unfilled matrix (Pukanszky and Voros, 1993).

Dynamic elastic modulus always shows higher values then the value obtained with the four point bending tests, due to the different velocity of the applied load to specimens. When the applied load speed is increased static elastic modulus tends towards values obtained through the dynamic method (Braem *et al.*, 1986; Sabbagh, 2002; Ramalho *et al.*, 2006).

Hence, addition of rigid particles to a polymer matrix can easily improve the modulus since the rigidity of inorganic fillers is generally much higher than that of organic polymers. The composite modulus consistently increases with increasing particle loading (Fu *et al.*, 2008).

Elastic modulus of composite materials results in a complex interaction between the mechanical properties of the two phases of the composite components. In the scientific literature, several theories and equations exist (Ahmed and Jones, 1990) which were developed to describe and predict the values of the composite elastic modulus as a function of the percentage filler fraction. From the theories and equations available, the most common are the ones due to: Einstein, Mooney, Guth, Voigt and Reuss (Ahmed and Jones, 1990; Nielsen, 1967; Fu *et al.*, 2008).

Reuss's theoretical equations for the elastic modulus are determined by the following the equations;

$$E_{\mathrm{C}}^{\mathrm{lower}} = E_{\mathrm{p}}E_{\mathrm{m}}(E_{\mathrm{p}}(1 - V_{\mathrm{p}}) + E_{\mathrm{m}}V_{\mathrm{p}}) \tag{2.1}$$

$$E_{\mathrm{C}}^{\mathrm{upper}} = E_{\mathrm{p}}V_{\mathrm{p}} + (E_{\mathrm{m}}(1 - V_{\mathrm{p}})) \tag{2.2}$$

Where, E_{C} and E_{m} represent composite elastic and matrix elastic modulus, and V_{p} inorganic filler volume percentage.

The simplest arrangements of fibers in a two-phase material containing continuous fibers and matrix are series (Reuss) and parallel (Voigt), and assuming iso-stress and iso-strain criteria for these two cases, respectively, a lower-bound of the composite modulus and an upper-bound (equation 2.1) can be derived. Voigt's model gives a linear relationship between E_{C} and V_{p} and a gross over estimate of E_{C}. The modulus of real composites lies between these two bounds. These upper- and lower-bound models are applicable to most particulate micro- and nano-composites. Generally, the modulus of composites should be lower than the upper-bound predicted by equation 2.1 and higher than the lower-bound by equation 2.2 (Fu *et al.*, 1998), although it is possible for a composite to violate the Voigt-Reuss bounds due to Poisson's effect (Ma *et al.*, 2003).

To obtain a satisfactory understanding of the mechanical behavior of restorative composites in a wide range of strain rates, compressive tests for restorative composites must be undertaken under low strain rate during static loading and high strain rate during dynamic loading. The stiffness of a material determines its usefulness in applications where mechanical forces act on the material, and where rupture or excessive deformation could cause loss of function. This allows understanding the importance of elastic modulus. The property in which dental composite is most conspicuously deficient in comparison to amalgam is elastic modulus, where composite is typically several times lower. This lower modulus may allow enhanced deformation and dimensional change on occlusal surfaces under high stress which may lead to defect formation or enhanced wear due to increased surface contact.

Hardness

In the mechanical characterization of dental restorative composites the indentation test has to be carried out at micro level (load between 0.5 and 10 N) so that the contact depth is sufficiently deep in order to determine the bulk mechanical properties of these materials (Yap *et al.*, 2004a).

The hardness or microhardness test is simple to conduct but very susceptible to various sources of error. Surface finish is one of the variables which would influence interpretation of indentation results especially at low penetration depth (Yap *et al.*, 2004b; Barber and Ciavarell, 2000; Bec *et al.*, 1996; Wang *et al.*, 2002). As the surface roughness is increased, the hardness measured at depths comparable with the roughness scale deviates increasingly from the actual hardness (Bobji and Biswas, 1999). This is because at low penetration depth, the indenter may only touch a few peaks and the apparent stiffness of the material is lower.

It was noted that the effect of roughness on material surface estimation is negligible if the indentation depth is much greater than the surface roughness (Tabor, 2000). However this effect has to be quantified when considering the size of the reinforced filler particles in dental composite resins as well as the bulk material response.

Hardness is a very important material property used to characterize and rank restorative dental materials. Due to the relationship between hardness and other physical properties (O' Neil, 1967), hardness testing has found universal application. Hardness tests by indentation have the advantage of being simple, cheap, reproducible, and relatively non-destructive (Lysaght and DeBellis, 1969). Regarding the applied loads, classical hardness indentation tests are usually classified in two categories: macro-indentation tests for loads greater then 1 kg, and micro-indentation tests for loads inferior to 1 kg. microhardness tests are used in dental composite materials (Chung, 1990; Willems, 1992; Mota *et al.*, 2006). The most common methods to measure hardness of restorative materials is through Knoop and Vickers micro-indentation tests (Attin *et al.*, 2009). The Vickers hardness is defined as the resistance to permanent and or, plastic deformation caused by indentation and can be calculated as the applied load divided by the projected surface area of the indent left after indentation.

Vickers's microhardness test allows good sensibility, small dimension of indentation marks and it is less sensible to surface conditions. The procedure for microhardness must respect the requirements of the Standard ASTM WK27978 — 10 Standard Test Method for Microindentation Hardness of Materials (2010). microhardness measurement is dependent of time and applied load, for plastics, there is a 50% to 70% recovery in indentation depth and 5% in diagonal dimensions (Crawford, 1982) after load removal. Taking this into account and considering the type of material in study, as well as applied load and test conditions used by other investigators (Willems, 1992; Matos et. al., 2003) this condition guarantees correct assessment and determination of hardness values.

Assessing hardness values of restorative resin composite is fundamental. The overall properties of a composite are influenced by the type, size, and volume fraction of the filler particles and the degree to which the filler is bonded to the resin matrix (Condon and Ferracane, 1997). The type of matrix and the degree to which conversion occurs during polymerization also influence the properties, especially when aging occurs in the oral environment (Condon and Ferracane, 1997). The presence of filler particles increases the compressive strength and hardness of the polymer matrix (Van Noort, 1994). Li *et al.*, (1985) reported that changing the level of filler in composite altered the properties of hardness, water sorption, compressive strength, elastic modulus, and wear resistance (Mandikos *et al.*, 2001).

2.3.2 Tribological properties

Teeth may need restoring for a variety of reasons. Destruction of tooth substance caused by dental caries may result in the loss of considerable quantities of enamel and dentine. Trauma may cause fracture and loss of parts of teeth. In this case the anterior teeth are most vulnerable and those teeth affected may be otherwise sound and caries-free. A third factor causing loss of tooth substance is wear.

The main categories of wear that contribute to the destruction of dental tissues and restorative materials are (Powers and Bayne, 1992): physiologic wear (vital life functions); pathologic wear (disease and abnormal conditions); prophylactic wear (preventive measures) and finishing procedure wear.

In all of these, the actual wear situation may vary significantly as the substrates, opposing wear surfaces, the lubrication systems involved, and the abrasive particles may differ. Table 2.4 presents a classification of wear situations in dentistry that result from the combination of the different types of wear and the diverse circumstances (Mandel, 1991).

This often arises due to over brushing using an abrasive dentifrice but may also arise due to a peculiarity of the diet, working environment or habits of the patient. High frequency of exposure of teeth to acids in food and drink or from regurgitated gastric juice is of growing concern in relation to the wear of teeth involved. The parts of teeth which require replacement by a restorative material vary in size, shape and location in the mouth. Thus, at one extreme, it may be necessary to restore a large cavity which extends over a large area of surfaces of a molar tooth. An entirely different situation is the restoration due to an accident with loss of dental material volume. The requirements of materials used in these and other applications vary and it is not surprising that no single restorative material is suitable for all cases. For some situations the strength and abrasion resistance of the material may be the prime consideration. In other situations appearance and adhesive properties may become more important (McCabe and Walls, 2008).

Two-body abrasion occurs in the mouth whenever there is tooth-to-tooth contact. This is what most dentists call attrition. Abrasive wear may also occur when there is an abrasive slurry interposed between two surfaces, such that the two solid surfaces are not actually in contact, this is called three-body abrasion, with food acting as the abrasive agent, and occurs in the mouth during mastication. Abrasion is the key physiological wear mechanism that is present in dental materials during normal masticatory function.

One of the main objectives in wear studies is to determine the nature of the dependency between the mechanical properties of materials and their tribological behavior of the surfaces in contact. As the service environment is the mouth, dental restorative materials, and teeth, are subjected to very specific service conditions (Said, 2000):

- Temperature: −10 to 50°C;

Table 2.4: Classification of wear situations in dentistry (Mandel, 1991).

Intraoral wear event	Wear Type	Lubricant	Substrate	Opponent	Abrasive
			Physiologic causes of wear		
Noncontact wear	3-body	Saliva/food	Tooth/restoration	—	Food
Direct contact wear	2-body	Saliva	Tooth/restoration	Tooth/restoration	—
Sliding contact wear	2-body	Saliva	Tooth/restoration	Tooth/restoration	—
			Pathologic causes of wear		
Bruxism	2-body	Saliva	Tooth/restoration	Tooth/restoration	—
Xerostomia	2-body	—	Tooth/restoration	Tooth/restoration	—
Erosion	—	Saliva	Tooth/restoration	—	—
Unusual habits	2-body	Saliva	Tooth/restoration	Foreign body	—
			Prophylactic causes of wear		
Toothbrush and Dentifrice	3-body	Water	Tooth/restoration	Toothbrush	Dentifrice
Prophylactic pastes	3-body	Water	Tooth/restoration	Polishing cup	Pumice
Scaling and cleaning	2-body	Water	Tooth/restoration	Instrument	—
			Cutting, finishing, polishing		
Cutting burs/diamonds	2-body	Water	Tooth/restoration	Bur	—
Finishing burs	2-body	Water	Tooth/restoration	Bur	—
Polishing pastes	3-body	Water	Tooth/restoration	Polishing cup	Abrasive slurry

- Saliva as lubricant:
    - Complex protein-containing salt solution;
- pH values ranging from 1 to 9;
- Contact load: from 1 to 700 N;
    - Mastication load: from 6 to 130 N;
    - Contact stress of 200 MPa;
- Loading rate: from 1 cycle/s to 1500 cycles/day;
- Sliding distance: 30 km in 50 years tooth lifetime;
    - 0.5 – 1 mm/cycle;
    - 0.6 km/year.

Direct restorative materials are subjected to high values of contact and masticatory loads, loading rates, sliding distances and particularly environmental conditions. In such contact conditions wear is the major failure mode of dental composites. Wear of dental composites includes such diverse phenomena as adhesion, abrasion and fatigue. These mechanisms may operate either alone or in combination.

Most of the performed studies involve commercial composite materials and focus on the effect of curing time, and their reflection on the abrasive wear behavior. The wear compatibility of both materials in contact should be one of the concerns of the wear studies. However, the majority of studies do not consider the wear produced on the antagonist material.

During the past decade not only clinicians, but also patients have developed an interest in posterior composite resins. This growth in interest has resulted from a desire for aesthetic restorations, as well as to distance the more negative aspects of amalgam, namely its' metal character and toxicity. The demand for restorations with natural appearance in the posterior region and the controversy as to the mercury action of amalgam, although be its' excellent mechanical properties, have attracted researchers to focus on the improvement of the resin composites in order to be applied in posterior teeth restorations.

The more reliable way to validate the behavior of the composite materials is *via in vivo* studies. These are long term studies, time consuming, and often involve a small number of patients; therefore it is very difficult to extract results likely to apply to the general public. Due to these difficulties, *in vitro* studies seem to be a reasonable alternative. The first problem is to validate the results attained *via in vitro* studies with the ones executed *in vivo*. This correlation is very complicated as there are no standards for mechanical characterization of these composites, namely for abrasion tests (Condon and Ferracane, 1996). There are a large number of variables involved in the *in vitro* studies, and the type of tests used in experimental approach vary greatly between investigating teams (Condon and Ferracane, 1996; Hu *et al.*, 1999; Suzuki *et al.*, 1996; Condon and Ferracane, 1997; Wassel *et al.*, 1994; Gee *et al.*, 1996a; Xu *et al.*, 2004; Lim *et al.*, 2002; Ruddell *et al.*, 2002; Kim J.W. *et al.*, 2002; Zantner *et al.*, 2004; Nagarajan *et al.*, 2004; Flanders *et al.*, 2003; Willems, 1992; Zheng *et al.*, 2003; Li and Zhou, 2002; Kawai and Leinfelder, 1995; Leinfelder and Suzuki, 1999; Yesil *et al.*, 2008).

To understand the multiplicity of approaches on this subject, a summary of the most important variables was elaborated. In a considerable number of recent studies the approaches are not unanimous, namely: on the geometry and nature of the materials used for the tests, on the abrasive solutions, on the type of contact/movement and on the method used to evaluate the wear.

Among previously referred studies, large differences can be observed on the contact conditions, counterface material and abrasive agent. Concerning the antagonist material, metals (Hu *et al.*, 1999; Gee *et al.*, 1996a; Xu *et al.*, 2004; Willems, 1992; Li and Zhou, 2002; Kawai and Leinfelder, 1995; Manhart *et al.*, 2000a) and enamel (Condon and Ferracane, 1996; Suzuki *et al.*, 1996; Condon and Ferracane, 1997; Wassel *et al.*, 1994; Lim *et al.*, 2002; Yesil et al, 2008) are most frequently tested. However, some studies use polymers (Ruddell *et al.*, 2002; Leinfelder and Suzuki, 1999) or ceramics (Kim J.W. *et al.*, 2002; Flanders *et al.*, 2003) and one of them uses titanium as antagonist (Zheng *et al.*, 2003).

The existence or not of abrasive particles such as poppy seeds, Poly(methyl methacrilate) PMMA beads mixture in deionized water, water, etc., on the contact surface is another parameter that varies. The parameters in which the studies are similar include type of contact geometry (plane-sphere) and type of wear measurement (depth of the wear transversal profile). Most of the studies are based on experiments with simple movements, unidirectional or reciprocate. However, some studies try to use a contact with complex movement more similar to what happens in the mouth, through cycles that involve impact rotation and contra-rotation or cycles with different loads and paths to attain different types of wear.

Clinical trials could certainly be the best option to determine material wear characteristics; however, such trials are expensive and time consuming. Preliminary testing, applying an *in vitro* approach is therefore a cheap and effective way to characterize new potential restorative materials. The major challenge to develop a laboratory test program, whose results could be accurately used to predict the wear behavior of a specific component, or biological practical cases, is certainly the selection of the type of contact, the relative movement and the operating variables. The complexity of the tooth contact makes it even more difficult to establish the most suitable technique. Different simple test types have been adopted. Yesil *et al.*, (2008) used the Oregon Health Sciences University (OHSU) oral wear simulator to produce abrasive wear and attrition; Manhart *et al.*, (2000a) used a fatigue simulator (Munich Artificial Mouth, Willytec, Munich, Germany), which simulates occlusal contact wear in a two-body sliding-wear test. Specific design equipment with cyclic sinusoidal pattern of loading in order to simulate the two-body wear, Shortall *et al.*, (2002); Leinfedler-Suzuki wear simulators; OHSU (Turssi *et al.*, 2005) and Ivoclar Vivadent are the more common chewing simulators (Heintze *et al.*, 2011). Some of the these wear methods/apparatus with elaborated movements are most similar to the tooth contact, however make it difficult to determine which wear mechanism produce specific damage, making it almost impossible to extrapolate or compare results obtained with different equipments.

In 2001 the International Organization for Standardization (ISO) technical specification on the wear by two-and/or three body contact describes eight different wear methods (ISO 14569-2, 2001). Furthermore, no detailed assessment of the eight methods had been carried out and no information has been given whether the methods are validated and the devices with which the methods are performed are qualified for that purpose (Heintze *et al.*, 2008).

A recent review on wear simulation *in vitro* concluded that — when following the United States Food and Drug Administration (FDA) guidelines on good laboratory practice (FDA Part 58 52 FR 33780, 2004) — only the expensive MTS wear simulator (Minnesota method) is a qualified machine for testing wear *in vitro* (Heintze, 2006). The force exerted by the hydraulic actuator is controlled and regulated during all movements of the stylus. All the other simulators lack control and regulation of force development during dynamic loading of the flat specimens. This may be an explanation for the high coefficient of variation of the results in some wear simulators for composite materials (28% – 40%) and the poor reproducibility of wear results if dental databases are searched for wear results of specific composite materials (difference of 22% – 72% for the same material). A round robin test evaluating the wear of ten dental materials (eight composite materials, one ceramic and one amalgam) with five wear simulation methods (ACTA, Munich, OHSU, Zurich, Ivoclar) showed that the results were not comparable, as all the methods follow different wear testing concepts (Heintze, 2006). A good compromise with regard to costs, practicability and robustness is the Willytec chewing simulator (Heintze, 2006), which uses weights as the force actuator and stepping motors for vertical and lateral movements (Willytec, 2001). Force measurements have revealed that in the beginning of the stylus/specimen contact phase the force impulse is 3 – 4 times higher during dynamic loading than during static loading (Heintze, 2006). Sliding is an essential component of a wear testing method, as a material is stressed in terms of micro-fatigue only when a stylus slides over the specimen. In the Ivoclar method, a lateral movement of 0.7 mm increases the wear of a specific composite material by about eight times (Heintze, 2006). As far as the number of loading cycles is concerned, tests with a number of composite materials subjected to the Ivoclar wear method have shown that about 40% of the final wear occurred during the first 10,000 cycles (Heintze, 2006). It has been well documented in the literature that wear increases with the increasing number of cycles. Most *in vitro* wear test methods demonstrate a running-in phase with a steep increase in wear in the initial phase and a flattening of the curve thereafter.

From a certain point onwards, wear increases in an even linear pattern (Kunzelmann *et al.*, 1998). When correlating material properties to the wear results of 23 composite resins subjected to the Ivoclar method, some parameters could be identified and incorporated into a formula to predict wear (Heintze *et al.*, 2007). In this wear formula: the following parameters were identified as contributing to a high wear rate: low fracture toughness, high modulus of elasticity, low Vickers hardness, high particle size and high volume content of inorganic components. In the

1970s and 1980s it was thought that *e.g.*, surface hardness of the ceramic material determines enamel wear (DeLong *et al.*, 1989). Studies in the 1990s, however, concluded that surface hardness is no predictor for wear of the opposing enamel (Seghi *et al.*, 1991; Magne *et al.*, 1999).

The use of biological materials, either in the abrasive slurries or as one of the contacting materials could be another problem because it is difficult to guarantee minimal control in shape, dimension and hardness; therefore the reproducibility of the test conditions could be a difficult task. Most published studies aim to investigate the wear of the material composites, but the wear of the opponent body is not considered. Knowing the wear resistance of the material in study is a key factor in materials development, but it is also very important to know how and how much the composite wears the antagonist material, natural tooth, restorative or prosthetic material. In the gathered studies not all evaluate the antagonist wear (Condon and Ferracane, 1996; Suzuki *et al.*, 1996; Condon and Ferracane, 1997; Williems, 1992; Zheng *et al.*, 2003, Yesil et al, 2008; Heintze *et al.*, 2007; Heintze *et al.*, 2011; Heintze *et al.*, 2008).

By definition wear is not a basic material property, but a system response of the material. Any material can wear by a multiplicity of mechanisms; adhesion, abrasion, fatigue and erosion. These mechanisms are influenced by factors such as, temperature, loading conditions, pH, presence of slurries and antagonist materials. The various mechanisms that result in wear are based on; i) physical mechanisms of material removal or displacement and ii) operational mechanisms such as mechanical action (rolling wear, sliding wear, etc.) and material interaction (metal versus metal, teeth versus resin composite, etc.).

Regarding physical mechanisms, in general, it is possible to distinguish four main types of wear processes':

Adhesive wear

Adhesive wear occurs when one surface bond to another, and with subsequent motion, rupture occurs in one of the materials. Therefore there is transfer of material from one surface to another. The sliding wear volume removed is proportional to, sliding distance, applied load, wear coefficient and inversely proportional to the hardness of the softer material. Wear coefficient can vary several magnitudes depending on the materials, the surface roughness, normal load, and the existence of particles between contacting surfaces.

Abrasive wear

Abrasive wear occurs when a hard asperities surface of a material or a hard, loose particle trapped between surfaces plastically deforms or cuts a surface as a result of motion. The former type of abrasion is termed two-body abrasion, whereas the latter is termed three-body abrasion. If the particles are carried by a gas stream or a flowing liquid then, in engineering, this is described as erosion. In general, abrasive wear is proportional to the hardness of the materials in contact, the geometry of the abrasive particles, the load and the sliding distance. As with adhesive wear, the wear coefficient can vary greatly and be influenced by the degree of freedom of the abrasive particle or asperity (Bayer, 1990). The resistance of a material to abrasive wear is fairly constant when abrasive is much harder then the material. As the hardness of both become similar and the abrasive action approaches polishing, wear resistance generally improves by one or two orders of magnitude (Bayer, 1990).

Fatigue wear

When one surface slides over another there is a zone of compression in the material ahead of the motion. Unlike abrasive and adhesive wear which are accompanied by loss or displacement of material; this type of wear requires multiple interactions. Plastic deformation of the material produces a zone of tension behind the motion. Cracks nucleate in the subsurface and propagate as a result of repeated cycles at a depth governed by the material properties'. Eventually these cracks propagate to the surface and the material that is surrounded by the cracks is lost. This displaced material may itself form wear debris and cause three-body abrasion.

Corrosive wear

If a chemical reaction layer forms on a surface then it may be scraped away by contact with the counterface. A fresh reaction layer forms on the exposed surface which is subsequently removed on the next encounter between the surfaces (Gahr, 1987). The material which is removed results in debris which may agglomerate into larger particles.

The interaction and simultaneous occurrence of several physical mechanisms in actual wear is very common. An adhesive wear fragment may be formed through surface weakened by fatigue, and in turn this fragment abrades the surface through several deformation cycles producing a larger fatigue wear particle.

The wear classification second to operational mechanisms is based on the materials, environment, and motion involved (Gahr, 1987);

- Dry or lubricated sliding wear;
- Rolling wear;
- Impact wear;
- Filtering;
- Metal/metal wear
- Mild wear;
- Severe wear;
- High temperature wear.

Each of these categories involves different combinations of basic wear mechanisms, thus illustrating the influence of the conditions of and around wear contact.

In dentistry it is very common to find wear terms such as, attrition, abrasion and erosion. These expressions are used to describe the wear of teeth and dental materials. Attrition describes surface loss at sites of occlusal contact and abrasion is used to describe wear at non-contacting sites together with a number of other situations which cannot be ascribed to erosion or attrition (Smith, 1989). However, it has long been recognized that it is difficult to designate many individual cases to any one category (Smith and Knight, 1984). The three terms have led to some confusion because they describe clinical manifestations rather than underlying mechanisms of wear.

Most dental structures are considered to be biphasic with one phase embedded in the other. Thus, enamel consists of prismatic enamel embedded in interprismatic enamel, amalgam consists of unreacted alloy cores embedded in the reaction alloys, and composite consist of glass fillers embedded in a polymer resin.

The wear of these structures can be understood by considering the relationship between slurry wear and sliding contact wear on the various materials.

Slurries tend to preferentially abrade the softer phase leaving harder material protruding from the surface. During sliding contact wear, there are a number of consequences for these protrusions. Regarding composites the hard filler particles may remain intact and transmit the sliding force to the surrounding matrix, resulting in micro-cracking. Eventually the cracked matrix is no longer able to retain the particles which are then displaced. With amalgams the surface protrusions are smeared over the remaining surface, resulting in the maintenance of a relatively smooth surface. Clinically, when active wear is taking place the wear facets appear smoother than the surrounding amalgam which has signs of corrosion. In materials such as enamel and porcelain the two phases of the materials are of relatively equal hardness and consequently slurry wear does not tend to cause protrusions. However, as discussed earlier, these materials may be subject to subsurface cracking as a result of fatigue. It appears that the dental tissues are sensitive to the environment and the wear rate of both enamel and dentine is increased in an acidic environment (Mair *et al.*, 1996).

Wear resistance of materials can be improved by decreasing the size of the interparticle spacing and the size of the particles (Mair *et al.*, 1996). The former decreases the effect of slurry wear, especially if the spacing is less than the size of the abrasive particles. Smaller particles result in smaller surface protrusions, which decrease the friction of sliding contact. These considerations have been very important in the development of the present generation of posterior composites which have filler particles with an average diameter inferior to 1 μm compared with 3 μm – 10 μm in the first generation of posterior composites. The action of both slurry and contact wear on dental materials play an important role, determining their potential to damage the opposing teeth or restorations. Protruding particles act as “sandpaper”, resulting in abrasion of the opposing surface (Mair *et al.*, 1996).

The composition of resin-based dental composites has evolved significantly since the materials were first introduced to dentistry more than 50 years ago. Until recently, the most important changes have involved the reinforcing filler, which has been purposely reduced in size to produce materials that are more easily and effectively polished and demonstrate greater wear resistance. Wear is considered to be a lesser problem for current materials as compared to those that were the standard of care a decade ago, in large part due to refinement in the size of the reinforcing fillers which significantly reduced the magnitude of abrasive wear (Ferracane, 2011).

“The days of wear tests which do not help our understanding should be behind us. It is essential that those who study wear, in dentistry, should liaise with tribologists who have many years experience with materials similar to those used in our profession” (Mair *et al.*, 1996).

2.4 Parameters which change composites behavior

The mechanical and tribological properties of dental composite systems are known to depend to a large degree on reinforcement filler content; volume or weight percentage, average particle size and filler size distribution.

2.4.1 Effect of filler content on wear

In the last decades filled polymers have gained special interest due to their superior mechanical properties.

Considering the complex clinical environment, the wear process of dental materials is very complicated. Traditionally, wear of composites has been explained simply in terms of the effects of the amount of filler, the nature of the matrix, or the coupling agent bond (Lim *et al.*, 2002;

Söderholm and Richard, 1998; Venhoven *et al.*, 1996; Masouras *et al.*, 2008). Due to applied investigations, many fillers systems, monomers systems, and coupling agents have been employed to improve the mechanical properties and wear resistance of dental composites. Many studies suggest that particle technology, particularly the composition, size and volume, occupied by the filler particles within a composite formulation, have the potential to influence the wear performance of a composite (Jøgersen *et al.*, 1979). Decreasing the inter-particle spacing, which is best, achieved with smaller filler particles, improves the wear resistance of composites. Reducing particle distance results in the protection of the softer resin matrix from abrasives, thus reducing composites wear. This reduction on inner-particle spacing in composites is achieved by two ways; decreasing filler size and increasing the volume fraction of inorganic composition. Researchers Jøgersen *et al.*, (1979) and Jøgersen and Asmussen, (1978) and several clinical research data sustain that the critical inter-particle spacing for dental composites is around 0.1 μm – 0.2 μm (Lim *et al.*, 2002; Lambrechts *et al.*, 2006a). Bayne *et al.*, (1992) suggested that in a microfilled composite, very little (< 6.0 vol.%) microfilled was required theoretically to provide matrix protection. Taking these studies into account Pallav *et al.*, (1989) state that; 15% in vol. should be the optimum value of filler reinforcement to achieve reasonable wear resistance for small-particle hybrid composites, if the fillers are well distributed.

Filler particle clustering is thought to be one of the disadvantageous factors on the performance of particle reinforced composites. Particle clustering may originate from the filler manufacturing process. According to Söderholm (1985), the silane coupling agent tends to form aggregates on the filler surface. Aggregates, however, do not form a very stable bond between filler and resin. Mohsen and Craig (1995) suggested that dispersion of the filler in the monomer mixtures involved wettability of the filler surface by the monomer, dispersion of the particles, and stabilization. If this is not achieved, microfilled particles may not be homogeneously dispersed in the resin matrix.

Jaarda (Jaarda *et al.*, 1993; Jaarda *et al.*, 1996) examined commercial composites through the use of SEM and digital imaging techniques to evaluate qualify and quantify composites in terms of the number, sizes, and area occupied by the inorganic phase. These studies revealed that commercial composites contained significant amounts of filler particles larger than stated in the manufactures literature.

Several studies suggest the importance of filler content and coupling agents in establishing parameters such as strength and abrasion resistance (Venhoven *et al.*, 1996; Condon and Ferracane, 1997; Condon and Ferracane, 1997a; Beatty *et al.*, 1998). Three-body abrasion involves the cutting of soft material by hard abrasive particles; therefore the increase of hard inorganic filler to soft resin matrix should improve the composite's overall resistance to wear. Coupling agents improve the adhesion between a polymeric phase and dense inorganic phase, leading to better load transfer and increasing wear resistance.

Beatty *et al.*, (1998) indicate that no direct relationship exists between filler pre-treatment and wear resistance for microfilled composites. It is possible that this phenomenon was due to filler-resin interaction or to a difference in distribution of filler clusters in the resin matrix (Lim *et al.*, 2002).

More recently, non-bonded microfillers have been added to composites to reduce polymerization contraction stress (Condon and Ferracane, 1998). Adding these particles that are neither treated nor coated with a non-functional silane did not have a negative effect on mechanical properties, and in fact usually improved fracture toughness (Hilton *et al.*, 1997).

Most commercial microfilled composites contain pre-polymerized resin fillers. However, the trend is to use homogeneous distributed nanoparticle dental composites. These particles are very similar in size to the microfillers used in current commercial dental composites.

From Jøgersen studies (1979, 1978), it may be concluded that the use of finer particles for fixed-volume-fraction of filler results in decreased inter-particles spacing and reduced wear. Abrasion is reduced through the "protection-hypothsis". The friction coefficient is reduced through increasing fracture toughness. In addition to inter-particle spacing, another key factor in wear of composites is good stress-transfer ability at the matrix, or increase in filler surface area.

In general, restorative dental composites which contain large reinforcement particles ($> 1\ \mu$m) have good resistance to two-body wear, but have unacceptably high abrasive (three body) wear rates (Condon and Ferracane, 1997). Microfilled and small particle hybrid composites tend to display abrasion resistance competitive with amalgam, but their two body abrasion sensitivity may predispose them to catastrophic fracture (Lim *et al.*, 2002; Mair *et al.*, 1996).

In the microfracture mechanism for wear, Roulet (1987) considered subsurface fatigue to be of major importance and demonstrated the presence of fatigue cracks on the composite surface.

Mazer *et al.*, (1992) also investigated the mechanisms of failure, particularly those containing submicron-sized fillers. It was determined that generalized wear-rate was linear, and it was shown that the marginal defect was cohesive in nature and that this type of defect, which is inherent in submicron-type posterior composites, was probably due to tensile fatigue failure. Due to higher modulus of the filler particles than the interposed resin matrix, filler particles were hypothesized to compress the intervening matrix during mastication and produced localized cracks. During cyclical loading, the surface is plastically deformed and microcracks are generated within the material. These microcracks eventually coalesce, resulting in a crack running parallel to the surface followed by the eventual loss of a wear particle (Wassel *et al.*, 1994).

2.4.2 Effect of particle content on the mechanical properties

In the last decades the size of the filler particles in dental resin composite materials has decreased considerably, from $8\ \mu\text{m} - 30\ \mu\text{m}$ in traditional composites' to $0.7\ \mu\text{m} - 3.6\ \mu\text{m}$ for modern small-particle composites'. An important reason for decreasing the filler particle size is the difficulty encountered when polishing coarse particle composites.

The results of previous study showed that, of the four evaluated parameters (tensile strength, hardness, *in vitro* wear and roughness); only the *in vitro* wear was dependent on the amount of microfine filler. It was concluded that the *in vitro* wear test was the most suitable for discriminating between differently filled composites.

Studies have shown the influence of the size and shape of the filler particles on the mechanical properties of dental composites (Sabbagh *et al.*, 2004; Kim K.H. *et al.*, 2002; Adabo *et al.*, 2003). These particle characteristics determine what Braem *et al.* (1986) called "maximum particle packing fraction", which is the ratio of true particle volume to the apparent volume occupied by the particles in the composite. According to the authors, important mechanical properties, such as Young's modulus, depend upon this ratio. Also, the presence of small spherical particles has been related to a high percentage of filler in the commercial composites, improving the mechanical properties (Kim K.H. *et al.*, 2002).

One of the most noticeable advances in composite filler technology involves the incorporation of silica fillers of nanometer size (Mitra *et al.*, 2003). Nanofillers are found in microfilled and some hybrid composites that can be considered predecessors of the newer nanoparticulate composites. A study evaluating the mechanical properties of experimental composites with or without nanofillers was carried out by Musanje and Ferracane (2004), who observed a positive effect of the presence of nanofiller particles, expressed by an improvement in flexural strength, surface hardness and fracture toughness (K_c). Nanoparticulate composites bring the added perspective of creating another category of universal resin composite that joins the optical properties and the polishability required for anterior restorations with the mechanical properties demanded for posterior restorations (Mitra *et al.*, 2003; Moszner and Klapdohr, 2004; Beun *et al.*, 2007). However, relatively little information about these new materials is available in the dental literature.

In a study by Rodrigues *et al.* (2008), the flexural strength of the composites was not affected by the differences of three orders of magnitude in average filler size between the two composites. This is in accordance with other studies that showed no significant difference in flexural strength between a nanofilled and some microhybrid composites (Musanje and Ferracane 2004; Moszner and Klapdohr, 2004; Beun *et al.*, 2007).

According to Mitra *et al.* (2003), a nano-filled composite with a high filler loading, was obtained due to the wide particle distribution and the spherical shape of the filler particles, equaling physical and mechanical properties of a microhybrid composites, including the flexural strength. The filler content of this composite is composed of 20 nm non-aggregated silica particles and nanoclusters of 75 nm agglomerated particles that are reported to reach a 0.6 μm $-$ 1.4 μm size range that, in turn, corresponds to the average size of the filler particles of the microfilled composite. In addition, both composites contain spherical-shaped particles that have been associated with reduced stress concentration as compared with the sharp edges present in irregular-shaped filler particles (Kim K.H. *et al.*, 2002). Other studies showed that mechanical properties such as Young's modulus and composite hardness depend mainly on the filler load

Venhoven *et al.*, (1996) studied the influence of average filler, using three different particle size dimensions on a three-body wear machine. They reported that filler size had a distinct effect on the wear. From the regression analysis it became clear that there was a significant linear coincidence when the wear rates of the composites containing 2.3 μm filler were compared with their composites with 1.3 μm reinforcement particle. These authors also report that a larger filler particle size had an adverse effect on the wear behavior, which indicates poorer mechanical coherence, attributing this to several effects. First, larger particles have a less favorable surface area-to-volume ratio. So *per* unit volume there are fewer interfaces between particle and resin, which can retain the particles in the composite. Second, larger particles will, on average, protrude further through the surface and as such their cantilever will be longer; this will lead to a higher angular momentum, causing earlier breaking out of the surface of a particle. Finally, the breaking out of larger filler particles will leave deeper holes. However, the relationship between wear and particle size is not linear (Venhoven *et al.*, 1996). Compared with composites containing glass-ceramic fillers of 1.3 μm and 2.3 μm, the composites containing the reinforcement particles with the intermediate size of 1.5 μm in all cases showed a higher wear rate than could be expected after interpolation between particle sizes.

The explanation may therefore be found in the inter-particle spacing, which depends on the filler particle size and filler load by volume. The shorter the distance between the particles, the more the matrix will be protected against the erosive activity from the hard fibers in the food bolus. A distinct decrease in wear conceivably occurs at the points where the inter-particle spacing drops below the average size of the food fibers. When the wear rates are interpreted this way, then this point may be somewhere between 1.3 μm and 1.5 μm.

It has been found that elastic modulus is the mechanical quantity most highly correlated with volumetric filler content (Draughn, 1981; Boyer *et al.*, 1982). This correlation has been quantified before by Boyer *et al.* (1982). They investigated the elastic modulus *vs.* the volumetric filler content of 10 composites and found a correlation coefficient of 0.91. Comparison of the elastic moduli of 30 products, as determined above, with volumetric filler percentages compiled from the literature showed an exponential regression between elastic modulus and the volume percent of inorganic filler. The correlation coefficient calculated from the logarithmic transformation is 0.92, which illustrates the accuracy and reliability of this new method. Although elastic modulus is supposed to be independent of the particle size, it should be dependent on the maximum particle packing fraction, which is defined as the ratio of true particle volume to the apparent volume occupied by the particles (Draughn, 1981). This ratio is determined by the particle shape and size distribution. This could explain why the ranking of the elastic moduli values does not perfectly match that of the volume percent of inorganic filler. Furthermore, the use of this ratio may well lead to the engineering of composites that retain close particle-to-particle distances, this type having been designated as resin-bonded ceramics by Cross *et al.* (1983). They result in high elastic moduli, since more energy is dissipated in the ceramic filler and less in the resin binder (Cross *et al.*, 1983). However, there is a significant risk with high filler fractions. If de-bonding occurs in such filler-rich composites, mechanical properties such as tensile strength and compressive strength will deteriorate more rapidly than otherwise, since the particles are close to, or even in contact with each other. Since there is no bond between them, the strength will be drastically diminished (Söderholm, 1985). This could explain why many of the posterior composites are in the elastic modulus range of the microfilled composites (Braem *et al.*, 1986). Although, clinically, these low-filler composites seem to be sufficiently wear-resistant in stress bearing areas (Lambrechts *et al.*, 1984), the percentage of collapsed fillings rises dramatically after four years of clinical service (Lambrechts *et al.*, 1985).

Filler size is only one of several parameters affecting the overall properties of a resin-composite. The filler type, shape and amount, as well as the efficient coupling of fillers and resin matrix, contribute to the material performance. Properties such as compressive or flexural strength, hardness and elastic modulus improve as the filler content increases. At the same time polymerization shrinkage decreases.

2.4.3 pH effect

The warm, wet nature of the mouth is a very specific environment that demands a great deal from resin restorative materials, especially in order for these materials to maintain reasonable stability in terms of mechanical and tribological behaviors. Bathed in saliva with an average pH near 7, humidity of 100% and constantly altered environmental conditions, namely temperature and pH, due to the introduction of food and even due to dental treatments, these resin restorative materials have to show their operating capabilities in such an environment. Within the last few years, several new types of resin composites have been introduced to the market. The new classes are packable (condensable) composites, universal composites, reinforced microfilled and nano-filled composites. The restorative materials and teeth are subjected to a high range of physical and chemical conditions. Some of these variables were already objects of study but their influence on the mechanical and tribological behavior is not well known. The warm, aqueous, chemical environment is one aspect of the oral environment that has an appreciable influence on the *in vivo* degradation of resin-composites. The *in vivo* evaluation of restorative materials is generally, besides ethical reasons, very complicated, time-consuming and expensive. Thus, *in vitro* aging studies are more often used and performed in various aging media. Among these, the most frequently used are water and ethanol/water solutions (Ferracane *et al.*, 1998; Wu and McKinney, 1982).

It is well established that the exposure of resin composites to an aqueous environment lowers their mechanical properties (Øysæd and Ruyter, 1986a; Calais and Söderholm, 1988; Calais and Söderholm, 1990). When stresses are applied to composites, these are absorbed by the resin matrix and transferred through the coupling agent to the stiffer, inorganic filler particles.

Several mechanisms have been suggested to explain the decrease of mechanical properties after aging in various liquids, mostly softening of the resin matrix and/or bond failures occurring in the outer layer of the filler, in the silane coating, at the silane-matrix interfacial region or within the matrix. It is not known where such “interphase” failures are induced, and which of the above regions can be regarded as the weakest links of a dental composite (Soderhölm and Roberts, 1990).

In the last decades, composite materials have shown good clinical longevity (Jokstad *et al.*, 1994), although problems due to fractures, increased surface roughness and micro leakage have been reported. Failures due to deteriorated mechanical properties and wear may be explained by the influence of moisture from the oral environment on the composite and bonding materials, leading to degradation and erosion (Øysæd and Ruyter, 1986a; Örtengren *et al.*, 2001; Geurtzen, 1998). Moisture in the oral environment may cause chemical degradation and erosion of composite resin materials due to hydrolysis or enzymatic hydrolysis (Larsen and Munksgaard, 1991). The sensitivity of dental composite resin materials to chemical degradation depends on the different monomers constituting the resin matrix and on the degree of its cross-linking (Geurtzen, 1998; Ferracane, 1994). Furthermore, the type of filler and its volume fraction will affect the water sorption and solubility behavior (Söderholm *et al.*, 1984; Øysæd and Ruyter, 1986b). Therefore, the presence of water is of crucial importance to the deterioration of composite resin materials as well as varying pH values in the oral environment and on tooth surfaces (Lingstrom *et al.*, 1993). The reduction of pH value as a consequence of sugared foods and drinks is well known. While enamel is partially able to remodel itself therefore resisting this kind of attack (Stookey, 2008), restorative materials should be insensible to pH variations although lower pH values have been known to affect negatively the wear resistance of composite resin materials (Chadwick *et al.*, 1990). However, the influence of pH on composites’ tribological behavior is not quite well understood, especially after aging.

Chapter 3

Materials, techniques and experimental procedures

3.1 Introduction

Chapter 3 is divided into three parts; materials, testing equipment and experimental procedures and a pH aging study.

In materials, presented are the composite materials investigated in the study as well as amalgam used for comparison. The section is divided into; commercial composites; produced composites; amalgam and antagonist materials and others.

Testing equipment is divided into two sections; first, a section where the equipment used to determine the mechanical properties of all studied material is presented, and second, the description of the apparatus associated to the tribological tests which are used to determine the behavior of the dental materials. Finally all experimental procedures and result analysis are exposed and explained.

3.2 Tested materials

3.2.1 Light curable commercial composites

The aim of this study is to characterize the mechanical and tribological behavior of commercial posterior restorative dental composites, and thus, the decision to select commercial composites that in general cover the major types of condensable composites. This selection should cover not only particle average dimension and matrix but also reinforcement type. “Packable” resin composites have been available since 1997, and dentists often use them as amalgam substitutes for the restoration of posterior teeth. They purportedly offer the advantages of having handling characteristics similar to those of amalgam, light curability in thicker increments than traditional resin composites, and less shrinkage.

The characterizations study focused on ten condensable resin composites used for posterior restorations. Table 3.1 and table 3.2 summarizes information regarding: matrix composition and reinforcement filler, the latter being subdivide into type, average particle dimension and percentage of fraction, in volume and/or weight.

Some of the studies and/or materials here presented are limited to the materials available in the market and also depended on the good will of manufactures and their official dealers.

Table 3.1: Main composition of the composite materials investigated as given by the manufacturers, matrix composition, type of reinforcement filler (constituents, dimension of particles and volume/weight fraction).

			Reinforcement filler		
Commercial designation	**Manufacturer**	**Matrix**	**Type**	**Dimension** [μm]	**Vol./Wt. Fraction** [%]
Filtek P60	3M Espe GmbH, Seefeld, Germany	TEGDMA Bis-EMA UDMA	Zirconia/silica	0.6 (0.01-3.5)	61/83
Prodigy Condensable	Kerr	Bis-GMA	Barium glass	0.6	59/79
Surefil	Dentsply/Caulk Inc. Milford, CT, USA	Urethane modified Bis-GMA, TEGDMA	Barium/silica glass	Mixture of different size	65.2/81.5
Synergy Compact	Coltène, Altstatten, Switzerland	TEGDMA Bis-GMA Bis-EMA	Strontium/ barium Silica	0.6 (0.04-2.5)	59/74
Quixfil	Dentsply, Konstanz, Germany	Bis-EMA, UDMA, TEGDMA, TMPTMA Di- and trimethacrylates	Silanated strontium aluminum sodium fluoride phosphate silicate glass	Mixture of different size particles	66/86
CeramX	DeTrey Dentsply GmbH, Constance, Germany	Methacrylate modified polysiloxane^{C}, dimethacrylate resin	barium-aluminum-borosilicate glass, methacrylate functionalised silicon dioxide nanofiller	Glass filler size: 1.1 – 1.5 μm; Nanoparticle size: 2.3 nm	57/76

Table 3.2: (Continued from table 3.1). Main composition of the composite materials investigated as given by the manufacturers, matrix composition, type of reinforcement filler (constituents, dimension of particles and volume/weight fraction).

			Reinforcement filler		
Commercial designation	**Manufacturer**	**Matrix**	**Type**	**Dimension** [μm]	**Vol./Wt. Fraction** [%]
Alert	Jeneric-Pentron, Wallingford, CT, USA	Bis-GMA, dimethacrylates groups	Microfilamentous glass fiber, silicon dioxide, Barium-borosilicate glass, microfine silica	0.8 μm irregular shape particles (glass fibers: 60-80 μm in length)	67/84
Filtek Supreme	3M Espe GmbH, Seefeld, Germany	Bis-GMA, Bis-EMA, urethane dimethacrylate, Triethylene glycol dimethacrylate	Silica nanofiller, zirconia/silica nanocluster	75 nm silica nanofiller and cluster size range is 0.6 to 1.4 μm	57.5/78.5
Pyramid Dentin	BISCO Schaumburg, IL, USA	Bisphenol-A diglycidylmethacrylate, Ethoxylated bisphenol A dimethacrylate, Triethyleneglycol dimethacrylate.	Glass filler	1 – 15 μm	80/75.2
Pyramid Enamel	BISCO, Schaumburg IL, USA	Ethoxylated bisphenol-A dimethacrylate, Triethyleneglycol dimethacrylate	Glass filler	1 – 15 μm	78/65.2

UDMA: Urethane dimethacrylate; Bis-GMA: Bisphenol A polyethylene glycol diether dimenthacrylate; TEGDMA: Tri[ethylene glycol] dimethacrylate; Bis-EMA: bisphenol A polyethyleneglycol diether dimethacrylate; TMPTMA: Trimethylol propane trimethacrylate.

All studied materials are packable composite resins, with volume percentages ranging from 59% to 70%, and in terms of weight from 73% to 86%. Although small range in filler fraction is not very different ≈ 10% (in weight and in volume) the manufactures' approach is not exactly the same concerning reinforcement material, varying in dimension and type.

From the selected composites two are clearly in terms of average particle dimension, nanofilled; CeramX and Filtek Supreme. CeramX, from Densply-DeTrey, presents barium-aluminium-borosilicate glass ranging from 1.1 μm to 1.5 μm and methacrylate functionalised silicon dioxide nanofiller of 2.3 nm. Filtek Supreme is characterized with reinforcement particles of zirconium oxide; of 2 nm – 5 nm and 20 nm – 75 nm and some nanoclusters ranging from 0.6 μm to 1.4 μm.

The other composites in the study have very similar average particle dimension ≈ 0.6 μm, and thus are considered to be all microfilled, despite some having wider ranges of particle dimension, namely the ones from Dentsply, QuiXfil (0.8 μm – 10 μm) and Surefil. Although manufacturers omit information regarding average particle distribution, from SEM observations, Surefil presents many large particles of *circa* 20 μm.

The majority of commercial composite materials are trade marks, and companies inform the consumer/users about their constituents but not the amount and percentage of each. This is true both for particle distribution size as well as organic matrix.

Organic matrix should be composed of one or more monomers to allow for good cross-linking when cured, in order to be resistant and stable. The most common dimethacrylate resin monomers for use in dental composite materials today include the aromatic Bis-phenol A derivative, Bis-GMA, and, in some cases, the aliphatic urethane dimethacrylate UDMA. In the group above the majority of the resins studied have in their constitution: Bis-GMA, UDMA, triethylene glycol dimethacrylate (TEGDMA), ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA).

Even though manufacturers indicate which elements constitute a composite they do not inform explicitly of the exact portions, thus commercial composites are treated like "black boxes". These material systems have to be approach, an evaluation of mechanical or physical is formulated based on the input-output characteristics of the system without consideration of the internal functioning of the system.

3.2.2 Produced composites

Filler content variation As stated before, results of mechanical/tribological properties of commercial composites are very difficult to correlate with their constitution taking into consideration that their exact design is not known (for users). In order to elaborate a parametric study of resin composite behavior it is very important to determine the influence of its main components; organic matrix and inorganic filler. In order to understand the influence of each component, a commercial matrix was fixed and the reinforcement particles were varied. This variation was first in volume percentage, of same filler material and same average particle dimension, and, afterwards the volume fraction was fixed but the average particle dimension was changed. For every combination of matrix/filler, mechanical and tribological behavior of the produced composites was evaluated. This study intended to evaluate the influence of the filler in the performance of the composite. Afterwards, with same average filler particle dimension and same volume fraction the matrix composition was altered.

For the first set of tests, where the influence of particles size was evaluated, the produced composites was composed of commercial polyester resin (U-Pol Plastik, London, UK), serving as a matrix, reinforced with particles of high purity silica. Polyester resin was used mainly because it enables the production of hand mixed composites with an extremely high reproducibility. On the other hand, silica was selected because it is available in a wide range of dimensions, guarantees good adhesion to the matrix and is very popular as reinforcement material in composites, namely dental composites. Table 3.3 resumes the combination of polyester resin and high purity silica, presenting: average size particle dimension, and filler volume fraction.

Table 3.3: Composite specimens used to evaluate filler volume fraction effect. Type of; matrix, filler, average mean particle dimension, fraction and designation.

Matrix	**Reinforcement material**			
	Type	**Average mean particle dimension [μm]**	**Filler volume fraction [%]**	**Composite designation**
Polyester resin	Silica	6	0	PR
			12	PR 12
			16	PR 16
			24	PR 24
			30	PR 30
			37	PR 37
			46	PR 46

In order to determine the influence of filler fraction, five specimens of each fraction were produced. With these specimens, and after determining the necessary time to allow for the stabilization of their mechanical properties (optimized by measuring hardness and dynamic Young's modulus through non-destructive mechanical tests) tribological and mechanical properties were assessed and hence the influence of the fillers on the composites performance. Resin specimens with 0% of silica served as reference, specimens designated as PR.

After this study it was necessary to understand how mean average particle size could influence the composite behavior. As to the effect of particle dimension, a 30% filler fraction was selected and all specimens had the same; filler fraction and matrix (polyester resin) but different mean average filler dimension. Here again a resin specimen served as reference. Table 3.4 presents the information regarding the study of particle size.

Table 3.4: Composite specimens used to evaluate filler average particle size effect for 30% filler volume fraction. Type of; matrix, filler, average mean particle dimension, fraction and designation.

Matrix	**Reinforcement material**			
	Type	**Filler volume fraction [%]**	**Average mean particle dimension [μm]**	**Composite designation**
Polyester resin	Silica	30	—	PR
			3	PR 30/3
			6	PR 30/6
			16	PR 30/16
			22	PR 30/22

After evaluating the effect of particle dimension for a 30% filler volume, and considering both the ever increasing trend in usage of nanofillers by all composite manufacturers and the fact that the commercial composites in the study also have nanofillers, it was decided that another study should be done including these types of particles. Realizing that the nanoparticles used (precipitated silica E) are characterized by a very high specific area, 172.2 m^2/g, it was necessary to test a filler volume fraction which corresponded to the wettability limit in the polyester resin used previously. Thus, a 10% volume filler fraction was used for each mean average particle dimension as well as a combination of nano and microparticles. Two lots of 10% volume fraction specimens with a mix of two particles sizes were produced; one with 70% microparticles of silica (average particle size 3 μm) and 30% nanoparticles of precipitated silica E (average particle size 0.13 μm), the second with 30% microparticles of silica and 70% nanoparticles of precipitated silica E. Table 3.5, presents the combinations of polyester resin and 10% in volume of reinforcement particles.

Table 3.5: Composite specimens used to evaluate filler average particle size effect for 10% volume fraction filler content. Type of; matrix, filler (nano and micro), fraction and designation.

Matrix	**Reinforcement material**		**Average mean particle dimension** [μm]	**Composite designation**
	Type	**Filler volume fraction [%]**		
Polyester resin	—	0	—	PR
	Precipitated silica E	10	0.13	PR 10/0.13
	Silica	10	3.00	PR 10/3
			6.00	PR 10/6
			16.00	PR 10/16
			22.00	PR 10/22
	70% Precipitated silica E+30% Silica	10	1.00	PR 10_70/0.13
	30% Precipitated silica E+70% Silica	10	2.14	PR 10_30/0.13

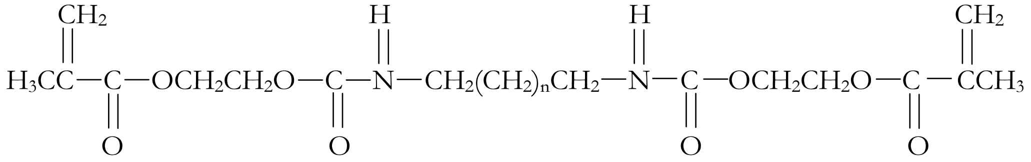
The aim of the present work is to evaluate the influence of the inorganic filler in the composite's mechanical properties and thus, for each one of the filler content the following mechanical properties were determined; hardness, flexural resistance (determined by bending tests), toughness and Young's modulus (determined both by dynamical methods and by bending tests). All of the results attained for the composites were compared with the ones achieved for polyester resin.

The composite specimens were shaped and cured in aluminium molds. The resin was processed according to the manufactures information. A pre-determined volume of resin (U-Pol Plastik) was placed in a container, followed by addition of the hardener (MEKPO), 2% of the initial volume of resin (as recommended by the manufacturer). The mixture was then well stirred and finally, the volume particles were progressively added and stirred again. The produced mixture was put in the mold. In order to obtain homogenous curing all specimens were placed in an oven at 40°C during 8 hours.

After removal from the respective mold all specimens were polished until the surfaces presented no imperfections and the dimensions of the specimens were homogenous. Because the hardness of this resin tends to increase with time, a previous study was done to determine the suitable number of days necessary to guarantee the stabilization of hardness value. It was determined that after 20 days no noticeable change in hardness was registered. The specimen's geometry was rectangular bars (50 mm × 6 mm) with 4 mm thickness.

Matrix variation The majority of commercial composite resins for dental restoration are trade marks, with very little information associated to their composition, never the less, it is known that there are three main factors to be considered in order to produce a novel composite resin: (i) the organic matrix; (ii) the filler and (iii) the interface between both the composite and the tooth itself (either to the organic or the inorganic moiety). The success of the final product is a sum of the contribution of the three items referred. After defining the study in terms of filler influence on the performance of produced composites, the next step was to evaluate the matrix influence on the overall performance of the composite in mechanical and tribological solicitations.

The main objective of this study was to evaluate and characterise the influence of different matrices. A new cross-linking agent, with two or more double bonds, associated the previous filler particles into functional groups, in order to obtain a resistant, stable and biocompatible material for dental restoration. A urethane dimethacrylate (UDMA) (fig. 3.1) containing two double bonds was synthesized by reacting the free −N=C=O groups present in a hexamethylene based diisocyanate biuret (Basonat) with the −OH groups of 2-Hydroxyethyl methacrylate (HEMA) in the presence of a catalyst, dibutyltin dilaurate (DBTDL). The main reasons for choosing a polyurethane dimethacrylate are that these molecules are known to lower resin viscosity, improve degree of conversion, and improve hardness of the material as well as its fracture toughness.



$$H_3C\overset{CH_2}{\overset{\|}{C}}-\underset{O}{\underset{\|}{C}}-OCH_2CH_2O-\underset{O}{\underset{\|}{C}}-\overset{H}{\overset{\|}{N}}-CH_2(CH_2)_nCH_2-\overset{H}{\overset{\|}{N}}-\underset{O}{\underset{\|}{C}}-OCH_2CH_2O-\underset{O}{\underset{\|}{C}}-\overset{CH_2}{\overset{\|}{C}}CH_3$$

Fig. 3.1: UDMA molecule.

Three resins containing different percentages of UDMA were prepared (rA, rB, rC) and three composites (cA, cB, cC) were prepared by adding 24% in volume of silica with mean average size of 6 μm to resins rA, rB and rC, respectively.

UDMA was prepared by mixing a hexamethylene based diisocyanate biuret (Basonat) (Sika Portugal, S.A.) with 2-Hydroxyethyl methacrylate (HEMA) in a ratio of 2 : 1 (mol) in the presence of a catalyst dibutyltin dilaurate (DBTDL), (Aldrich Chem. Co.). The conditions under which the reaction occurred are demonstrated in fig. 3.2.

Besides UDMA, the organic matrix contained Bis-GMA (Aldrich Chem. Co.) and TEGDMA (Aldrich Chem. Co.). These dimethacrylates commonly used in the preparation of dental composites were used as received without further purification. To make the samples light curable, 2 mol % of camphorquinone (CQ) (Aldrich Chem. Co.) and 2 mol % of N-phenylglycine (Aldrich Chem. Co.) were added to each sample. Methyl methacrylate (MMA) (Aldrich Chem. Co.) was also added to the organic matrix in order to increase the viscosity of the resin specimens and to facilitate the mixing of the solid photo-initiator/photo-sensitizer system. The resins were prepared by mixing all the monomers together followed by transferal to dark containers to avoid

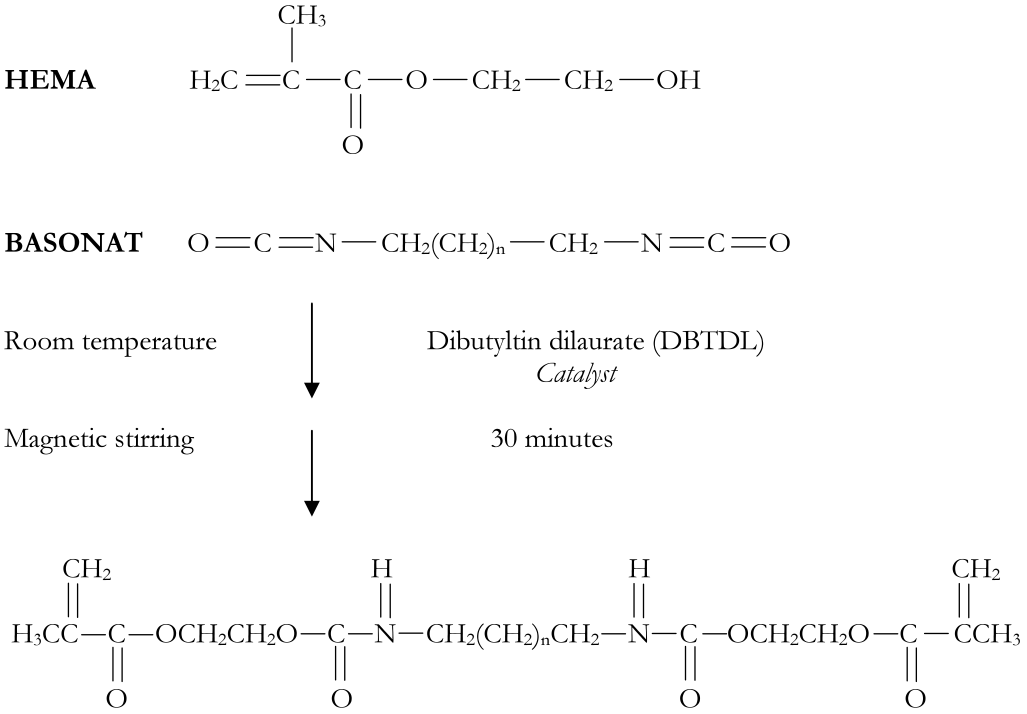


Fig. 3.2: Preparation of UDMA.

unintentional curing. CQ and N-phenylglycine were finally added to the mixture and well stirred to ensure total dissolution. Composites cA, cB and cC were prepared by progressively adding and stirring manually the silica particles (24 vol. %) to resins rA, rB and rC, respectively. The compositions of the resins and composites are shown in table 3.6.

Table 3.6: Designations and compositions of specimens used in this study.

Material	**Filler volume fraction** [%]	**Average particle dimension** [μm]	**Composition (mol %)** Bis-GMA	TEGDMA	MMA	UDMA	**Designation**
Resin	—	—	63	26	11	0	rA
	—	—	57	23	10	10	rB
	—	—	50	21	9	20	rC
Composite	24	6	63	26	11	0	cA
	24	6	57	23	10	10	cB
	24	6	50	21	9	20	cC

Since these composites and resins are light sensitive their preparation and production is slightly different from those previously produced.

Specimen's geometry and processing procedures for these materials was as described previously for the other composite materials.

3.2.3 Amalgam

For comparative purposes, a few samples of amalgam with identical geometry were prepared. The main objective was to have a reference and to know how the restorative packable composites behave in relation to restorative material used for over 150 years.

In this study the dental amalgam, Tytin FC from KerrDental, USA was used. Tytin FC was provided in two-part plastic capsules separated by a membrane that must be broken by squeezing before they were mixed with liquid mercury in a mechanical vibrator, (Automix, KerrDental) to efficiently mix the surface of the particles. The powder alloy composition of Tytin is silver 61%, tin 26% and copper 13%, the mercury-to-alloy ratio being approximately 43%. After triturating it was cast into the same molds as the commercial resin composites. Thus, the geometry of the specimens was maintained in accordance with tests at which the material was subjected. Parallelepiped specimens were used only in impulse excitation of vibration, for the determination of Young's modulus. Cylindrical specimens were used for measuring Vickers hardness and to perform reciprocating wear tests. All specimens' surfaces were finished by grinding on abrasive SiC paper up to 1200 grit, to remove any excess of material and to guaranty homogenous dimension in every direction.

3.2.4 Other materials

For the tribological behavior studies, reciprocating wear tests were conducted on composite materials (commercial composites, produced composites and reference materials (resins and/or amalgam) against spherical ended specimens of two different materials: glass and human premolar teeth.

Glass spheres (Kugelfabrik Gebauer GmbH, Fulda, Germany) used as counterbody (fig. 3.3a) were standard in accordance with DIN 5401 part II, concerning the control in the geometry and dimensions, table 3.7.

Table 3.7: Characteristics of glass spheres and dimensions.

Material	**Density** [kg/m^3]	**Hardness** [MPa] **(STD)**	**Average diameter** [mm]	**Diameter tolerance** [μm]
Soft glass	2,500	5,177 (116)	10	14

The teeth used in the present study were sound premolars extracted mainly for orthodontic reasons, and were supplied by the Faculty of Medicine of Coimbra University. All teeth were properly washed and stored until their usage. On all teeth hardness, Vickers indenter was measured in ten different locations of the enamel layer. The average hardness, in thirty teeth, was 3,259 MPa with standard deviation (STD) of 451. Concerning tooth roughness, at point of contact, Ra was of 0.09 μm (STD, 0.01). The high value of standard deviation in the determination of microhardness expresses one of the inconveniences when using biological materials.

Testing required specific tooth preparation in order to obtain the desired geometry. To guarantee similar contact geometry from test to test and in both pairs of materials, the teeth were prepared to ensure a contact surface radius of 5 mm, fig. 3.3 a). This preparation consisted of root removal and subsequent halfing of each tooth. Afterwards, each one of these halves was glued in acrylic cylinders and put in contact with a rotating mold of the desired radius. Application of constant pressure to the contact point as well as addition of abrasive pastes of several granulometries permitted obtention of the desired shape. Each one of the tooth specimens was then polished with zircon powder against felt in order to remove scratches produced by the abrasive pastes, fig. 3.3 b).

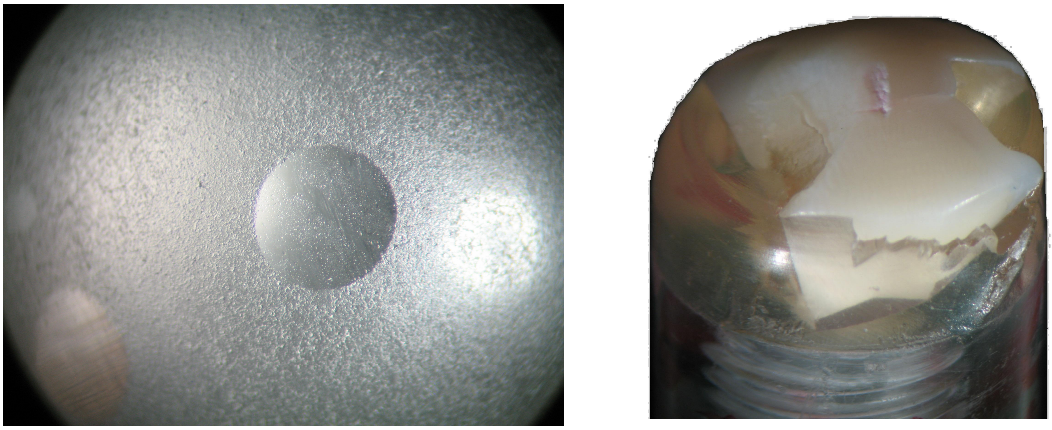

(a) (b)

Fig. 3.3: Reciprocating antagonists; a) glass sphere with wear scar and b) premolar human tooth.

For the evaluation of transition wear regime, from mild to severe using the load-scanning test, the antagonist material used was AISI 52100 steel spheres with 5 mm radius. In order to ensure different values of roughness, the steel spheres where chemically etched. In terms of Ra values of the sphere they were of; 0.21 μm; 0.66 μm and 8.66 μm, for the smooth, medium and rough sphere respectively. A new sphere was used for each specimen. The smooth sphere was not chemically etched.

3.3 Testing equipment and experimental procedures

Due to the developments in recent years of the dental composite industry a great variety of composites has emerged. The increase in aesthetics concern as well as preoccupation of amalgam toxicity has launched a global debate over the selection of amalgam alternatives. Several composite materials are in the market without an *in vivo* evaluation, long term evaluations of clinical results, both qualitative and quantitative.

It is easy to understand that *in vivo* tests are time consuming and the extracted results are mainly qualitative. These results depend on human intervention and physiological conditions (age, sex, diet, etc.) as well as the role of the varying environmental conditions were said restorative materials are located (mouth with different temp, pH and sliding distance values).

In vivo studies must be supported by preliminary *in vitro* researches to confirm and direct the investigation of these materials. Thus, to do so, materials have to be well characterized with simple, expedited and reproducible tests which allow not only a qualitative appreciation, but also, and fundamentally, a quantitative assessment of their properties/features.

Properties evaluated in this study were selected in order to allow an analysis of the major reasons for restorative composite failure. To reach an understanding of failure mechanisms and the characteristics which influence most of the composite's behavior it is fundamental to understand the role of each component of resin composite materials; matrix, reinforcement particles and the interface between both. Besides materials' intrinsic influences it is also fundamental to identify external entities/parameters which affect composites in its complex working environment, the mouth. Factors such as; aging and pH, and understand its influence on the mechanical and tribological characteristics' of this restorative materials. For all this a set of mechanical and tribological tests were selected.

To begin, an introduction explaining how the testing equipment used for the study will be presented. As stated before, for the characterization of the studied composites two fields were explored: mechanical and tribological characterization.

Concerning mechanical characterization table 3.8 illustrates both the measured properties as well as the tests which allowed characterization of the materials studied.

Table 3.8: Mechanical tests and assessed properties of materials.

	Tests		
Properties	**Vickers hardness**	**4 point bending**	**Impulse excitation of vibration (IEV)**
Hardness	■	□	□
Dynamic Young's Modulus	□	□	■
Static Young's Modulus	□	■	□
Flexural resistance	□	■	□
Work-of-fracture	□	■	□

Tribological characterization was done through two *in vitro* tests; reciprocating wear and load scanning tests. Table 3.9 shows the properties/features determined by each test.

Table 3.9: Tribological tests and assessed properties of materials.

	Tests	
Properties/Feature	**Reciprocating wear**	**Load scanning**
Wear /wear resistance	■	□
Friction coefficient	■	□
Wear volume	■	□
Regime transition in friction by point contact	□	■

Afterwards it will be presented, first all mechanical test apparatus and afterwards the tests used to characterize the tribological behavior. In the subsequent points are presented all experimental procedure done to evaluate and assess results obtained from mechanical and tribological tests.

3.3.1 Mechanical tests

Mechanical properties such as hardness, flexural resistance, work of fracture, static and dynamic Young's modulus of the resin composites have been studied in this thesis. For the determination of these properties the following tests were chosen: Vickers microhardness, four point bending and impulse excitation of vibration.

Hardness test Due to the characteristics Struers Duramin testing equipment (Struers, Denmark, (fig. 3.4)) was selected to determine the microhardness of materials in study (commercial composites, produced resin composite, amalgam) and antagonist bodies (glass spheres and teeth). Vickers microhardness test was selected due to; good sensibility, small dimension of indentation marks and its' reduced sensitivity to surface conditions. A microhardness test was prepared because in the case of commercial resin composites, both diagonals of the indentation are much larger than the singularity of the composites. The procedure followed respects the requirements of the standard test method for micro-indentation hardness of materials (ASTM WK27978, 2010). A load of 0.20 kgf (1.962 N) [$HV_{0.2}$] has been applied for a period of 40 seconds. Loading dwell time of 40 seconds was selected to assure a steady state deformation regime (Shahdad *et al.*, 2007). Microhardness measurement is dependent of time and applied load, for plastics, there is a 50% to 70% recovery in indentation depth and 5% in diagonal dimensions (Crawford, 1982) after load removal, taking this into account and considering the type of material in study, applied load and test conditions used by other investigators (Willems, 1992; Matos *et al.*, 2003) this condition guarantees a correct assessment and determination of hardness values.

Every surface was correctly polished prior to the hardness measure. For the light cured materials hardness was measured on the surface directly exposed to the curing light. At least ten indentations were made in each of the specimen or materials to determine the average hardness. Each specimen's microhardness data measured was expressed through an average value, a standard deviation, and the confidence interval for a confidence level of 90 %, assuming a normal distribution.

Fig. 3.4: Struers hardness testing equipment, model Duramin used to perform Vickers microhardness tests.

Impulse excitation of vibration (IEV) For resin composite materials the conventional measurement of Young's modulus, i.e. via tensile testing (ASTM E 111-04, 2004), is difficult:

the linear proportional regime such that measuring Young's modulus with the tangent to the initial slope of the stress-train curve is often difficult and usually inaccurate.

Dynamic measurement of the Young's modulus is an alternative to quasi-static tensile tests. The strain interval used for the dynamic measurement of Young's modulus is small, meaning that dislocation activity is negligible, as is the build-up of internal damage. The sample then truly behaves more as a linear elastic solid (Hauert *et al.*, 2009).

In the determination of the Young's modulus as described by Braem *et al.*, (1986) and according to the standard; Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio for Advanced Ceramics by Impulse Excitation of Vibration (ASTM C1259-96, 1996), each specimen was set in free flexural vibration by a light mechanical impulse. A strain-gage, glued to the specimen's surface, captured the flexural vibration signal. The fundamental frequency of the first flexural vibration mode was determined analyzing the vibration response by Fast Fourier Transform (FFT).

Young's modulus was calculated as a function of the frequency of the first flexural vibration mode using equation 3.1.

$$E = 0.9465\left(\frac{mf_t^2}{d}\right)\left(\frac{l^3}{t^3}\right)T_1 \tag{3.1}$$

Where l and d are the length and width of the bar, m their mass and f_t is the fundamental frequency. According to ASTM C1259-96 standard, T_1 is a correction factor to take into account the finite dimensions of specimens. For the calculation of T_1 a constant Poisson ratio of 0.3 was used.

For each specimen the average dimensions have been calculated from ten measurements of the three directions. Each sample was weighed on a precision scale (Ohaus Analytical Plus, AP110, USA). Ten impulse excitation signals acquisitions were considered in order to determine through numerical methods the average Young's modulus. For each Young's modulus is presented also standard deviations and confidence interval for 90% certainty.

Four point bending test The matrix of dental composite materials is a mixture of polymers, reinforced with one or more inorganic fillers (quartz, barium silicate, strontium borosilicate, etc.) or a mixture of glass particles with colloidal silica. Although these materials may withstand the complex nature of masticatory forces in aggressive oral environments without significant wear, they fail in a brittle manner.

With materials that exhibit non-reproducible mechanical properties, subject to technique sensitivity, it is essential to strive for a combination of cavity design and appropriate materials with an acceptably low failure rate during service. This is not always easy to achieve on the basis of limited laboratory data.

Flaw distribution, specimen size and shape, environmental effects, and test conditions may play significant roles in the response of a dental restoration. Thus, the issues of material property characterization and reliability prediction are particularly important in view of the different geometries of dental restorations.

The use of linear elastic fracture mechanics to understand the failure characteristics and clinical properties of dental composite materials has increased in the past ten years. Most of the published work (Lloyd and Ianetta, 1982; Pilliar *et al.*, 1986; Ferracane *et al.*, 1987; Chadwick *et al.*, 1990; Söderholm and Roberts, 1990; Kovarik *et al.*, 1991; Ferracane and Marker, 1992) is concerned with the effects of air, water, ethanol, and other-environments on fracture strength, flexure modulus, and mode I fracture toughness with various compositions. The large scatter of mechanical properties, commonly observed in these materials, is described using Weibull statistics.

Failure of a dental restoration occurs when its load bearing capacity is diminished due to material degradation in the oral environment. This process is usually assisted by pre-existing voids, imperfect interfaces, and residual stresses. Under the continuous application of mechanical and/or environmental loads, progressive degradation eventually leads to crack initiation and growth that results in failure of a dental restoration. Thus, resistance to crack initiation and growth is an important consideration for the reliable assessment of dental restorations.

The objectives of this study were aimed at characterizing the fracture properties of selected dental restorative composites, commercial and produced in the laboratory. Loading conditions and specimen's geometry were constant. Testing also evaluated aging effect and pH variation.

The results of the mechanical properties related to strength and fracture of all restorative composites in the laboratory environment are reported. Prismatic bars (6 × 4 × 50 mm) were prepared for flexure strength tests, figs. 3.5 a) and 3.5 b).


(a) (b)

Fig. 3.5: a) Dental composite specimen's prismatic shape; b) Experimental assembly with specimens in place during test.

All experiments were conducted on a universal servo-hydraulic testing machine (Instron Model 4206, USA), controlled by digital electronics at room temperature (≈ 21°C) in ambient air, with load capacity of 100 KN. A 500 N load cell (Bongshin, model DBBP-500, Korea, with a rated output of 3 mV/V), was used to maximize the sensitivity of the outputs. This cell was interposed in the upper tie. On one end of the S-beam load cell, the upper spam was bolted and on the other end, a threaded rod gripped to the upper machine's claw, which applied the load directly to the specimen. The electronic Instron equipment controlled the displacement velocity while the load cell was connected to acquisition data equipment Spider8 (Hottinger Baldwin Messtechinik GMBH, Germany), with a 10 Hz acquisition rate for the applied load. The adopted criterion for failure was the specimens' fracture.

Bending tests experiments were performed under displacement control mode with a constant crosshead speed of 0.5 mm/min considering the scatter of mechanical properties in brittle materials, four specimens, were tested under the same conditions to provide sufficient representative information. The number of repetitions is small considering the type of material, due to limitations associated with the commercial material cost.

Four point bending tests were performed according to standard ASTM C1161-96 (1996). Samples were loaded using a loading span support of 20 mm and a 40 mm for the lower span, fig. 3.6. Bending tests allow for three different results, namely: flexural resistance, static Young's modulus and a toughness parameter, work-of-fracture (WOF), which corresponds to the specific energy required to fracture the specimen, obtained from the area under the load-displacement curve divided by the specimens' cross-section area.

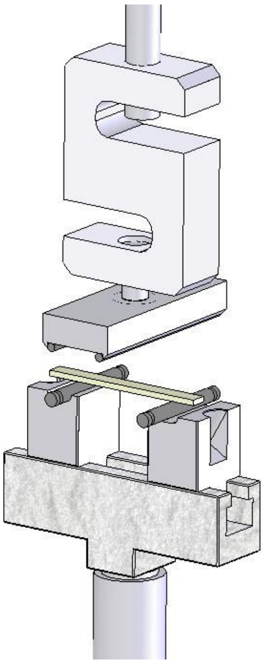


Fig. 3.6: Assembly used in the four point bending tests.

The four point bending configuration was loaded symmetrically at two locations with the distance between the loading points. Flexural strength S and elastic modulus E were determined from simple beam theory (Gere and Timoshenko, 1984).

The flexural strength (S) was determined using equation 3.2, where P is the break load, L the outer span and d and t respectively the width and the thickness of the specimen. The work-of-fracture was calculated by the area below the flexural curve that can be used as a comparative value of the toughness.

$$S = \frac{3PL}{4dt^2} \tag{3.2}$$

where t is the specimen height, I is the moment of inertia of the cross section.

The static elastic moduli for, four point bending tests, were determined with the use of the following equation 3.3 (Broek, 1987):

$$E = \frac{PL^3}{4dt^3\delta} \tag{3.3}$$

Where d is the width and t is the height of the specimen. The load P and the corresponding deflection δ were measured directly. Results of flexural strength and static elastic modulus were obtained from the four point bending test in MPa and GPa respectively.

All composite specimens were prepared for each test using a bipartite aluminum mold (bolted to an acrylic base), positioned over a glass slide and a polyester strip and filled with composites material, inserted in several increments. Another polyester strip was positioned and pressed against the restorative material with a glass slide for removal of excess before polymerization. The specimens were irradiated only on the top surface, with light exposures of 40 s, by a halogen curing unit, Demetron Optilux 501 (Kerr, Orange, CA, USA), with a power density of

850 (±50) mW/cm^2, with an output wavelength ranging from 400 nm to 505 nm. The specimens were finished with metallographic abrasive paper and stored at room temperature during 4 weeks before the bending tests.

The specimen's dimensions were measured with a digital caliper (Mitutoyo Co., Kawasaki, Japan) before testing.

After each test, the fractured surfaces of the specimens were observed to check for the existence of pores in the fracture surfaces. Results were considered only for the specimens without holes under naked eye inspection.

3.3.2 Tribological tests

When the intent is to study wear behavior between materials it is necessary to understand the environment in which they work, as well as the mechanisms involved in the processes which are the most important and finally conceive and/or use equipment adapted to the aim of the study.

Taking into account previous studies, namely with ball-cratering (presented elsewhere), and results later obtained, wear behavior of composite (dental commercial restorative materials or manufactured one') tested either against human teeth and/or glass spheres was studied. The ultimate goal of this type of study is to establish the predictability of wear behavior between the binome tooth-composite, based on the results of laboratory tests involving the contact of composite with synthetic material.

The evaluation of tribological behavior was assessed through short stroke reciprocating sliding contact, with geometry sphere-plane contact. The testing system used for the study allows a wide range of test speeds, loads and test environment. The measurement system includes acquisition of data and directly or indirectly allows for the estimation of the following main parameters: coefficient of friction, energy dissipation, wear rate, volume of material removed by wear from the pairs in study and wear resistance.

Besides the reciprocating technique another tribological test was used: a load-scanning test. This unidirectional sliding test allows for the changing of loads and coefficient of friction along the test as well as correlating these parameters with stress distribution and contact morphology. In the scope of the present study, load-scanning test was used to verify factors that led some pair of materials in the study to not show a transition wear regime from mild to severe.

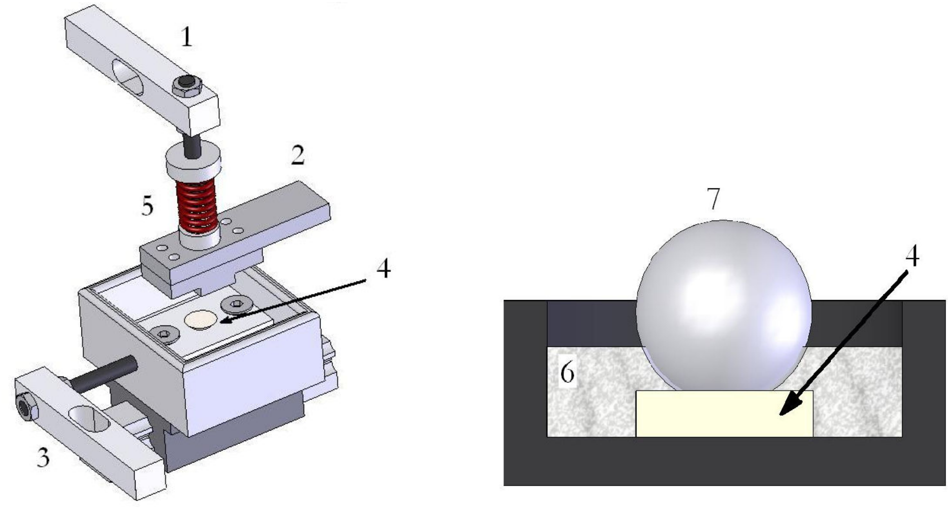
In each one of the tests, the results analysis was always accompanied by a systematic SEM observation of the morphologies of the produced contact scars.

Reciprocating wear tests As seen before the parameters which affect composite's wear performance are great in number and hard to separate by degree of influence. With such an enormous number of variables parameters, *e.g.*, material properties (particle size, matrix material, particle volume fraction, particle distribution, etc.) and/or contact mechanisms (two or three body wear) and/or conditions (normal load, sliding distance, aging, environment conditions, etc.) it is very difficult to assess the influence of each parameter in the wear behavior.

After considering all the involving aspects of wear experiments which were presented previously, the selected wear test was reciprocating type, with contact geometry plane-sphere. The test was selected primarily due to similitude with the natural movement occurred in the mouth and secondly, as it allows for variations in the amplitude of movement, normal load and test environment. The possibility of evaluating wear of both materials in contact is also an important advantage of this type of test.

Reciprocating motion of the surfaces in contact was done in distilled water/artificial saliva baths or abrasive slurry. Both antagonist bodies used had a 5 mm radii; this value was selected because it corresponds to the average curvature radius of molar teeth (Lambrechts et al., 2006b).

The reciprocating test was performed to determine the wear resistance of the chosen composite material as well as the wear produced on both contact surfaces. This technique comprises a sliding contact of a spherical body in reciprocating motion against a flat specimen of composite material (fig. 3.7) (Ramalho and Antunes, 2007).



(a) (b)

Fig. 3.7: Reciprocating equipment for sphere-plane contact.

Fig. 3.7 indicates the elements that comprise the reciprocating apparatus. The sphere or tooth (7) is connected to the moving stage (2) and is kept in permanent contact against the horizontal surface of the stationary specimen (4). The normal load is applied by a spindle-spring (5), which is connected to the normal load cell (1) to measure the normal force applied. In the scope of the present study, the nominal value of the normal load was 5 N. However, to analyze the effect of the normal load on the wear behavior, values of 3, 5, 6 and 8 N were applied to the contact pointglass-composite or tooth-composite. A harmonic wave, generated by an eccentric rod mechanism that was set with stroke length of 2 mm and frequency of 1 Hz (Lewis and Dwyer-Joyce, 2005), imposed a reciprocating movement to the upper specimen carrier (2). The composite specimen was placed in a container, which was filled with distilled water/artificial saliva or abrasive slurry (6). The lower specimen holder was connected to a slider guided by ball linear bearings to allow movement in the direction of the motion. A stationary load cell (3) was used to equilibrate the lower specimen obtaining friction force values along the test.

During the chewing process of human beings, the magnitude of mastigatory force in the oral cavity ranges from 3 N to 36 N but can reach peak values of 135 N (Dowson, 1998; Goldmann and Himmlova, 2008). According to the current study test geometry, the surfaces interact theoretically by point contact and higher loads occur in the mouth sporadically; therefore, the normal load was fixed near the minimum referred values.

Due to the fact that there were two types of environmental media in for the reciprocating sliding contact; artificial saliva (or distilled water) and abrasive slurry, and in order to simulate a two- and three-body contact the duration of the two tests varied due to the differences in wear rate severity of this distinct environments. Nominal test duration with distilled water environment was of 10,500 cycles. Abrasive slurry tests, had smaller duration, of about 2,600 cycles, in order to create a measurable damage and long enough to allow the determination of a "stable" coefficient of friction (COF) for each material pair in study.

Initially tests were done with artificial saliva, but due to the similarity between the results obtained with distilled water and considering the higher preparation time for artificial saliva, distilled water replaced the latter. These results were expected considering the materials in play, i.e., resin composites after cure are inert as well as the antagonist bodies used, glass spheres and natural teeth. Besides that fact, test duration was not very prolonged thus avoiding formation of oxides. The replacement of artificial saliva with distilled water also lestened human manipulation and thus eliminated introduction of other variables.

Table 3.10 illustrates for reciprocating wear test the conditions used for both possible test condition environment, abrasive slurry or saliva/distilled water done with composites against glass spheres.

Table 3.10: Characterizations of the two types of wear tests.

<table>
<tr><th rowspan="2">Test conditions</th><th colspan="2">Type of test</th></tr>
<tr><th>Abrasive slurry</th><th>Artificial saliva/
Distilled water</th></tr>
<tr><td>Stroke (peak-to-peak) [mm]</td><td colspan="2">2</td></tr>
<tr><td>Frequency [Hz]</td><td colspan="2">1</td></tr>
<tr><td>Test duration [Cycles]</td><td>2,600</td><td>10,500</td></tr>
<tr><td>Normal load [N]</td><td colspan="2">5</td></tr>
<tr><td>Antagonist body</td><td colspan="2">Ø10 mm, Glass sphere</td></tr>
<tr><td>Environmental media</td><td>Aqueous suspension of 0.35 g of glass micro-spheres (≈ Ø4 μm) per ml of distilled water)</td><td>0.7 and 1.2 g/l of NaCl and KCl respectively in distilled water</td></tr>
</table>

The values of test duration for the two pair of materials, glass-composite and tooth-composite were selected, first, through an evaluation of the wear marks. Due to the fact that typically, the tooth produces smaller associated damage, in itself and in the composite, the test duration for this pair of material varied from 6,000 to 20,000 cycles. Previous studies revealed that duration of less than 6,000, especially for low normal loads, did not allow the system to create sufficient wear volume, on both composites and counterbody, in order to be visualized and measured.

As for the pair glass-composite, cycle duration ranged from 2,000 to 12,000. For this pair of materials, these durations were combined with the values of normal load of: 3, 5, 6 and 8 Newton. In all cases the reciprocating tests were done in distilled water bath at room temperature.

Table 3.11 resumes all the test conditions used for both pairs of materials. The tests are sorted by the increasing energy input. The product of load by number of cycles was considered as a degree of severity of the test.

After the reciprocating wear tests terminated, the scars produced on the composite specimen were scanned by Roddenstock RM 600 laser 3D profilometer. The scanning of all tested specimens was transversal to the sliding direction and the distance between profiles ranged from 18 μm to 25 μm, depending on the length of the wear scar. The areas of the 2-D profiles were integrated along the length of the wear mark, allowing the determination of the volume removed by wear of composite dental material (Blanpain et al., 1993).

The counterbody, glass sphere and teeth, presented wear scars with spherical-caps shape and the diameter of their surface was measured in two orthogonal directions: the direction of motion and the direction perpendicular to it. The average values of crater radius, r, as well as

Table 3.11: Test conditions used in the characterization of the two pairs of material.

Material pair					
Glass sphere-Composite			**Tooth-Composite**		
Test designation	Normal load [N]	Duration [Cycles]	Test designation	Normal load [N]	Duration [Cycles]
A	8	2,000	J	8	6,000
B	3	6,000	K	5	10,500
C	5	6,000	L	6	10,000
D	8	4,000	M	3	20,000
E	6	6,000	N	8	9,000
F	8	6,000	O	8	12,000
G	5	10,500	P	6	20,000
H	8	9,000	—	—	—
I	8	12,000	—	—	—

the sphere radius, R, were then used to calculate the scar depth, h, and volume, V, of removed material, using equations 3.4 and 3.5.

$$h = R - \sqrt{R^2 - r^2} \tag{3.4}$$

$$V = \frac{\pi}{3} h^2 (3R - h) \tag{3.5}$$

The energy dissipated by friction between the bodies in contact can be considered the major energy source of wear of materials in sliding contacts. Energy dissipated by friction generates wear damage, in spite of the wear mechanism involved, for instance in cases of fracturing, plastic deformation or tribochemical reactions. Thus, the energy dissipation could be directly associated with wear. According to Czichos (1978), concepts similar to thermodynamic analysis could be applied in wear analysis, at least at a qualitative level. From the energetic approach the energy dissipation by friction along the test is directly proportional to the wear volume (Huq and Celis, 2002; Ramalho and Miranda, 2006).

The Coulomb friction model establishes that the friction force is proportional to the normal load, therefore, assuming a constant friction coefficient, a proportional relationship can be established between the wear volume and friction force. From the energetic approach the energy dissipation is also directly proportional to the wear volume (Hamilton, 1983; Johnson, 1985).

The tangential force to calculate the dissipated energy was obtained through periodic acquisition along every test. The energy dissipation, which is therefore associated to the wear in each test, is computed along the test as the work of the tangential force.

The interval between acquisitions was of 300 cycles and a vector of 3,000 values was saved *per* acquisition. Three loops of time-force were computed in each acquisition. These values allow for the calculation of the average work between acquisitions and thus obtain the total energy dissipated by friction through the integration of average work along the tests. Values of energy were then correlated with the volume of material removed during the tests. This approach was applied both to the composite and the antagonist. For each one of the acquisitions the average tangential force (the root mean square average) was also calculated. After attaining a steady-state regime the average tangential force of every acquisition was used to calculate the friction coefficient.

To calculate the energy dissipated, the tangential force was obtained through periodic acquisition along every test. The energy dissipation, which is therefore associated to the wear in each test, is computed along the test as the work of the tangential force.

The surface of the wear marks was examined by SEM. All the tested specimens were sputter-coated with gold in order to allow for better observation. The images were attained with secondary and backscattered electron detectors to allow for the observation of particle dimension and distribution and the identification of the wear mechanisms occurred throughout the tests.

Load-scanning test Due to the variation of the failure modes verified in reciprocating contact sphere-plane, it was necessary to investigate the factors that lead to this transition from a mild to a severe wear regime.

The cases where the transition occurred display always a simultaneously increase in the friction. Therefore our hypothesis is that this variation of degradation modes was probably due to the variation of stress distribution, leading to different location for the appearance of the first fractures. As the evolution of the friction force seems be directly involved in the change of the mechanisms it was necessary to conceive a test where it was possible to vary friction coefficient in a large range of normal load.

In order to manage all that it was decided to carry out a test with the same contact geometry, sphere-plane, where the stress distribution is well known (Hertzian stress distribution). A load-scanning type test was chosen. The characteristics of this test allow unidirectional contact, which maintains the geometry of contacting bodies along the test with fresh surfaces; possibility of measuring, with precision, the normal and tangential loads along the test; ability to observe the scars generated during the test allowing to associate to each point the contacting loads, in both normal and tangential directions.

Therefore, load-scanning tests were done considering a steel sphere against a dental composite. The roughness of the steel sphere was varied by chemical etching from low to high values in order to induce a variation of the friction coefficient.

The objective of the tests was to determine the factors that lead to a regime transition in friction by point contact; therefore, the evaluation test had geometry of the contact plane-sphere, with unidirectional motion and increasing normal load. The composite specimen was attached to an X-Y moving table, and the specimen holder had a three way load cell connected to it, in order to acquire the normal and tangential loads along the test. This type of test allows the correlation the wear mark to the acquired values of normal and tangential loads (Ramalho, 2004).

The load cycle is imposed by a spring and a controlled movement of the upper sphere along the axis Z. A complete single unidirectional pass consists of four steps, fig. 3.8.

The test was performed in a computed numerically controlled machine (CNC) in order to allow a precise displacement and load control. As shown in the above picture the spherical antagonist material approached the flat specimen, in point 2, in which they would start the contact, during a sliding distance of 10 mm, with increasing normal load up to a maximum of 330 Newton. The sliding velocity was of 0.74 mm/s and the established load rate of 2 N/s. After reaching the normal maximum load the sphere was pull up away of the sphere from the composite specimen.

Normal and tangential loads were acquired along the test by a three-component load cell, which was attached to the composite specimen.

For each material in study it was used smooth, medium and rough spheres normal and tangential loads were acquired along the tests. Considering the Amontons-Coulomb friction model, which establish a linear evolution of the friction force with the normal applied load,

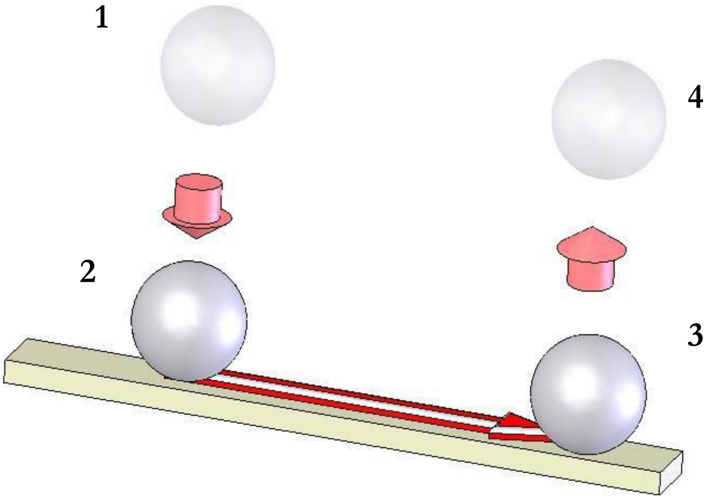


Fig. 3.8: Representation of the scanning load cycle.

plotting the tangential force against the normal force should leads to a linear evolution, being the coefficient of friction the slope.

The acquired data allowed, also, representing normal and tangential loads along the displacement of the sphere. Relating these graphics with the wear scar produced by each sphere on the dental composite allows us to establish a relationship between the observed morphology features and the values of the loads that occurred on those specific places. From the analysis of the previous graphs assembled along with the assembled SEM picture scar' surface of the composite, permitted to know the exact location of the fractures produced by the increasing loading produced by the distinct roughness surface spheres.

3.4 Aging conditions: pH values and aging periods

In order to determine the influence of pH and storage time on the composites tribological and mechanical behavior, seven commercial composite materials were used. Previously these same composite were tested without aging. In order to obtain more reliable test results two batches of composites were produced. Filtek P60 (3M), Prodigy Condensable (Kerr), Surefil (Dentsply), Synergy Compact (Coltène), Quixfil (Dentsply), CeramX (Dentsply) and Alert (Jeneric-Pentron). After being processed and before being put in the aging recipients all were subjected to the non destructive tests, namely microhardness and impulse excitation vibration tests.

A paralelipipedical specimens shape was chosen due to the fact that these specimens were to be used in the determination of mechanical properties, before and after aging. Specimen dimension were of 50 mm in length, 6 mm width and 4 mm thick. In order to determine the dynamic elastic modulus all flat specimens were finished with the appropriate polishing so their dimensions in thickness, length and width were homogeneous. Their weight was also determined on a precision scale — Ohaus analytical plus. The description of how specimens were processed was described previously.

To assess the influence of aging effect, different values of pH were considered for the commercial composites. All materials were tested without aging (0 months) in order to establish a reference value pertaining to mechanical and tribological properties. One batch of specimens was produced in order to be removed from the three buffer solutions bath — acid, neutral and alkaline — at the 3rd, 6th and 22th month and tested in terms of its wear resistance and mechanical properties. Specimens were kept in hermetic containers with buffer solutions. The pH of each container was verified every week with a pH meter from Crison, model GLP 21. Containers were immersed in a distilled water bath at a controlled temperature of 37 ± 1°C.

In order to guarantee that water sorption would not interfere in the determination of the mechanical-tribological properties, due to possible swelling of the cross linked polymer network and a consequent reduction in properties, and because the specimens tested previously were tested dry, all specimens removed from the pH containers, after aging time ended, were dried out in a P Selecta oven, model DIGITHEAT, during 12 hours at 30°C. Specimens were kept in a control environment at room temperature and protected from light during 24 hours before testing.

Chapter 4

Mechanical properties, results and discussion

4.1 Introduction

This chapter allows for the presentation of all preliminary tests executed in order to establish; test apparatus; proceedings; mechanical characterization of materials tested and the main parameters to study. After the presentation of preliminary studies and results the chapter is then organized with the presentation of mechanical test results. Regarding mechanical tests, results for Vickers hardness, impulse excitation of vibration (IEV) and four point bending tests will be discussed. The chapter is focused on the presentation of mechanical result tests and derived conclusions concerning commercial restorative composites and produced composites. As to commercial restorative composites materials the results of aging and pH effects are also presented along with the reference conditions, *i.e.*, prior to aging. Conclusions concerning these effects are done subsequently.

4.2 Mechanical tests — Preliminary results

Before the final definition of all work presented it was necessary to pre-select all materials, tests and procedures. Concerning materials, initially the study was focused on commercial posterior restorative composite materials. Taking into account the large number of composites in the market, selection of a reasonable number of possible composites was done. The first selection criterion was composite more commonly used in the market. The faculty of medicine having been involved in a research project in this area was of great assistance in narrowing the list of selected composites. The final list of composites was composed of not only the more commercially representative including packable nano- and microfilled particle reinforced composites but also a fiber reinforced composite, not very much used in Portugal.

After material selection it was necessary to determine properties of most interest and respective experimental procedures for the *in vivo* tests.

Because the main objective of this study was focused on mechanical and tribological tests this small outline will be divided into these main areas. As soon as the study was started and the first results emerged one thing was clear, not all variables were within our control, making it very difficult to compare composites formulations from different manufactures, or even from the same producer. Thus, in order to understand the mechanical and tribological behavior of these selected materials it became mandatory to include a complementary path. One which was more controllable, *i.e.* one were the matrix was well known and which allowed a controlled addition of reinforced material, concerning both fraction content and filler size.

This new parametric approach opened the possibility to study and understand, in a controlled manner, how each one of the composite constituents influences the restorative system in their mechanical behavior.

Effect of curing and storing time In this step of the study the first concern was to define the post-curing time to reach stable properties. Several specimens were cured and stored within water and air in vessel opaque to light while others allowed light to penetrate. Their hardness was evaluated every day until this property was stable and thus a period of time was established after which post-cure had no influence over the mechanical test results.

Regarding the characterization of commercial composites initial studies start with the influence of curing time duration on hardness and wear, work published in Wear (Antunes and Ramalho, 2003). Tests performed were: Vickers microhardness test and ball-cratering. For each commercial material several specimens were produced, each one light cured from 10 s to 80 s and then mechanical and tribological tested.

Preliminary testing evaluated the influence of cure on the hardness of composites. Several specimens were cured, cut in half and their hardness measured in depth, along microhardness profiles, from the cured surface towards uncured surface.

An evaluation of light power density variation was also performed. Curing equipment, with halogen light, which allowed the selection of 300 mW/mm^2 and 500 mW/mm^2 was used to cure several specimens of the same composite, and these were tested in hardness and ball-catering tests. The main objective was to understand the influence of light intensity on hardness and wear resistance.

The abrasion test selected initially was not the most convenient; first, because surface interaction mechanics are not very similar to tooth-to-tooth contact, secondly, the impossibility to simulate the composite-tooth contact and finally there are more suitable types of contact with more accurate wear results, namely reciprocating tests. Ball-cratering tests did not allow for very precise evaluation of antagonist material nor the use of material more similar to teeth, in hardness, and more oxide free as soft glass. Considering the previously pointed out limitations of ball-cratering, it was concluded that reciprocating wear tests would be the best alternative and the test procedures were established. This test allowed for suitable control of environment parameters such as the possibility to regulate temperature of the abrasive solution at contact point as well as a precise evaluation of friction and normal forces during the duration of the contact. This test also permitted a very easy and reliable measure of the wear scars on the bodies/surfaces in contact.

Results obtained for commercial restorative composites showed that in some way we were dealing with complex systems similar to “black boxes”, *i.e.*, did not allow a direct approach cause effect, due to that fact that the constitution variables were not free to vary.

After defining all mechanical and tribological tests it was necessary to find a composite which was controllable and easy to process. The choice was a current polyester resin with the addition of silica particles. Due to the fact that this resin was chemically cured the percentage of catalytic product was evaluated which allowed more hardness, and a determination of curing time to assess when the resin was physically “stable”. Mixing process was also very well studied in order to establish a simple and stable procedure which did not introduce any more parameters/influences in the study.

All these preliminary studies allowed for the evaluation of the main properties of interest within the study and established the trend of the final study. The results here presented are the corollary of this preliminary outline.

4.3 Microhardness

The results here presented concern Vickers hardness tests of all materials used in study, with several volume fraction of reinforcement, particle dimension and/or matrix variation. Values of Vickers hardness are also presented for the natural human tooth, amalgam and soft glass sphere (used as antagonist of restorative materials).

A Struers Duramin testing equipment was used to apply a load of 0.20 kgf (1.962 N) for a period of 40 seconds [$HV_{0.2}$]. Each materials results regarding measured microhardness data are given in MPa through the average value of all tests and the corresponding confidence interval, assuming a normal distribution and 90% confidence level.

4.3.1 Commercial composites

Concerning commercial composites, and although not all were subjected to the complete study, results for microhardness tests are presented for all restorative materials. Some were only tested, for example, in reciprocating wear test and others subject to the aging effect study. For the latter, the values of Vickers hardness test will show all aging periods and pH conditions considered.

The values presented for 0 months are reference values. These values represent the average values of all hardness measurements for each material without aging. For aging effect study, two batches of specimens were used for each variable: pH condition and aging period. For each batch of twelve specimens, hardness was measured ten times according to the ASTM C1327-08 (2008), standard for advanced ceramic. Twelve specimens times two batches; times 10 measurements for each material corresponds to the average values presented for each material, before aging. After each aging period two specimens of, each pH and aging conditions, were again, tested and with 10 indentations for the Vickers hardness test. Values for materials used in the aging study are presented first, and afterwards materials involved in other studies as well as an amalgam which was used as comparative material.

Table 4.1: Average Vickers hardness values [MPa] and confidence interval (CI) for Filtek P60 from 3M.

pH	**Filtek P60**			
	0 months	**3 months**	**6 months**	**22 months**
3	920.6 (69.3)	869.9 (47.1)	888.3 (25.5)	857.7 (91.2)
7		863.6(67.3)	860.2 (34.1)	822.2 (40.2)
9		874.1 (50.8)	896.8 (41.6)	846.2 (93.0)

From the results analysis it is possible to see that Filtek P60 (table 4.1) is not very much affected by neither pH nor aging time. All values of microhardness registered are inferior to the average values of the composite before aging. The biggest variation occurs for pH 7 particularly at 22 months, corresponding to 11% reduction in hardness value relatively to the reference value for Filtek, 920.6 MPa. All other variations are smaller than 10%.

Table 4.2, Prodigy hardness is most affected after 22 months aging, but only for 3 and 9 pH values, with registered differences of 33% and 17% respectively. All other microhardness values diminish less then 10% for every pH condition and aging time.

In table 4.3 shows Surefil composites it is noticeable that the specimens aged in pH 3 are more susceptible of reduction hardness values than those aged in the other buffer solutions. For

Table 4.2: Average Vickers hardness values [MPa] and confidence interval (CI) for Prodigy Condensable from Kerr.

pH	**Prodigy Condensable**			
	0 months	**3 months**	**6 months**	**22 months**
3	602.8 (57.6)	546.6 (42.9)	547.9 (40.2)	403.3 (61.7)
7		568.8 (31.1)	593.2 (32.1)	566.6 (25.9)
8		569.5 (27.9)	562.2 (39.7)	500.9 (49.4)

Table 4.3: Average Vickers hardness values [MPa] and confidence interval (CI) for Surefil from Dentsply.

pH	**Surefil**			
	0 months	**3 months**	**6 months**	**22 months**
3	895.9 (52.8)	780.5 (58.1)	785.8 (51.6)	500.6 (153.8)
7		830.5 (62.3)	875.9 (58.7)	762.7 (62.2)
9		844.9 (38.1)	844.3 (57.1)	719.7 (41.2)

pH 3 the decrease is of 13%, up to 6 months fall to 44% less hardness at the 22$^{\text{nd}}$ month. Aging time also affects specimens significantly, for pH 7 and pH 9 with a decrease in hardness values of 15% and 20% respectively, for the last aging period.

Table 4.4, concerning Synergy the specimens most affected are the ones removed form the aging bath at the 22$^{\text{nd}}$ month for pH 3 and pH 9. These microhardness measurements registered a decrease of 30% and 22% respectively. All other values of microhardness decreased with a variation of 10%. Increase in hardness was registered at three month aging period for all pH 3, pH 6 and pH 9. This increase was of 3%, 1% and 8% relatively to 554.0 MPa reference hardness value.

Table 4.4: Average Vickers hardness values [MPa] and confidence interval (CI) for Synergy from Coltène.

pH	**Synergy**			
	0 months	**3 months**	**6 months**	**22 months**
3	554.0 (50.7)	571.7 (26.0)	523.9 (39.8)	385.4 (49.7)
7		556.9 (24.5)	544.3 (57.4)	515.5 (47.3)
9		600.7 (28.6)	564.7 (23.3)	432.9 (31.1)

After analyzing hardness results of QuixFil (table 4.5) specimens it is possible to understand that this composite is very affected by aging time and pH values. Curiously 6 months aging time was less affected than 3 months. The decrease of hardness was always less than the previous aging time, and there was even an increase in hardness for pH 3 and 6 months. Specimens aged in pH 9 bath were affected mostly at aging times of 3 and 22 months (less 31% of 889.4 MPa), while for pH 7 there is an increase of hardness for increasing period of aging time. The worst result obtained was for 22 month aging at pH 3, less 47%.

Table 4.5: Average Vickers hardness values [MPa] and confidence interval (CI) for QuixFil from Densply.

pH	**QuixFil**			
	0 months	**3 months**	**6 months**	**22 months**
3	889.4 (73.1)	718.5 (68.4)	934.8 (45.9)	470.6 (37.0)
7		791.7 (59.5)	832.6 (80.5)	860.6 (47.2)
9		613.6 (34.6)	792.0 (71.4)	616.8 (79.2)

In table 4.6, CeramX also shows a large decrease in hardness for 22 months and pH 3 conditions (less 44%), while for pH 7 the decrease was approximately the same for 3 periods of aging time (≈ 10%). Hardness values at pH 9 were less affected for intermediate aging period (6 months) while for 22 months the reduction was of 13%.

Table 4.6: Average Vickers hardness values [MPa] and confidence interval (CI) for CeramX from Densply.

pH	**CeramX**			
	0 months	**3 months**	**6 months**	**22 months**
3	631.6 (80.5)	532.8 (29.6)	547.3 (30.3)	350.9 (53.8)
7		569.4 (15.7)	569.3 (35.8)	579.3 (26.3)
9		588.1 (38.2)	627.4 (29.3)	547.9 (18.3)

Regarding Alert (table 4.7), and contrary to other composites evidences a slight increase in hardness, 1% – 3%, for specimens aged in pH solutions of 7 for the three aging periods. Specimens aged in pH solutions of 9 were not very much affected. The pH value which affected Alert hardness the most was buffer solution of pH 3, reducing hardness 15%, 12% and 24% for 3, 6 and 22 months respectively.

Table 4.7: Average Vickers hardness values [MPa] and confidence interval (CI) for Alert from Pentron.

pH	**Alert**			
	0 months	**3 months**	**6 months**	**22 months**
3	749.0 (41.7)	635.8 (33.1)	660.8 (49.1)	567.3 (46.0)
7		760.7 (61.7)	771.4 (63.4)	759.9 (37.4)
9		764.0 (44.4)	702.2 (64.2)	732.8 (51.9)

Table 4.8 is representative of hardness values of the composites which were not subject to the aging study, although were part of other analysis. Table 4.8 also shows the hardness value

of an amalgam used in the study which is 1.8 to 3.1 times higher than that assessed for all composites in the study.

Table 4.8: Average Vickers hardness values [MPa] and confidence interval (CI) for Filtek Supreme (Dentsply), Pyramid Enamel (Bisco), Pyramid Dentin (Bisco) and amalgam Tytin (Kerr).

Filtek Supreme	**Pyramid Enamel**	**Pyramid Dentin**	**Tytin**
0 months			
779.8 (83.9)	608.9 (22.64)	535.8 (11.41)	1695.9 (196.4)

4.3.2 Produced composites

I. Filler content variation

As explained before a great number of variations in volume fraction percentage and matrix variation were elaborated to understand the influence of the main components of composites, and therefore, we will start first with the study of filler volume fraction variation for the same average particle dimension. Afterwards two volume filler percentages will be studied and the particle average dimension varied. Finally results for the matrix variation will be presented.

II. Filler volume fraction variation

For the determination of the effect of variation of filler volume fraction, composites were produced mixing the commercial polyester resin with 6 μm average particle dimension silica. Thus the mixtures consisted of 12%, 16%, 24%, 30%, 37% and 46% in volume of silica. Some specimens of polyester resin only (0% filler volume fraction) were also produced to serve as comparison to composites specimens. Table 4.9, presents hardness values for the produced composite specimens with several filler volume fractions.

From the observation of table 4.9 one can conclude that hardness values increase linearly with increasing filler volume fraction. Regarding elastic modulus and hardness, Braem *et al.* (1987) showed that the modulus of a composite increased monotonically with filler level. This is consistent with results of the present study showing that the modulus and hardness of resins increases significantly with the addition of an inorganic filler. Also, Li *et al.* (1985) reported that changing the level of filler in composite altered the properties of hardness, water sorption, compressive strength, elastic modulus, and wear resistance.

III. Average filler size particle dimension

After the evaluation of volume filler fraction percentage we chose to evaluate the effect of average particle size dimension while maintaining the filler volume fraction unvaried. Initially the intention was to study only one percentage of volume filler fraction (30% in volume), but being nanoparticles the latest trend we decide to use them, and due to its characteristically, very high particle contact area, the initial volume fraction was impossible to attain using the proposed method of mixing particles. Therefore in order maintain the same variables constant,

Table 4.9: Average Vickers harness values [MPa] and standard deviation (STD) resin composites with 6 μm average particle dimension and six values of volume filler fraction.

Filler volume fraction [%]	**Polyester resin and 6 μm silica particles**		
	Designation	**Hardness [MPa]**	**STD**
0	PR	208.4	0.87
12	PR 12	248.4	1.26
16	PR 16	276.6	0.54
24	PR 24	298.9	0.41
30	PR 30	324.3	0.67
37	PR 37	367.0	1.20
46	PR 46	410.4	2.24

i.e., resin, material particle and mixing procedure, a volume filler fraction of 10% corresponded to the maximum capacity of resin and silica nanoparticles.

i. 30% volume filler fraction

Table 4.10, presents the average values of Vickers hardness for polyester resin matrix composite specimens with filler volume of 30% and average particle dimension of; 3 μm, 6 μm, 16 μm and 22 μm.

Table 4.10: Average Vickers hardness values [MPa] and standard deviation (STD) for polyester resin matrix composite specimens with 30% of filler volume and different average particle dimension.

Filler average dimension [μm]	**Composite with polyester matrix and 30% silica volume fraction**		
	Designation	**Hardness [MPa]**	**STD**
0	PR	208.4	0.89
3	PR 30/3	329.3	4.18
6	PR 30/6	324.3	6.60
16	PR 30/16	327.3	1.13
22	PR 30/22	323.8	2.51

From the analysis of the hardness results, the value of the resin hardness is much smaller than the hardness values of composites with 30% of filler fraction whatever the average filler sizes. The difference between them PR 30/3, PR 30/6, PR 30/16 and PR 30/22 is inferior to 6 MPa, thus, reinforcing the idea that hardness is influenced by filler fraction and not filler average particle dimensions. Due to the proximity of hardness values for the composites in study, it is natural to determine an average hardness value for these specimens. Therefore average value for 30% volume filler fraction is 326.2 MPa (excluding the resin specimens which do not have any inorganic filler content).

ii. 10% volume filler fraction

As explained before, due to the very high values of contact area of nanoparticles, another batch of specimens had to be elaborated to study the produced composites with this variety of particles. From the microhardness tests of the specimens previously presented the results are shown in the table 4.11.

Table 4.11: Average Vickers hardness values [MPa] and standard deviation (STD) for composite specimens with 10% of filler volume and a polyester resin matrix with different average particle dimension.

Filler average dimension [μm]	**Composite with polyester matrix and 10% silica, nano and micro silica, volume fraction**		
	Designation	**Hardness [MPa]**	**STD**
0	PR	208.4	0.87
0.13	PR 10/0.13	238.3	7.27
1	PR 10_70/0.13	243.9	15.67
2.14	PR 10_30/0.13	251.3	23.42
3	PR 10/3	242.0	9.69
6	PR 10/6	243.8	15.61
16	PR 10/16	245.2	7.38
22	PR 10/22	243.1	8.84

Again form the values obtained the conclusion extracted from the previous point, 30% in filler fraction volume, corresponds to the same hardness value. Here the difference between composites hardness values is bigger, there are also a higher number of specimens, hardness values range from 238.3 to 251.3 ($\approx$ 13 MPa).

Considering the average hardness of the resin (208.4 MPa) and resin composites with 10% (243.9 MPa) and 30% (326.2 MPa) in filler volume, and comparing them to the results obtained for filler volume fraction variation the relation between hardness and volume filler fraction is almost the same. A slope of about 4 (MPa)/% filler fraction was obtained in this case which is comparable to the value presented in table 4.9, previously obtained for the Polyester resin with 6 μm average silica particles, and several filler volume percentages.

IV. Matrix variation

For the determination of microhardness the procedures used for these materials were the same as used before. Prior to obtain the hardness results for these materials and due to the fact that exposure to light, resins tend to increase hardness in time, a continuous study, for all materials, with periodic hardness measures, was done to determine the number of days necessary to guarantee the stabilization of hardness. For these materials are present stabilized hardness values (table 4.12):

From table 4.12 it is obvious, and as expected, hardness values for all resins are smaller then the one obtained with increment of 24% in volume of inorganic filler. One of the main reasons for mixing inorganic particles together with the organic matrix is to increase the hardness of the material and after mixing 24% in volume the results show that for all resins.

Resin rA containing no UDMA is characterized by the lowest value of hardness followed by the hardness value for resin rC and the organic matrix containing 10 mol % of UDMA is the resin with the highest value of hardness. The composite containing 10 mol % of UDMA (cB) continues to show the highest hardness value but in contrast, composite cC has a lower hardness value than the composite obtained from resin rA. This result may be due to a poorer bonding between the organic and inorganic components of composite cC, or possibly the solid photo-initiator/photo-sensitizer system fail to light cure the composite in question.

Table 4.12: Average Vickers hardness values [MPa] and standard deviation (STD) for composite and resin specimens with 24% of filler volume and three distinct chemical compositions.

Material	**Designation**	**Particle dimension** [μm]	**Filler volume fraction** [%]	**UDMA** (mol %)	**Hardness** [MPa]	**STD**
Resin	PR	—	—	—	208.4	0.87
	rA			0	176.7	0.25
	rB			10	208.7	1.17
	rC			20	194.7	0.3
Composite	PR 24	6	24	—	298.9	0.41
	cA			0	272.1	0.68
	cB			10	283.4	0.42
	cC			20	263.1	0.48

The three resins considered show very similar results between them and also comparing to the previous polyester resin (298.9 MPa). Regarding the composites cA, cB and cC their hardness values are also very similar characterized with 7% difference between the hardest and the softest. These composites differ manly in the UDMA percentage 0 mol %, 10 mol % and 20 mol % for cA, cB and cC respectively.

In regard to the polyester composite resin, with the same volume filler percentage PR 24, hardness values decrease; of 10% to cA, 5% to cB and 14% to cC composites.

4.3.3 Antagonist materials

The teeth used in the present study were sound premolar extracted for mainly orthodontic reasons, and were supplied by the Faculty of Medicine of Coimbra University. All the teeth were properly washed and stored until its in vitro usage. In all hardness, Vickers by indenter was measured in ten different locations of the enamel layer. The average hardness, in 30 teeth, was 3,259 MPa with standard deviation (STD) of 451 and 43.6 for 90% confidence interval. Concerning the teeth roughness, in the location where the contact was effectuated, Ra was of 0.09 μm (STD, 0.01). The high value of standard deviation in the determination of microhardness expresses one of the main inconveniences of biological materials usage. Table 4.13, presents glass spheres physical characteristics and dimensions.

Table 4.13: Characteristics of glass spheres and dimensions.

Material	**Desnsity** [kg/m^3]	**Hardness** [MPa] (STD)	**Average diameter** [mm]	**Diameter tolerance** [μm]
Soft glass	2,500	5,131 (84.6)	10	14

In spite of higher values of hardness then human enamel glass spheres are materials oxide free and their properties vary less then biological materials. Willems (1992), reported Vickers hardness values for human enamel of 4,008 MPa a little higher then other authors for the same test conditions (Ryge *et al.*, 1961; Anusavice, 1982).

4.4 Impulse excitation of vibration (IEV)

To determine the dynamic elastic modulus was used the impulse excitation of vibration (IEV) as described by ASTM C1259-96 standard (1996). According to it each specimen is set in free flexural vibration by a light mechanical impulse and the displacement response signal acquired. This technique was chosen due to its simplicity and good reproducibility. First it will be presented the results for commercial composite materials (including materials characterization after aging in medium with different pH variation), afterwards the results obtained for the produced composites, with all filler and matrix variation, will be presented and discussed.

4.4.1 Commercial composites

Table 4.14 to table 4.21 present the dynamic elastic modulus results of the commercial composites included in the study. The first seven composites were select to be part of the study effect of aging and pH effect, therefore the values presented concern a control batch, corresponding to no aging and no pH values (0 months) and the dynamic elastic modulus for 3, 6 and 22 months for every pH values defined: 3, 7 and 9.

The description used for microhardness measures is also valid for dynamic elastic modulus of the materials here presented. The values, for each material here present for 0 months are used as reference and serve as control relatively to the results of elastic modulus of aged specimens. The number of measurements used in microhardness is the same as used here. Again, first are presented the value for materials utilized in the aging study and afterwards materials involved in other studies and an amalgam which was used as reference.

In table 4.14, pH values and aging time do not affect very much dynamic elastic modulus of the Filtek P60 specimens, although that generally there is a decrease. The greatest reduction occurs for 22 months and pH 3 (≈ 11%), other values decrease, relatively to reference value for Filtek, less then 9%.

Table 4.14: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for Filtek P60 from 3M.

pH	**Filtek P60**			
	0 months	**3 months**	**6 months**	**22 months**
3	22.1 (0.77)	20.9 (0.19)	20.9 (0.11)	19.7 (0.13)
7		22.2 (0.17)	20.7 (0.14)	20.9 (0.12)
9		21.0 (0.20)	20.6 (0.09)	21.1 (0.09)

Table 4.15, average values of dynamic elastic modulus obtain for Prodigy specimens are not very much altered for pH 3, pH 7 and pH 9 nor for aging times of 3, 6 and 22 months. Variation in the analyzed property has a maximum of 5%. Contrarily to hardness values and other specimens elastic modulus results Prodigy presents a general increase for almost all pH conditions and aging periods, only the average values of specimens aged during 6 months in pH 3 solution conditions decreased 1% relatively to 15.04 GPa non aged reference.

Surefil specimens generally registered a small decrease in dynamic elastic modulus, table 4.16. For 3 and 6 months conditions and pH 7 and 3 months and pH 9 no variation occurred. For the other conditions variations, with decreasing values, ranged from 1% to 7% of the reference value

Table 4.15: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for Prodigy Condensable from Kerr.

pH	**Prodigy Condensable**			
	0 months	**3 months**	**6 months**	**22 months**
3	15.04 (0.65)	15.57 (0.11)	14.90 (0.12)	15.50 (0.08)
7		15.11 (0.09)	14.97 (0.06)	15.46 (0.18)
9		15.78 (0.12)	15.70 (0.12)	15.52 (0.06)

of dynamic elastic modulus 20.0 GPa. The smallest value was registered for the 22^{nd} month and pH 9 conditions, −7%.

Table 4.16: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for Surefil from Dentsply.

pH	**Surefil**			
	0 months	**3 months**	**6 months**	**22 months**
3	20.0 (0.68)	18.7 (0.13)	19.5 (0.04)	19.4 (0.09)
7		20.0 (0.04)	20.1 (0.03)	19.3 (0.07)
9		20.1 (0.04)	19.8 (0.07)	18.6 (0.09)

From the observation of dynamic elastic modulus of Synergy specimens there is a small increase for 3 and 6 months and pH 9 and also 3 months and pH 7, of 4% and 8% respectively, table 4.17. For all the other conditions there is a decrease, generally small (1% – 8%), except for 22 months and pH 9 which demonstrated a reduction of 62% relatively to reference value of 15.5 GPa.

Table 4.17: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for Synergy from Coltène.

pH	**Synergy**			
	0 months	**3 months**	**6 months**	**22 months**
3	15.5 (1.10)	15.1 (0.06)	14.7 (0.09)	14.6 (0.07)
7		16.8 (0.11)	15.4 (0.10)	14.2 (0.05)
9		16.1 (0.10)	16.2 (0.13)	5.9 (0.06)

Generally all values of dynamic elastic modulus of Quixfil decrease for all aging periods and pH values, table 4.18. The decreases for pH 3 and pH 7 and for all aging periods vary, relatively to average reference values up to 9% less. For pH 9 decreases of 7%, 17% and 56% are registered for aging periods of 3, 6 and 22 months respectively.

The obtained values of dynamic elastic modulus for CeramX variation register a small increase of 1% and 3% for conditions pH 9 and aging periods of 3 and 6 months, for this pH

Table 4.18: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for QuixFil from Densply.

pH	**QuixFil**			
	0 months	**3 months**	**6 months**	**22 months**
3	26.3 (0.61)	24.9 (0.13)	25.6 (0.12)	24.3 (0.09)
7		25.4 (0.13)	25.1 (0.05)	24.0 (0.10)
9		24.4 (0.13)	21.9 (0.19)	11.5 (0.06)

condition a reduction of 4% was measured, table 4.19. For pH 7 the reductions were of 2%, 8% and 9% relatively to 3, 6 and 22 months. Condition of pH 3 and for the 22$^{\text{nd}}$ month registered the larger decrease 13% relatively to the 15.2 GPa reference value.

Table 4.19: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for CeramX from Densply.

pH	**CeramX**			
	0 months	**3 months**	**6 months**	**22 months**
3	15.2 (0.74)	14.3 (0.07)	14.6 (0.12)	13.3 (0.07)
7		14.9 (0.10)	14.0 (0.06)	13.9 (0.01)
9		15.3 (0.12)	15.6 (0.11)	14.6 (0.07)

In table 4.20, regarding the elastic values for the several aging periods and pH conditions Alert did not suffer a very big decrease, except for the conditions of pH 3 and 22 months aging, which presented a reduction of 13%. All the other reduction values ranged from 1% to a maximum of 6%.

Table 4.20: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for Alert from Pentron.

pH	**Alert**			
	0 months	**3 months**	**6 months**	**22 months**
3	18.8 (0.99)	19.4 (0.11)	18.3 (0.08)	16.3 (0.08)
7		18.5 (0.11)	18.0 (0.15)	18.3 (0.13)
9		17.7 (0.07)	18.6 (0.10)	17.8 (0.20)

The three composites presented in table 4.21 have very similar filler weight percentage, 78%, 78% and 80%, for Filtek Supreme, Pyramid Enamel and Pyramid Dentin respectively, and the average dynamic elastic modulus was of 16 GPa, 18.1 GPa and 15.1 GPa in the same order.

For the only amalgam (Tytin) presented in the study the average value is 3 up to 4.5 times greater then the values of dynamic elastic modulus obtained for the commercial light cured composites.

Table 4.21: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for Filtek Supreme (Dentsply), Pyramid Enamel (Bisco), Pyramid Dentin (Bisco), Filtek Supreme (Kerr) and amalgam Tytin (Kerr).

pH	**Filtek Supreme**	**Pyramid Enamel**	**Pyramid Dentin**	**Tytin**
			0 months	
—	16.0 (0.29)	18.1 (0.11)	15.1 (0.23)	67.6 (1.79)

4.4.2 Produced composites

I. Filler content variation

As done previously for the microhardness values the same structure will be used for the dynamic elastic modulus. Thus, first the composites with same particle dimension and volume filler fraction variation, secondly, the same volume filler percentage, 30% and 10% wright fraction presentation of elastic modulus results regarding filler content variation.

II. Filler volume fraction variation

For the determination of the effect of variation of filler volume fraction composites were produced mixing the commercial polyester resin and a 6 μm average silica particle dimension. Mixtures of 12%, 16%, 24%, 30%, 37% and 46% in volume of silica were tested. Some specimens of only polyester resin were also produced to serve of comparison to the composites specimens. Table 4.22, presents the dynamic elastic modulus of resin composites with average particle dimension of 6 μm and six volume filler fractions.

Table 4.22: Average dynamic elastic modulus values [GPa] and standard deviation (STD) resin composites with 6 μm average particle dimension and six volume filler fractions.

Filler volume fraction [%]	**Polyester resin and** 6 μ**m silica particles**		
	Designation	**Dynamic elastic modulus** [GPa]	**STD**
0	PR	4.51	0.34
12	PR 12	6.24	0.27
16	PR 16	6.91	0.07
24	PR 24	8.60	0.19
30	PR 30	9.25	0.94
37	PR 37	12.6	0.18
46	PR 46	15.8	0.11

As observed for the hardness, and now for the dynamic elastic modulus there is a linear relation between inorganic filler fraction and elastic modulus. Again the results were expectable, as referred in the hardness analysis, and observing from the literature citations a very well known relation, several authors showed that mechanical properties such as Young's modulus and composite hardness depend mainly on the filler load (Harrison and Draughn, 1976; Braem *et al.*, 1987).

A positive correlation has also been established between the hardness and the inorganic filler content (Boyer *et al.*, 1982; Raptis *et al.*, 1979; Roberts and Shaw, 1984).

III. Average filler size particle dimension

For what regards the effect of average particle dimension in dynamic elastic modulus for volume filler fraction of 30% and 10% a parametric analysis was done. First are presented the results for 30% silica fraction, for the several particle dimensions and the same thing for 10% reinforcement particles. The second analysis regards the effect of matrix; again the three produced matrices are compared with the polyester resin and also these matrices with composites with the same matrix compositions and reinforcement particles of 6 μm and 24% filler volume fraction.

i. 30% volume filler fraction

Table 4.23, presents the average values of dynamic elastic modulus for polyester resin matrix composite specimens with filler volume of 30% and average particle dimension of; 3 μm, 6 μm, 16 μm and 22 μm.

Table 4.23: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for composite specimens with 30% of filler volume and a polyester resin matrix with different average particle dimension.

Filler average	**Composite with polyester matrix and 30% silica volume fraction**		
dimension [μm]	**Designation**	**Dynamic elastic modulus** [GPa]	**STD**
0	PR	4.51	0.02
3	PR 30/3	9.74	0.49
6	PR 30/6	9.25	0.95
16	PR 30/16	9.01	0.04
22	PR 30/22	9.24	0.06

Concerning dynamic elastic modulus again the values for 30% in filler fraction is almost independent from particle dimension. Results show, also, the effectiveness of inorganic filler doubling elastic modulus. The difference between composites with different average particle dimension is very small from 5% to 7% less then PR 30/3, the composite with higher average elastic modulus. Average elastic modulus for 30% filler volume fraction, regardless from particle dimension, 9.31 (0.31) GPa.

ii. 10% volume filler fraction

From the IEV tests for composite specimens with silica filler volume of 10% and polyester resin matrix specimens with different average particle dimension; 0.13 μm, 1 μm, 2.14 μm, 3 μm, 6 μm, 16 μm and 22 μm, dynamic elastic modulus values are presented in table 4.24.

In table 4.24, for 10% in filler fraction volume, with several particle dimensions elastic modulus ranges from 6.15 GPa and 6.77 GPa ($\approx$ 0.62 GPa) which represents less then 10% of the higher average dynamic elastic modulus. Considering the average of all compositions used in these batch the average dynamic elastic modulus is 6.35 (0.21) GPa.

Considering the resin elastic modulus (4.51 GPa) and resin composites with 10% (6.77 GPa) and 30% (9.31 GPa) in filler volume, resin is more than half the value obtained for 30% filler

Table 4.24: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for composite specimens with 10% of filler volume and a polyester resin matrix with different average particle dimension.

Filler average dimension [μm]	**Composite with polyester matrix and 10% volume filler fraction, nano and micro silica**		
	Designation	**Dynamic elastic modulus** [GPa]	**STD**
0	PR	4.51	0.020
0.13	PR 10/0.13	6.18	0.024
1	PR 10_70/0.13	6.77	0.027
2.14	PR 10_30/0.13	6.42	0.036
3	PR 10/3	6.23	0.016
6	PR 10/6	6.34	0.004
16	PR 10/16	6.15	0.032
22	PR 10/22	6.33	0.028

volume and elastic modulus for 10% is 41% higher.

It has been found that Young's modulus is the mechanical quantity most highly correlated with volumetric filler content (Draughn, 1981; Boyer *et al.*, 1982). This correlation has been quantified before by Boyer *et al.* (1982).

Although Young's modulus is supposed to be independent of the particle size, it should be dependent on the maximum particle packing fraction, which is defined as the ratio of true particle volume to the apparent volume occupied by the particles (Draughn, 1981). This ratio is determined by the particle shape and size distribution. This could explain why the ranking of the Young's moduli values does not perfectly match that of the volume percent of inorganic filler (Braem *et al.*, 1986).

IV. Matrix variation

For the analysis of matrix influence, the results for dynamic elastic modulus are shown in table 4.25.

Table 4.25: Average dynamic elastic modulus values [GPa] and standard deviation (STD) for three: resins and composite specimens. Resin matrix with different UDMA mol percentage and composites with average particle 6 μm and 24% of filler volume.

Material	**Designation**	**Particle dimension** [μm]	**Filler volume fraction** [%]	**UDMA** (mol %)	**Dynamic elastic modulus** [MPa]	**STD**
Resin	PR	—	—	—	4.51	0.02
	rA			0	4.37	0.25
	rB			10	4.56	1.17
	rC			20	4.72	0.30
Composite	PR 24	6	24	—	8.60	0.19
	cA			0	11.40	0.68
	cB			10	11.51	0.42
	cC			20	9.57	0.48

The average elastic modulus values obtained for the resins and composites prepared are presented in table 4.25. There is a small difference between the values of the dynamic elastic modulus for the four resins, with a tendency to increase with the amount of the UDMA component. Elastic modulus for the polyester resin is also very similar to the resins with UDMA. As expected, table 4.25 shows higher values of dynamic elastic modulus for composites cA, cB and cC, prepared by adding to the three resins 24% volume fraction of inorganic particles. The results obtained for composites cA and cB are similar to each other whereas for composite cC, containing the highest amount of UDMA, there is a significant decrease (≈ 20%), thus a similar trend as was seen before for the microhardness test results. Comparing the elastic modulus with values obtained for the polyester resin with the same filler volume percentage, results shows a smaller value; this is related to the matrix composition. Differences in resin formulations among manufacturers were also known to affect degree of conversion and cross linkage, (Ruyter and Svendsen, 1978; Vankerckhoven *et al.*, 1981; Asmussen 1982; Cook and Standish, 1983; Caughman *et al.*, 1991; Davidson-Kaban *et al.*, 1997; Asmussen and Peutzfeldt, 1998).

Composites cA, cB and cC are constituted by organic matrix with Bis-GMA and TEGDMA photo-initiator/photo-sensitizer and cross-linking agent, a urethane dimethacrylate (UDMA). This complex matrix system, in all similar to commercial restorative composite materials, is the reason for the difference to the dynamic elastic modulus value. Has reported by Chung (1990) seems plausible that it be assumed that the filler concentration and the nature of bonding between filler particle and resinous matrix play a prominent role in determining the properties of contemporary dental composites (Wu and McKinney, 1982; Söderholm, 1985; Calais and Söderholm, 1988; Glenn, 1982).

4.5 Four point bending test

In this test three properties are determined: flexural resistance [MPa], work-of-fracture [J/m^2] and static elastic modulus [GPa].

4.5.1 Commercial composites

Initially it was intended to evaluate the flexural properties of commercial composites, but in order to have a significant number of results in the aging periods considered a great number of specimens had to be produced for each; material, aging period and pH condition. Due to high price of commercial composite materials given to us, it was decided to evaluate these properties only without aging, only seven specimens of each commercial restorative material was used to assess each of the mechanical properties. Although the number is not very elevated, taking into account that these are not totally homogeneous materials and its processing depends very much in the person producing it, due to a poor filling of the mould or even a not very careful curing procedure. In table 4.26, are presented the significant properties regarding the four point bending test, the fact that seven of all composites used in the several studies are utilized in the aging and pH study the result presentation and discussion will be done for each one of these properties for each restorative commercial material.

Observing the results from table 4.26, flexural strength results range from 44.7 MPa to 90.4 MPa being these extreme results obtained respectively for CeramX and Pyramid Enamel. Considering the flexural results in interva MPals up to 50 MPa the composite materials Prodigy and CeramX had average results of 48.4 MPa and 44.77 respectively. In the interval of 50 MPa to 60 MPa were the restorative materials, Surefil, Synergy, QuixFil and Pyramid Dentin with results of; 58.68 MPa, 58.78 MPa, 56.16 MPa and 59.02 MPa respectively. More then 60 MPa

Table 4.26: Average flexural strength [MPa], work-of-fracture [J/m^2] and static elastic modulus [GPa] for commercial resin composites, standard deviation (STD).

Commercial composite	**Flexural strength** [MPa]	**Work-of-fracture** [J/m^2]	**Static elastic modulus** [GPa]
Filtek P60	68.70 (7.44)	1.68×10^3 (255.29)	12.20 (0.81)
Prodigy Condensable	48.40 (7.38)	1.52×10^3 (178.18)	9.91 (0.66)
Surefil	58.68 (6.42)	1.22×10^3 (189.01)	13.27 (1.37)
Synergy Compact	58.78 (7.95)	2.24×10^3 (150.32)	8.94 (0.86)
QuixFil	56.16 (6.47)	0.83×10^3 (35.25)	16.42 (1.46)
CeramX	44.70 (4.26)	1.11×10^3 (169.17)	8.59 (0.81)
Alert	68.60 (7.20)	2.27×10^3 (223.27)	11.83 (1.19)
Filtek Supreme	78.54 (3.24)	4.22×10^3 (120.07)	8.69 (0.24)
Pyramid Enamel	90.40 (6.35)	4.36×10^3 (254.71)	10.21 (0.88)
Pyramid Dentin	59.03 (4.94)	4.03×10^3 (223.27)	6.61 (0.37)

and minus then 70 MPa only two composites had average results ranging these values, Filtek P60 and Alert. More than 70 MPa only the average values of specimens of Filtek Supreme and Pyramid Dentin. Although some author, Braem *et al.* (1989); Chung and Greener (1990) and Kim *et al.*, (1994) have reported positive correlation between mechanical properties and volume fraction filler, for these particular results is not noticeable a clear tendency. Chung *et al.*, (2004) reported a ranking of flexural strength values from lowest to in accordance to filler fraction of the tested composites, although all of them were from the same manufacturer and had very similar matrix composition.

It is also important to understand that the composites here tested are very different in terms of filler content, *i.e.*, not only in average particle dimension, particle size distribution and also the existence of fibers, but also their matrices are distinct.

Concerning the mechanical properties of work-of-fracture (WOF) for the tested composites can be observed that the evolution of these properties is very similar to the progress results, flexural strength and WOF, values for the composites can be observed in the fig. 4.1.

Concerning the static elastic modulus obtained form bending tests there is a group of composites that evidences higher results relatively to the rest, these composites are, by decreasing order of elastic modulus, QuixFil, Surefil, Filtek and Alert. It is important to notice that these resin composites all have volume filler fraction higher then 80%, generally higher volume filler fractions represent higher elastic modulus. Static elastic moduli are smaller then the ones obtain dynamically but their tendency is very similar.

4.5.2 Produced composites

The influence of particle content, volume fraction and particle dimension is very important to the mechanical and tribological behavior, however, the mechanisms of influence are not yet well established. Through a parametric approach is intended to quantify the direct influence of; filler fraction, particle dimension and matrix composition in flexural behavior of composites and resins using four point bending test. In this test three properties have been used to evaluate the bending material performance: flexural resistance, work-of-fracture and static elastic modulus. First it will presented the results concerning volume percentage filler content, afterwards particle dimension (for 30% and 10% filler content) and finally the influence of matrix composition.

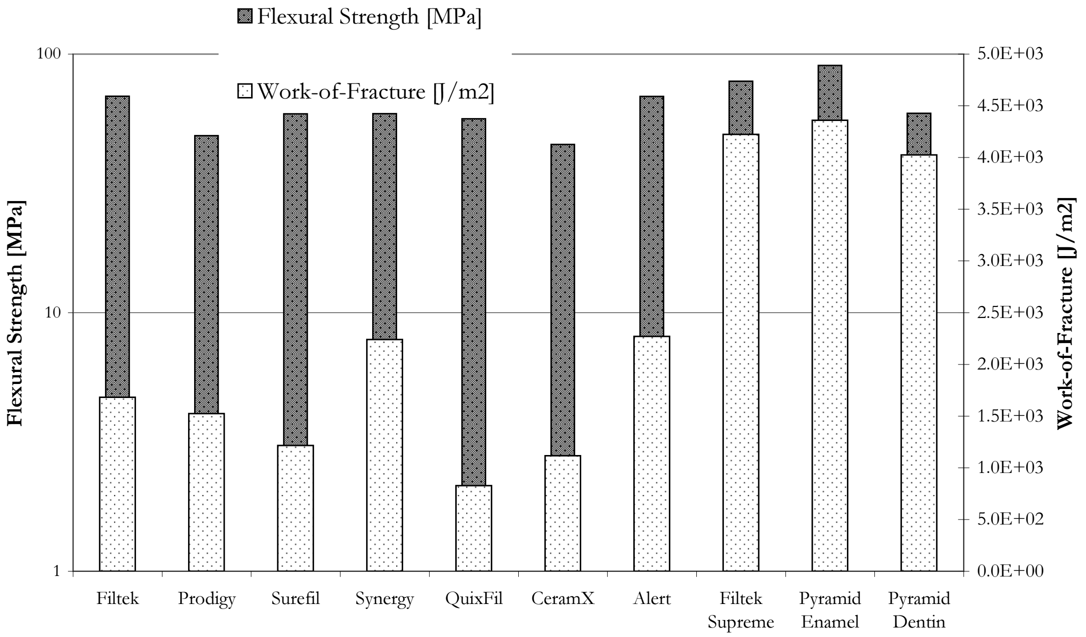


Fig. 4.1: Representation of average flexural strength [MPa] and work-of-fracture [J/m^2] for the restorative composites evaluated by four point bending tests.

I. Filler content variation

To analyze bending test properties; flexural resistance [MPa], work-of-fracture [J/m^2] and static elastic modulus [GPa] for produced composites, filler volume fraction and average particles dimension were modified. Specimen composites with same particle dimension and volume filler fraction variation were produced, afterwards, for constant volume filler fractions, 30% and 10%, average particle dimension was altered.

II. Filler volume fraction variation

The displayed results, table 4.27, generally, show that with increasing values of particles content values for ultimate break load (flexural strength [MPa]) and consequently displacement are smaller and the flexural strength diminishes. Therefore, although a raise in the static elastic modulus an increase in particles volume fraction leads to a reduction in work-of-fracture values.

Hence, addition of rigid particles to a polymer matrix can easily improve the modulus since the rigidity of inorganic fillers is generally much higher than that of organic polymers. The composite modulus consistently increases with increasing particle content (Fu *et al.*, 2008), in this case for 10% filler volume fraction elastic modulus increased almost 50% in relation to the unfilled matrix (Pukanszky and Voros, 1993).

From the analysis of the table 4.27 static elastic modulus increases with increasing filler volume fraction, this was also observed when the impulse excitation technique was used. Dynamic elastic modulus shows always higher values then the value obtained with the four point bending tests this is due to the different velocity of the applied load to specimens. When the applied load speed is increased static elastic modulus tends to values obtained through the dynamic method (Braem et al 1986; Sabbagh, 2002).

Table 4.28, presents, static and dynamic elastic modulus for; resin composites specimens with 6 μm average particle dimension filler and several volume fractions.

Table 4.27: Average flexural strength [MPa], work-of-fracture [J/m^2] and static elastic modulus [GPa] for resin composites with 6 μm average particle dimension and six volume filler fractions.

Filler volume fraction [%]	**Polyester resin and 6 μm silica particles**			
	Designation	**Flexural strength** [MPa]	**Work-of-fracture** [J/m 2]	**Static elastic modulus** [GPa]
0	PR	54.2	4.3×10^3	2.93
12	PR 12	44.05	1.8×10^3	4.38
16	PR 16	36.69	1.4×10^3	4.52
24	PR 24	36.01	1.1×10^3	5.24
30	PR 30	27.05	5.7×10^2	5.72
37	PR 37	23.61	3.3×10^2	7.30
46	PR 46	24.93	3.0×10^2	9.52

The elastic modulus of the material tested results from a complex interaction between the mechanical properties of the two phases of the composite components. In the scientific literature several theories and equations exist, which were developed to describe and predict the values of the composite elastic modulus depending on the percentage volume of particles.

From the comparison of the theoretical equations and the experimental data obtained for the elastic modulus the equation developed by Reuss, equation 2.1; are in agreement with the experimental results, fig. 4.2.

In general, and for the results of the dynamic and static tests, there is an increase in these properties that corresponds to a rise in the percentage of the volume of reinforcement particles. However, the increasing of particle contents leads to lower flexural resistance and smaller break-load displacement. Therefore, in spite of higher elastic modulus, the work-to-fracture diminishes with the rise of particle contents. Another important conclusion is the fact that the Reuss model, for elastic modulus, agree well with the experimental results, therefore can be used to forecast the expected values for new compositions.

Table 4.28: Comparison of static and dynamic elastic modulus [GPa] for resin composites with 6 μm average particle dimension and six values of weight/volume filler fractions.

Filler fraction [%]		**Dynamic elastic modulus**	**Static elastic modulus**
Vol.	**Wt.**	[GPa]	
0.00	0.0	4.51	2.93
0.12	30.0	6.24	4.38
0.16	40.0	6.91	4.52
0.24	50.0	8.60	5.24
0.30	60.0	9.25	5.72
0.37	70.0	12.6	7.30
0.46	80.0	15.8	9.52

III. Average filler size particle dimension

After presenting test results for volume filler fraction variation a parametric analysis was done for fix fraction of 30% and 10% of silica and several particle dimensions for each volume

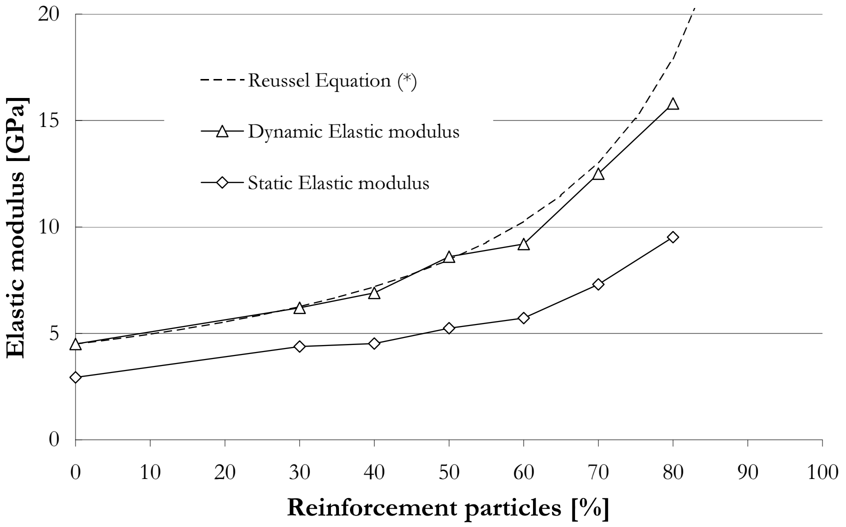


Fig. 4.2: Representation of the Reussel model, for elastic modulus of particle composites, and experimental data for dynamic and static elastic modulus in function of particles volume fraction.

filler fraction considered.

i. 30% volume filler fraction

As previously explained the first results regard specimens with 30% filler fraction and average particles dimension of 3 μm, 6 μm, 16 μm and 22 μm. Table 4.29, presents properties of four point bending tests.

Table 4.29: Average flexural strength [MPa], work-of-fracture [J/m 2] and static elastic modulus for composite specimens with 30% of filler volume and a polyester resin matrix with different average particle dimension.

Filler average dimension [μm]	**Composite with polyester matrix and 30% silica volume fraction**			
	Designation	**Flexural resistance** [MPa]	**Work-of-fracture** [J/m^2]	**Static elastic modulus** [GPa]
0	PR	55.20	4.3×10^3	2.93
3	PR 30/3	24.22	0.32×10^3	5.70
6	PR 30/6	27.05	0.30×10^3	5.72
16	PR 30/16	41.43	1.72×10^3	5.13
22	PR 30/22	44.13	1.66×10^3	5.23

From the analysis of the obtained values for bending tests properties; flexural resistance and work-of-fracture have the same type of evolution. These properties tend to increase with increasing average particle dimension and therefore distance between particles increase, for the same filler volume fraction. On the other hand static elastic modulus has almost the same values, ranging from 5.13 GPa to 5.72 GPa. This tendency was already verified for the dynamic elastic modulus. Thus, for the same filler content and increasing particle dimension flexural resistance and work-of-fracture increase while elastic modulus maintain its value.

ii. 10% volume filler fraction

In the table 4.30 are presented the results of bending tests, along with average properties results of flexural strength [MPa], work-of-fracture [J/m^2] and static elastic modulus for composites with 10% filler volume fraction and several particle dimension, 0.13 μm, 1 μm, 2.14 μm, 3 μm, 6 μm, 16 μm and 22 μm, and also a mixture of nano and micro silica particles.

Table 4.30: Average flexural strength [MPa], work-of-fracture [J/m^2] and static elastic modulus for composite specimens with 10% of filler volume and a polyester resin matrix with different average particle dimensions.

Filler average dimension [μm]	**Composite with polyester matrix and 10% volume filler fraction, nano and micro silica**			
	Designation	**Flexural strength** [MPa]	**Work-of-fracture** [J/m^2]	**Static elastic modulus** [GPa]
0	PR	55.20	4.3×10^3	2.93
0.13	PR 10/0.13	22.12	0.63×10^3	3.16
1	PR 10_70/0.13	23.29	0.83×10^3	3.34
2.14	PR 10_30/0.13	28.21	1.2×10^3	3.39
3	PR 10/3	38.88	1.6×10^3	3.02
6	PR 10/6	43.31	2.2×10^3	3.15
16	PR 10/16	49.92	2.6×10^3	3.59
22	PR 10/22	55.19	3.1×10^3	3.50

According with what was demonstrated for 30% filler volume fraction, and has it should be expected, the flexural strength and work-of-fracture tend to increase with increase of filler particle dimension. Concerning elastic modulus, static as well as dynamic, the values are very similar, ranging from 3.02 GPa to 3.59 GPa for the static elastic modulus of the composites with 10% volume filler fraction. This kind of results are reported by Bowen (1956, 1963 and 1964) and have shown that increased filler fraction also increased the elastic modulus and strength, while it reduced setting contraction and thermal expansion.

Ikejima *et al.*, (2003) reported that when filler volume fraction was increased, flexural strength, flexural modulus and shear strength increased up to about 50%. Other authors reported that, the fracture toughness tends to decrease with reduction in filler volume/weight fraction (Hara and Nemoto, 1986; McCabe and Wassell, 1999; Braem *et al.* 1989; Ferracane *et al.*, 1998)

IV. Matrix variation

For the matrix influence analysis the results for four point bending test are shown in table 4.31. In this table (4.31) there are also present a polyester resin and a composite with the same resin and a same filler fraction so they could serve as comparison materials.

Bending tests allow three different results, namely: flexural resistance, elastic modulus and work-of-fracture (the energy required to fracture the specimen, obtained from the area under the load-displacement curve divided by the specimens' cross-section area). The values of elastic modulus presented in the table 4.31 were obtained by bending test corresponding to the linear part of the graph load *vs.* displacement, *i.e.*, slope of curve load-displacement under static conditions.

These values are obtained at a higher strain than the elastic modulus values obtained by means of dynamic tests. Following the same pattern as of the values of the dynamic elastic

Table 4.31: Average dynamic elastic modulus values [GPa] for three: resins and composite specimens. Resin matrix with different UDMA mol % and composites with average particle 6 μm and 24% of filler volume.

Material	**Designation**	**Filler volume fraction** [%]	**UDMA** (mol %)	**Flexural strength** [MPa]	**WOF** [J/m^2]	**Static elastic modulus** [GPa]
Resin	PR	—	—	54.20	4.27×10^3	2.93
	rA		0	52.04	4.34×10^3	2.40
	rB		10	58.42	1.01×10^4	2.78
	rC		20	59.62	7.96×10^3	3.17
Composite	PR 24	24	—	36.01	1.10×10^3	5.24
	cA		0	26.86	4.41×10^2	7.35
	cB		10	40.42	1.05×10^3	7.07
	cC		20	36.30	1.03×10^3	5.81

modulus, the static elastic modulus for the three resins also increases with the UDMA content and the values for composites cA and cB are similar to each other while composite cC shows a significant decrease.

The remaining results show that the average flexural strength for resins containing UDMA (rB and rC) is higher than that of resin rA and that the work-of-fracture for resin rB is significantly higher than of the other two resins. The advantages of UDMA have been reported to be lower viscosity and greater flexibility of the urethane linkage, which may improve the toughness of resin composites based on this monomer (Glenn, 1982). Thus, by adding the inorganic part to the prepared resins, values of the ultimate break load displacement become lower and the flexural strength diminishes. Despite having a lower static elastic modulus than composite cA, composite cB containing 10 mol % of UDMA possesses the highest values for average flexural strength and work-of-fracture despite the reported increase of flexural strength with increasing UDMA (Asmussen and Peutzeldt, 1998; Ruyter and Øysæd, 1987), reported that due to in the rather flexible nature of UDMA molecules it is possible a decrease of flexural resistance with increasing content of UDMA.

4.6 Partial conclusions

I. Hardness

i. Commercial composites

Commercial composites are very difficult to compare due to the difference in their composition, namely matrix components, type of filler and filler volume fraction. Even so, assuming the announced values of inorganic filler fraction are correct, generally the tendency is to present an increase in hardness for composite with higher values of filler volume fraction. Hardness of tested materials ranged from 535 MPa to 920 MPa.

Concerning aging and pH effect on hardness, generally the composites more affected were Surefil, QuixFil and CeramX, *i.e.* observing the 3 aging periods and all pH values in study. Acid solution (pH 3) was the more aggressive to composites. The more affected were Alert, CeramX, QuixFil, Surefil, Synergy and Prodigy, taking into account the more extended aging period hardness reduction, relatively to their reference, was at least of 33%. QuixFil registered the highest decrease with 47%, Surefil and CeramX reduced hardness in 44%. Curiously the composites most affect by acid solution are from the same manufacturer, Dentsply.

Specimens aged in pH 9 buffer solutions were also affected, but not in so great extend, Surefil, Synergy and QuixFil presented reductions of 20%, 22% and 31% respectively all for the longest aging period. The neutral solution was the one which least affected composite's hardness. Constantinescu *et al.*, (2007) have concluded that the effect of acid medium in acrylic resins induce surfaces with higher roughness compared to higher pH media.

ii. Produced composites

Concerning produced composites, and, taking into account the parameters in study which affect hardness can be concluded that:

- Hardness rises with increase of filler fraction, from the seven different filler fractions in study average values were all different and a composite with higher values of inorganic material had higher values of hardness;
- Average filler particle dimension did not affect composite's hardness values. Considering the five average filer particle dimension and even a mixture of nano- and microfiller, for the same filler fraction, no variation in hardness was registered;
- Matrix variation affected hardness values. Resins produced for the study showed variation in hardness depending on the different percentage of UDMA (0%, 10% and 20%). Composites produced with these matrices showed an increase with the adding of filler and again as occurred for resins composites hardness varied in the same manner as resins. This evidences a dependence of hardness in respect to the matrix constitution.

Although there are differences in the molecular structure and composition in the resinous matrix of the composites tested, positive relationships were determined between volume fraction of filler and Vickers hardness number. It thus seems plausible that it be assumed that the filler concentration and the nature of bonding between filler particle and resinous matrix play a prominent role in determining the properties of the composites (Wu and McKinney, 1982; Soderholm, 1985; Calais and Soderholm, 1988).

II. Elastic modulus

i. Commercial composites

As observed with hardness, there is a general tendency to increase elastic modulus with filler fraction.

Concerning the effect of aging and pH solutions their influence in the composites elastic modulus was not as intense as occurred for hardness. In this case fewer composites were affected and also in less extend. Most affected composites were Synergy and QuixFil. For what concerns elastic modulus the decrease in properties values was more noted for the last aging period and for the basic solution, pH 9. Synergy and Quixfil suffered an elastic modulus reduction of 62% and 56% respectively. All other buffer solutions and aging periods were not very much aggressive. Thus, pH does not affect very much the elastic response of these restorative materials.

From the results presented and analyzed can be concluded that the composites modulus of elasticity (Peutzfeld, 1997, Wolter et al 1994) increase when filler volume fraction is increased.

The results of the work of Ikejima *et al.*, (2003) clearly demonstrated this effect of filler content, filler particle size and filler silanazation on mechanical properties. Also Papadogiannis *et al.*, (2003) reported in a study with packable resin composites that the higher values of elastic modulus obtained by Alert could be attributed to the higher filler load and to the content of large-size irregular glass fibers Lakes *et al.*, (2002).

ii. Produced composites

Concerning the dynamic elastic modulus for these types of resin and composites, regarding the evaluation of filler fraction and particle size variation can be concluded that:

- With the introduction of increasing values of filler volume fraction in polyester resin a rise in elastic modulus is registered;
- Again it was possible to observe that average particle dimension variation, with constant filler volume fraction, did not have any influence in specimen's average dynamic elastic modulus. This was true also for composite with a mixture percentage 30% – 70% and 70% – 30% of nanoparticles.
- Matrix composition, for the filler volume fraction considered had no noticeable influence in elastic modulus values. Although composites specimens with 20% mol UDMA had smaller elastic modulus than specimens with 10% and resin specimens with these UDMA percentages did not behave exactly the same exact way.
- There is a clear relation between dynamic elastic modulus and static elastic modulus. The evolution of the elastic modulus has the same tendency values differ only due to technique used, when IEV is used higher values elastic modulus were obtained.

III. Flexural strength, work-of-fracture and static elastic modulus

i. Commercial composites

Observing the bending test results there is no relation between filler volume fraction and any of the three properties analyzed in this flexural test. It is possible to conclude that flexural strength and work-of-fracture have the same tendency for all composites in study. Elastic moduli obtained from static bending tests have the same tendency that is registered for dynamic test ones. As these composites have great number of variables constituents, and thus possible variables, matrix composition, filler fraction, and filler size distribution, mixture of different percentage and diverse monomers it is very difficult to establish a cause effect relation between its components and its behavior.

Regarding this matter Manhart *et al.* (2000a) suggested that the fillers themselves, the filler load level, and the filler-matrix interactions probably have a greater influence on the fracture parameters of dental composites than the structure of the organic matrix.

Boyer *et al.* (1982) studied ten commercial composites, including microfilled resin composites, and reported that tensile strength and filler concentration had a negative correlation coefficient. The tensile and compressive strengths were reported to be superior for a lower (45%) rather than a higher (55%) filler-volume fraction (Draughn, 1981). The negative effects were assumed to be related to inherent flaws, especially air porosity included in the composite material (Smith, 1985). In addition, a critical filler concentration is needed for reinforcement and significant improvement in the properties of composites. Atsuta and Turner (1982) reported that with increasing loading of the silicate filler, an abrupt decrease in strength was found for composites with greater than 83 wt % silanated Li $AlSiO_4$ particles, Chung (1990).

ii. Produced composites

Regarding the flexural behavior of produced composites it is possible to establish some conclusions due to the parametric approach used. When evaluated the filler volume fraction it was possible to establish that;

- increasing filler content produced an exponential decrease composite's flexural strength and work-of-fracture and the opposite effect was determined for elastic modulus (exponential increase);
- When average particle dimension was increased, maintaining constant particle filler volume fraction, it produced a linear increase in flexural strength and work-of-fracture. As previously observed static elastic modulus was not affected by average particle dimension.
- Regarding the effect of matrix it is possible to conclude that matrices with higher values of % mol UDMA increase flexural strength and elastic modulus but on the other hand decrease work-of-fracture. The introduction of inorganic filler in the previous matrices leads to a decrease in flexural strength and work-of-fracture of composites and, conversely, an increase in elastic modulus values. Concerning elastic modulus % mol UDMA have a contraries effect in resin and in the composites; for elastic modulus and work-of-fracture increasing percentage of UDMA make resin have higher values of these properties while for composites these values decrease. Only for flexural strength the increase in mol % of UDMA has the same effect in resins and in composites.

Chapter 5

Tribological behavior, results and discussion

5.1 Introduction

This chapter begins with the validation of the main experimental methodology used to assess the wear of dental composite materials. This validation concerns mainly the use of glass sphere as antagonist material in the reciprocating wear tests. The use of glass as an antagonist material derives from its advantages; no oxidation, hardness values similar to tooth enamel and constancy of properties. Even with these advantages it was necessary, to first validate wear tests with glass spheres instead of teeth. To validate the usage of this material it was necessary to assess if tests results using this binome, composite-glass sphere, were possible to correlate and extrapolate with tests done with composite-natural human tooth.

Two methods have been adopted to analyze the results: first, methodology based on Archard's wear law and second, the energetic approach. This validation study was elaborated through the use of three commercial posterior condensable composites in the same environment, distilled water.

After validating reciprocating wear tests, the influence of two types of environment, artificial saliva or abrasive slurry at point of contact was evaluated. For this particular study eight commercial restorative composites were tested against glass spheres, under normal load condition. The goal of this part of the study was the determination of wear resistance under different wear mechanisms: abrasion and attrition. The evaluation of environmental influence on these tests allows for the understanding of composite behavior under reciprocating contact through the measurement of wear volumes of the contact pair and analyzing the removal mechanisms involved in the wear process.

Analyzing the previous tests, and as already expected, it was concluded that commercial restorative materials are closed systems where nothing can be altered, therefore making it very difficult to establish a cause effect concept. Laboratory produced composites make it possible to contour this difficulty, and, therefore change composite parameters such as; filler volume fraction, average particle dimension and matrix composition.

Due to the fact that analysis of some composite-glass pair had shown slight discrepancy in results a complementary study involving three commercial composites was done. Load-scanning tests were used to understand and explain the regime transition of these materials using an energetic approach occurred in reciprocating wear tests. This test made it possible to understand wear/fracture mechanisms induced by the values of coefficient of friction.

The final study regarded application of the implemented methodology with the intention of evaluating the effect of aging time in baths with different pH values on seven commercial composites as well as evaluating their performance in reciprocating wear test. Commercial restorative composites were evaluated after three aging periods, 3, 6 and 22 months in 3, 7 and 9 pH buffer solutions. All these studies involve directly or indirectly wear process with removal mechanisms and thus all SEM observations were done at the contacting surfaces.

5.2 Reciprocating wear test and methodology validation

The first step was to validate the usage of glass spheres as antagonist material in order to understand and apply relations found within several variables of the study in general, and then transposes and apply then in practical terms. Three commercial composites, Surefil, Synergy and Alert, were chosen to evaluate the applicability of standard materials such as glass spheres instead of premolar human teeth.

After the justification and presentation of the test proceedings, an energetic approach parallel to conventional wear evaluation will be presented. The energy dissipated during the test is directly related to material removed by wear and the basic idea was to find a way to predict the result of glass against material composites and afterwards extrapolate these results as if the composite in study were to be tested against human teeth. This validation would allow for understanding of what to expect of the composites' performance when this would be tested against human teeth, *in vitro* or even *in vivo*.

A classic approach was done through Archard's law relating the volume of wear material with normal load and sliding distance. The two wear parameters are correlated by the coefficient of friction. The energetic approach was used to relate the wear/energy of both material pairs; tooth-composite and glass-composite. In order to determine the relationship between the two pairs of materials the tests were conducted for several normal load conditions and duration tests. This allowed for the determination, of wear coefficient of the two pairs of materials and energetic relationships. Wear depends as much on sliding conditions (normal load and sliding velocity) as on properties of materials.

The earliest contributions to the wear constitutive equations were made by Holm (1946). Holm established a relationship for the volume of the material removed by wear (V) in the sliding distance (s) and related it to the true area of contact. Archard (1953) formulated the wear equation of the form: volume of the material removed (V) is directly proportional to the sliding distance (s), normal load (N) and a dimensionless wear coefficient (k), and inversely proportional to the hardness of the surface being worn away (H).

Today in accordance to Archard's law, it is generally recognized that wear can be quantified using the wear coefficient, which in turn depends on normal load and the sliding distance.

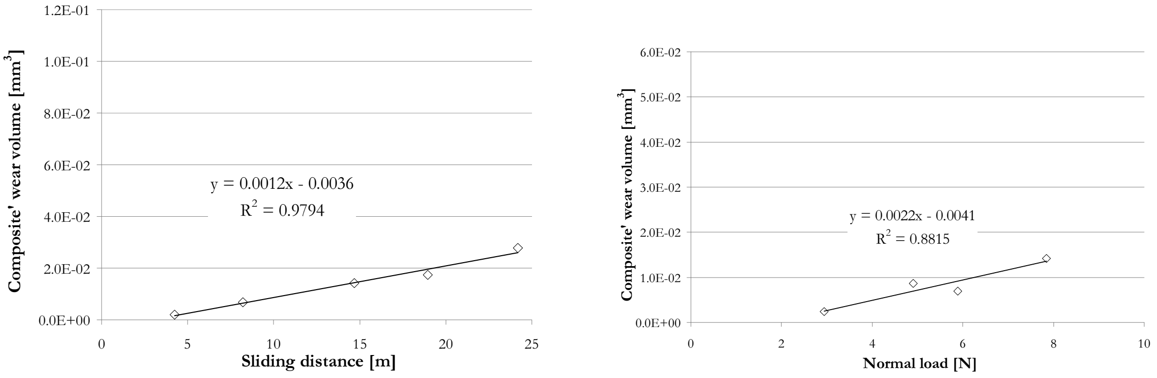
Considering Archard's law and taking into account the wear conditions previously determined, one can deduce that there is an existing proportionality between wear, sliding distances, and normal loads.

For the pair Surefil and glass sphere fig. 5.1 presents a linear relation for wear volumes and both sliding distance and normal loads utilized in the reciprocating wear tests.

Fig. 5.2 plots the same variables for the tribological pair Synergy against glass spheres. Results for restorative composite Alert versus glass spheres are plotted in the graph of fig. 5.3.

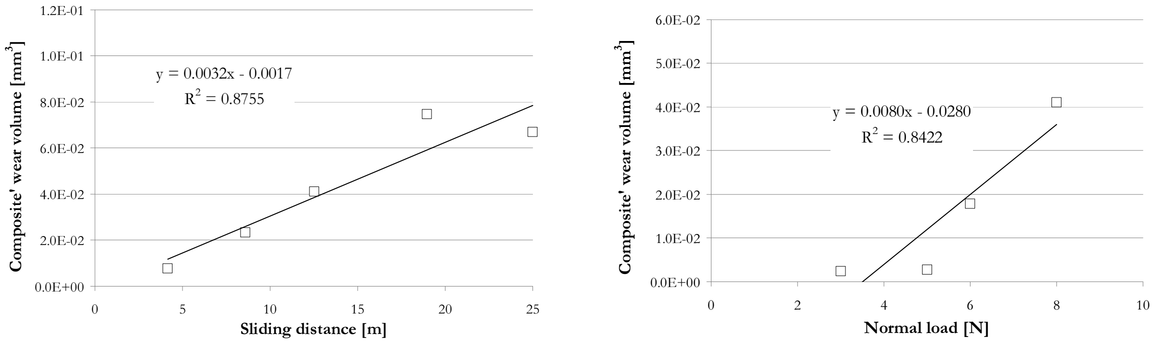
Results regarding reciprocating wear tests, presented in fig. 5.1 to fig. 5.3, show, for all materials testes against soft glass spheres:

- a linear relation between: removed material by wear and sliding distance, considering the tests under a constant normal load, fig. 5.1 a), fig. 5.2 a) and fig. 5.3 a);



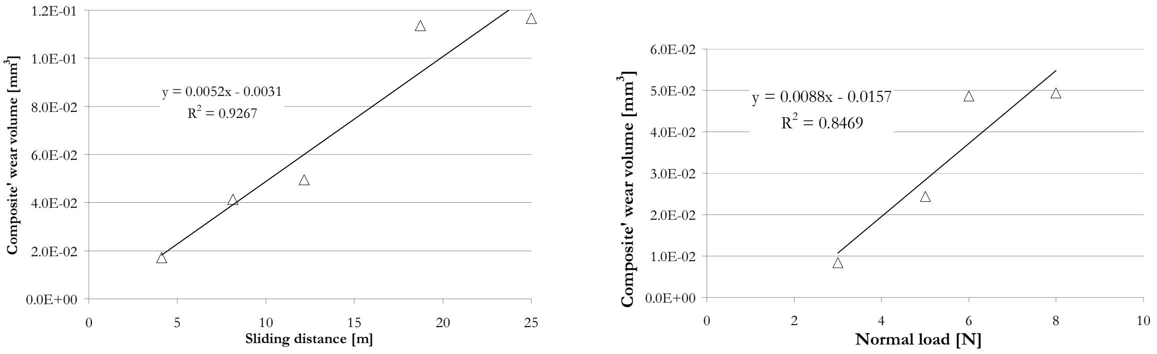
(a) (b)

Fig. 5.1: Relation between composite wear volumes and; a) sliding distance, and b) normal load, constant sliding distance for the pair Surefil against glass sphere.



(a) (b)

Fig. 5.2: Relation between composite wear volumes and; a) sliding distance, and b) normal load, for the pair Synergy against glass sphere.



(a) (b)

Fig. 5.3: Relation between composite wear volumes and; a) sliding distance, and b) normal load, for the pair Alert against glass sphere.

- an increasing linear relation between material removed by wear and increasing normal load applied, considering the tests be done under constant sliding distance, fig. 5.1 b), fig. 5.2 b) and fig. 5.3 b).

A linear relation between the wear volume, the applied load and the sliding distance is in accordance with the Archard's wear equation; $V \propto N \cdot s$. The ratio between wear volume and normal load times sliding distance represents the wear coefficient for the materials in study, considering a classical approach.

The energetic approach establishes a linear relationship between the wear volume and the energy dissipated by friction; $V \propto$ Energy. This energy is obtained by multiplying friction force by the sliding distance.

A linear relation between wear volume and friction force on composites wear varies linearly with sliding distance, and the dissipated energy is obtained by friction force times sliding distance, thus composites wear volume is linear to energy, $V \propto F \cdot s$. Therefore this material pair requires respect and is suitable to be analyzed by the exposed methodology.

Duration test, for two pair of materials, glass-composite and tooth-composite were selected, first, through an evaluation of the wear marks. Typically the tooth produces a smaller associated damage, in itself and in the composite, with the test duration for this pair of materials varied from 6,000 to 20,000 cycles, tests designation from J to P. Previous studies revealed that duration of less than 6,000, especially for low normal loads, did not allow the system to create sufficient wear volume, on both composites and counterbody, in order to be visualized and measured.

Concerning the pair glass-composite, the duration ranged from 2,000 to 12,000 cycles. For this pair of materials, these durations were combined with the values of normal load of: 3, 5, 6 and 8 N. In these reciprocating wear tests distilled water bath at room temperature was used, tests designation ranges from A to I.

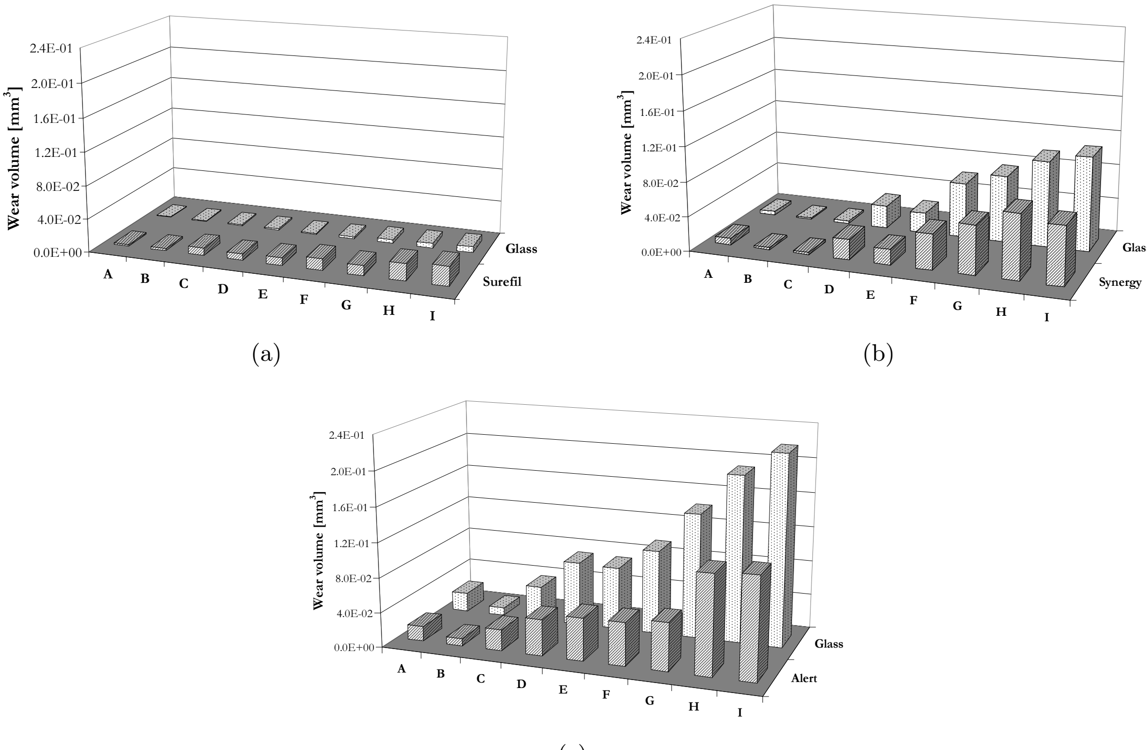
For both two material pairs tests are sorted by the increasing energy input, *i.e.*, the product of normal load by number of cycles (sliding distance), this was considered as a degree of severity of the test.

I. Pair's glass-composite

Generally the values of wear of the composite and antagonist increase with the product of normal load by number of cycles, *i.e.* sliding distance.

Therefore, different amounts of wear were generated as a function of the test conditions. Fig. 5.4 displays the obtained results for the three studied composites against glass; each presents the wear volumes of the composites and their glass sphere antagonists. Tests were classed from A to I by increasing test severity and in general the wear amount fit the same sort. For Surefil, exceptions are tests: C and F. Test C has higher value of composite volume then D and E. Test F, which has more normal load, although the number of cycles is smaller, 6,000 against the 10,500 of test G. Values of wear measured for the antagonist body, glass sphere, have almost the same evolution as the resisted for the wear volume of the composite, generally there is an increase with the rise of product normal load by number of cycles. Synergy has tests B and C with smaller values then test A and test E has a bit less wear then D, for the rest there is an increase in the amount of material removed by wear with increasing severity. Regarding Alert only test B has less when then it would be expected the rest of the results are as aspect.

For the same conditions of severity Surefil produces much less wear volumes, in the composites and antagonist, after is Synergy and clearly Alert-glass is the material pair with more removed material. It is also possible to notice that Synergy and Alert are more aggressive to glass then Surefil, when comparing the amounts of material removed by wear glass has a greater volume then the composites material. This two pairs (Synergy-glass and Alert-glass) wear more and the composites are more aggressive to their antagonist.



(a)

(b)

(c)

Fig. 5.4: Wear volumes of the restorative material and antagonist body, glass sphere, in reciprocating test with distillate water; a) Surefil, b) Synergy, and c) Alert.

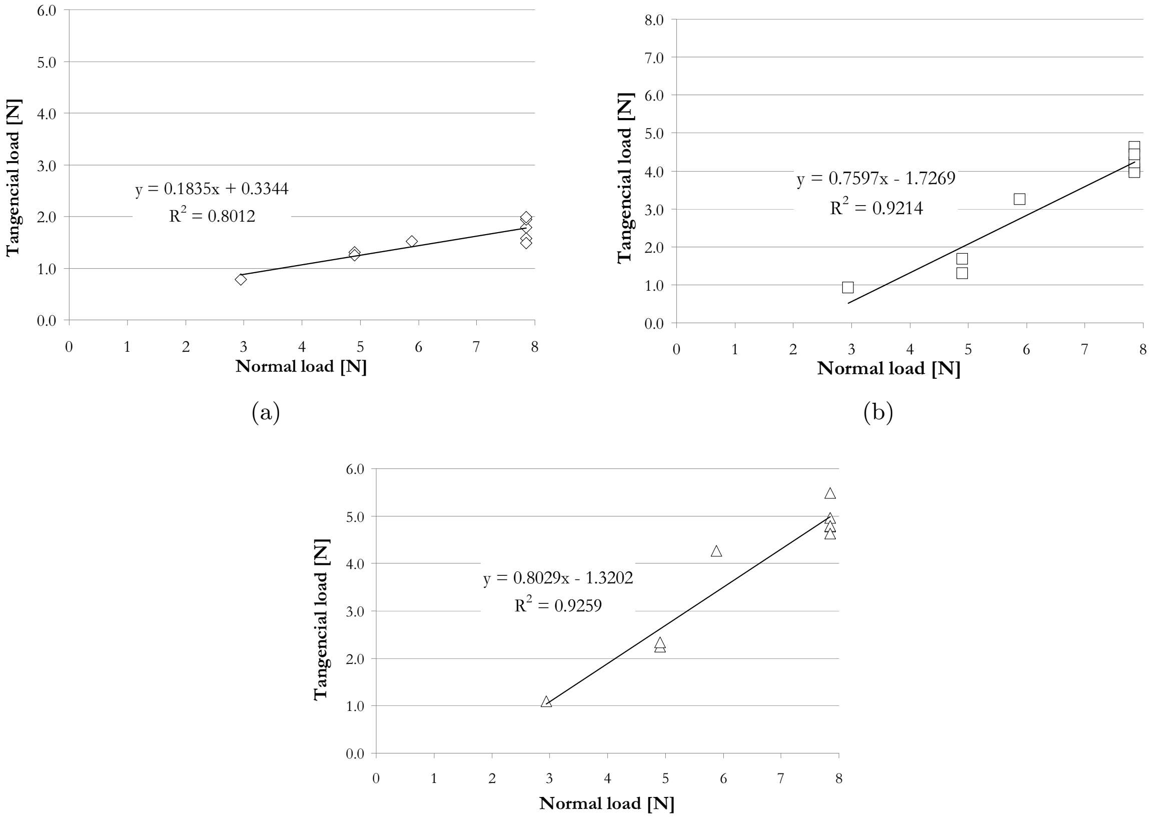
Fig. 5.4 represents average value of friction force plotted against the normal applied load, for the pair glass-composite, R^2 represents the coefficient of determination for the linear fitting of the data. The results clearly fit reasonably at linear evolution; therefore, this pair agrees with Amontons-Coulomb linear behavior, and the slope of the straight line fitted by the experimental results, is a good approach for the friction coefficient. In this case values of 0.18, 0.76 and 0.80 for glass-Surefil, glass-Synergy and glass-Alert respectively were obtained.

Table 5.1, presents, for all composite-glass pair testing, the average coefficients of friction calculated from the average value of the tangential force during each test.

For each material pair, the energy dissipated by friction was correlated to material removed by wear, fig. 5.6. All graphs representative of material pairs' show results fitting a linear evolution with high correlation. Considering the energetic approach, the slope of the straight lines (volume ratio/energy, VRE) represents composite volume removed by unity of energy and could be used as a material performance parameter. VRE obtained for glass-composite pairs were; 2.26×10^{-4}, 3.95×10^{-4}, and 6.50×10^{-4} [mm^3/J] for Surefil, Synergy and Alert respectively.

Fig 5.7 is similar to the figure 5.6, however it correlates the amount of antagonist material removed by wear as a function of the energy dissipated for each pair glass-composite.

It correlates wear volume of antagonist material versus energy dissipated by friction from the respective test, fig. 5.7. All values of removed material and dissipated energy are plotted in the graph (fig. 5.7), and these plotted points allow for determination of trend line and its slopes.



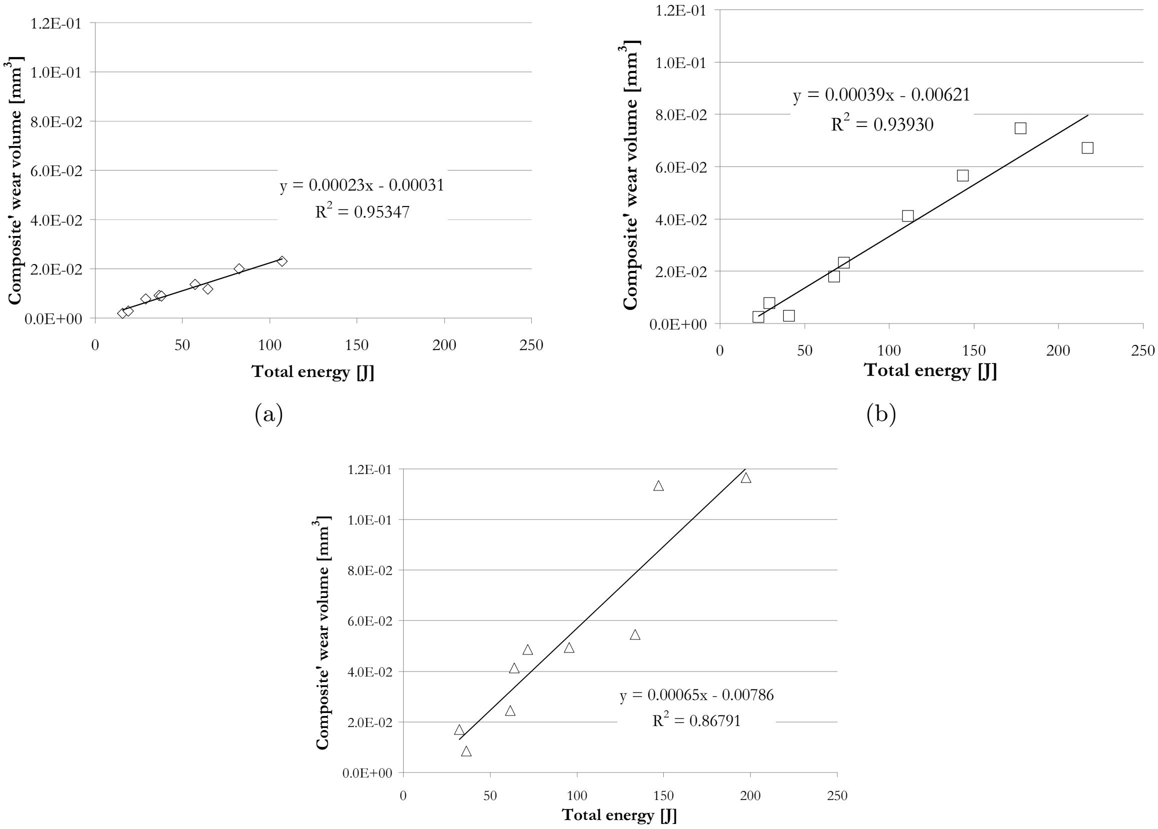
(a) (b)

(c)

Fig. 5.5: Representation of coefficient of friction for the pair glass-composite; a) Surefil, b) Synergy and c) Alert.

Table 5.1: Coefficient of friction (COF) for the pair's glass-composite.

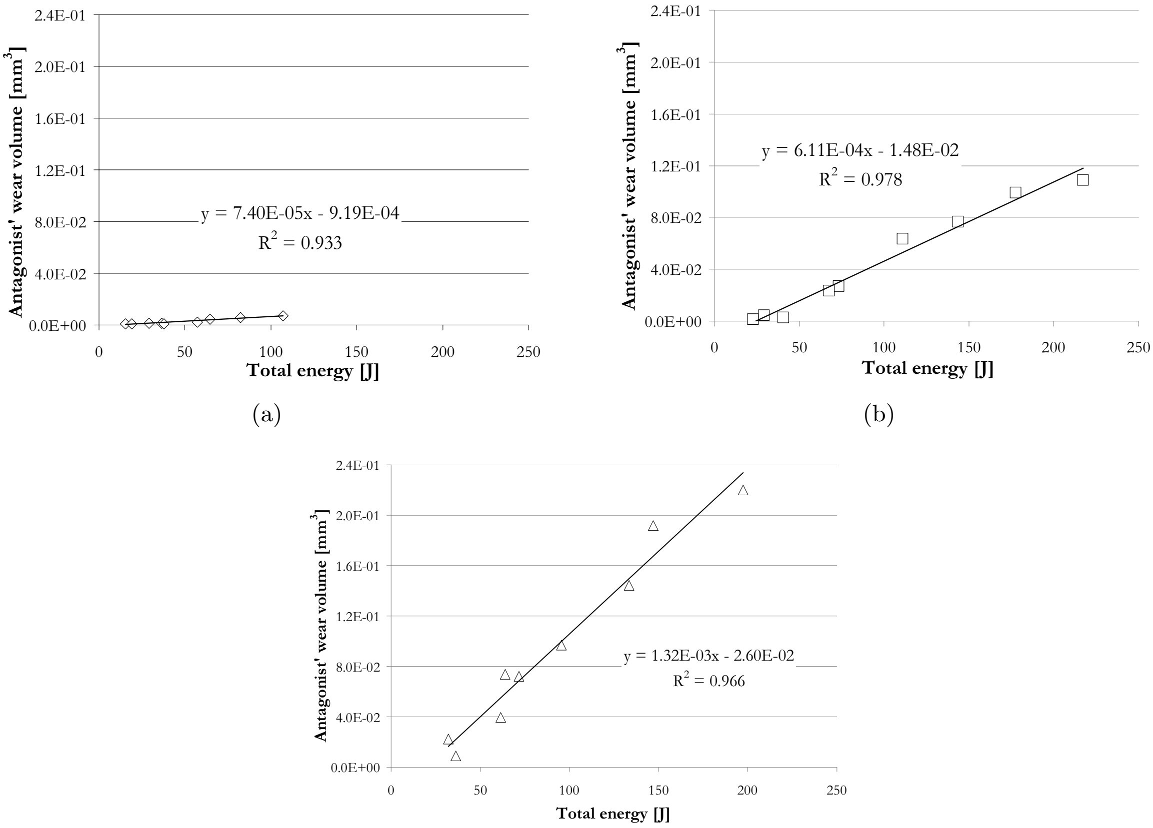
Glass-Composites			
Test designation (Normal load [N]; n. cycles)	**Alert**	**Synergy**	**Surefil**
A (8; 2,000)	0.63	0.52	0.20
B (3; 6,000)	0.37	0.31	0.26
C (5; 6,000)	0.46	0.34	0.27
D (8; 4,000)	0.61	0.59	0.19
E (6; 6,000)	0.72	0.55	0.26
F (8; 6,000)	0.61	0.50	0.23
G (5; 10,500)	0.48	0.51	0.24
H (8; 9,000)	0.70	0.54	0.25
I (8; 12,000)	0.59	0.57	0.25



(a) (b)

(c)

Fig. 5.6: Representation of total energy and composite wear for the pair glass-composite; a) Surefil, b) Synergy, and c) Alert.



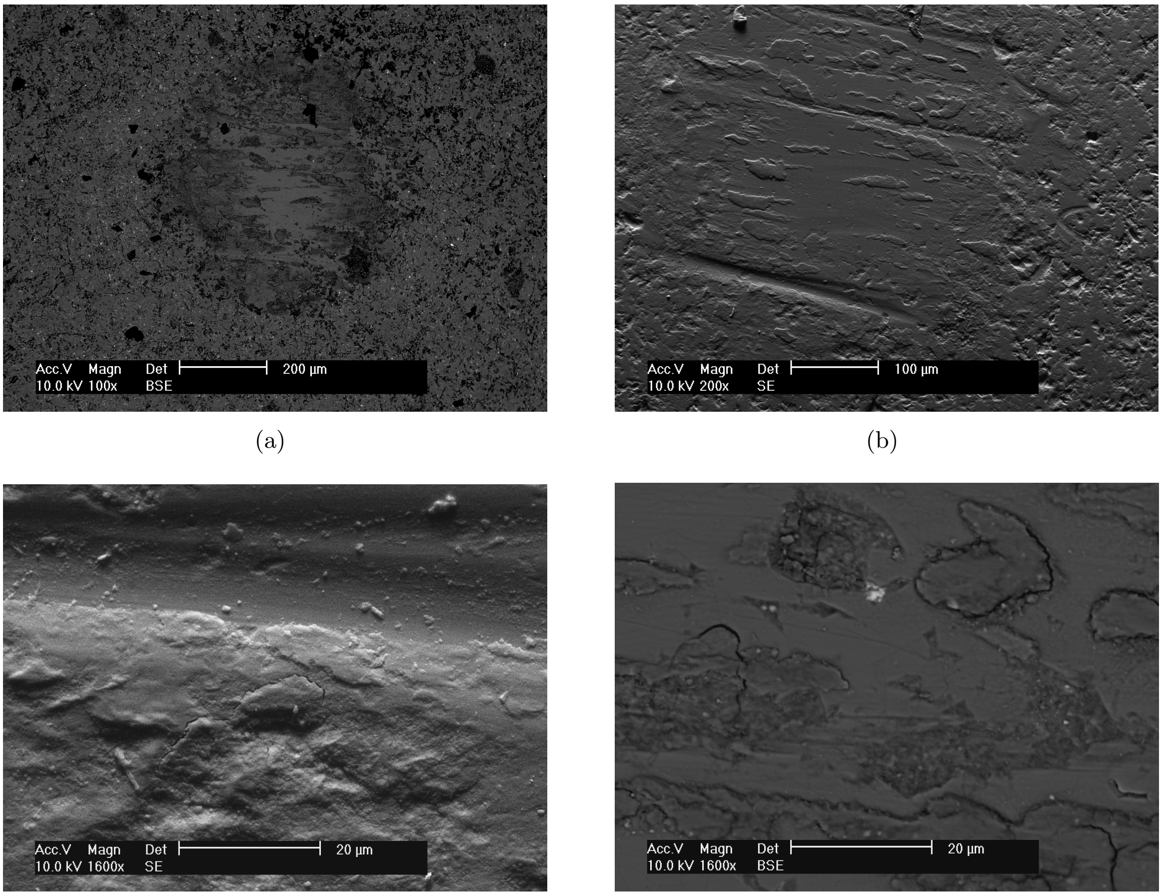
(a) (b)

(c)

Fig. 5.7: Representation of total energy and antagonist wear for the pair's glass-composite; a) Surefil, b) Synergy, and c) Alert.

For the antagonist materials tested against the three commercial composite studied the results are the following; 7.40×10^{-5}, 6.10×10^{-4}, and 1.30×10^{-3} [mm^3/J] for Surefil, Synergy and Alert respectively.

Concerning the morphology of composites and glass spheres tested in reciprocating wear tests, surface appearance is analogous in all specimens observed, composites and antagonist bodies. Comparing the different test conditions, for what concerns glass spheres tested against each of the specimens of the three composites in study, no significant differences were observed. Fig. 5.8 shows four images from the antagonist body tested against Surefil. The morphology of the glass spheres was characterized by few scratches and agglomeration of plasticized material, glass, fig 5.8 b). In fig. 5.8 c) a detail of a scratch is shown, and it is possible to observe adhesion deposition of matrix material of the composite. These surfaces are also characterized by hertzian fractures due to the contact of the reinforcement particles trapped between the two surfaces, fig. 5.8 d). In the last image it is possible to see that the debris of matrix stays preferentially in the series of fractures. Images for fig. 5.8 a) and fig. d) in back-scattered electrons (BSE) mode.



(a) (b)

(c) (d)

Fig. 5.8: Morphology of the glass sphere in the reciprocating test K (5 N; 10,500 cycles) against Surefil; a) total view of the wear mark, BSE; b) partial view with SE, c) ridge with incrusted particles, and d) hertzian fractures, BSE.

Fig. 5.9 presents the typical morphology obtained by composite specimens tested against glass. Surefils' morphology was characterized by a continuous removal process of matrix and reinforcement particles with almost no detachment of large particles. Fig. 5.9 a) presents the wear mark correspondent to the reciprocating test K (5 N and 10,500 cycles), one can observe at the center of the scar a homogeneous wear of the matrix and reinforcement particles. Surefil was characterized by mixture of reinforcement particles of different sizes, in fig. 5.9 b) it is possible to observe fractured particles, and some contact surfaces presented scratching due to the particles trapped between both surfaces, possibly caused by particle detachment from the composite. Surefil presented the lowest wear volume and wear rate of the three composite materials.

In fig. 5.9 c) Alert contact surface is showed. The majority of the contacting composite surfaces presented a tribo-layer constituted by matrix and reinforcement particles of the composite which remained trapped within the contact. Synergy is characterized by small particles of almost the same size and in some of the contact area the tribo-layer is broken. Alert, was characterized by highest wear rates and volumes of removed material. Fig. 5.9 d) shows us that due to the existence of fiber glass as reinforcement material, the mechanic behavior of reinforcement particles was the same as for Synergy, but because of its larger particle dimensions and its higher hardness it was not possible to form a protective tribo-layer that separated the core of the composite from the antagonist body. Therefore, Alerts' reinforcement fibers served as an abrasive material which remained trapped between the contacting surfaces ploughing both of them.

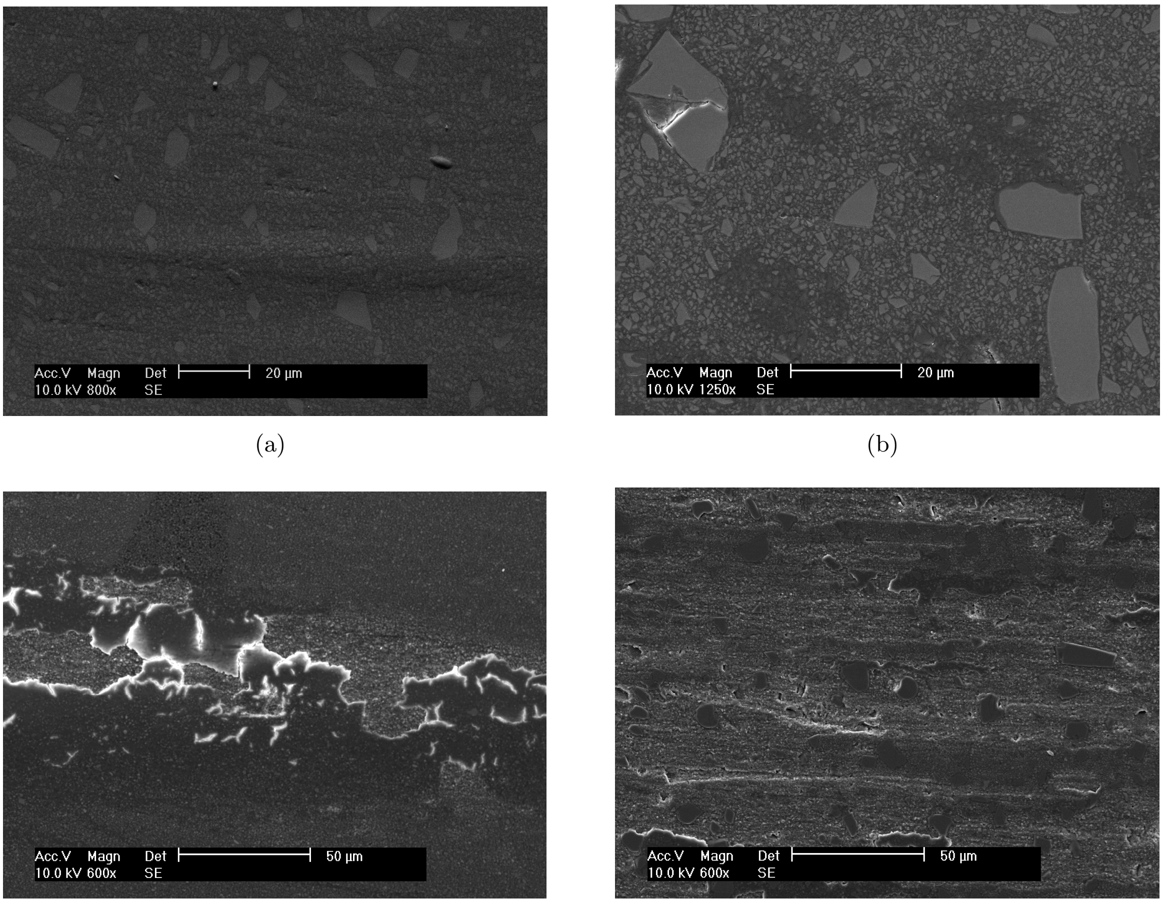
II. Pair's tooth-composite

Fig. 5.10 represents reciprocating wear tests for the pairs of material composites *vs.* tooth. Fig. 5.10 a) presents tooth-Surefil test results. Test condition J, K, L, and M present much smaller wear volumes than the other three conditions, N, O and P, and this is valid for both the composite and the antagonist body, tooth. There isn't a well-defined tendency as for the glass-composite, but as before, the wear loss of the composite is greater than the one registered in the antagonist body. The condition which presents greater composite wear is P (6 N and 20,000 cycles), but not for the tooth which has smaller wear than condition O (8 N and 12,000 cycles).

Concerning the other two pairs, tooth-Synergy and tooth-Alert there is an increase with increasing test severity, except for tests L and M which both have the same product $60,000$ N$\times$ cycle (6 N$\times 10,000$ cycles and 3 N$\times 20,000$cycles). These two wear conditions have very similar wear volumes in the three composites and their antagonists. It is possible to observe that Alert has more material removed and also removes more material from antagonist teeth. Synergy produces less wear on its antagonist and composite wear is smaller than Alert. Surefil has two distinct wear rates, very small for less severe tests and higher wear volumes of composite for more severe loads and number of wear cycles.

In table 5.2 the average values of coefficient of friction for each one of the wear tests of the pairs tooth-composite are shown. Contrary to what occurs to the pair glass-composite, the pair tooth-composite results disagree with a linear model. The tests J, K, L and M have average values similar to those of the pair's glass-composite, and all smaller than 0.3, while tests N, O and P have average friction coefficients higher than 0.3. As seen before Alert and Synergy have very consistent results with their COF values being very constant. Tooth *vs.* Alert, COF values range from 0.81 to 0.97 and for the pair tooth *vs.* Synergy COF values vary from 0.51 to 0.62. For both, the exceptional high values were registered for normal load of 6 newton and 10,000 wear cycles.

Fig. 5.11 shows a good correlation between normal load and tangential force values for reciprocating wear tests of teeth versus Synergy and Alert (coefficient of determination higher



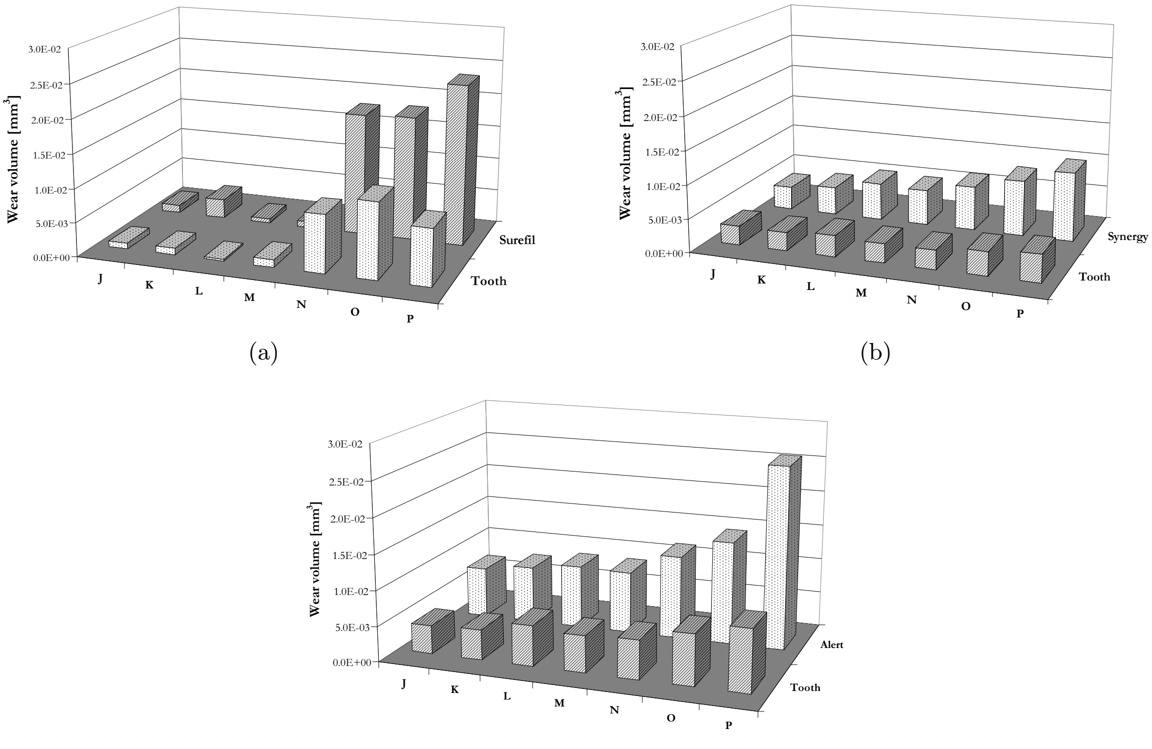
(a) (b)

(c) (d)

Fig. 5.9: Composites' wear scar morphology in reciprocating test; a) Synergy wear scar whit homogeneous wear in the centre of contact, K (5 N and 10,500 cycles), b) Surefil wear scar with fractured reinforcement particle, mixture of reinforcement particles with different sizes, c) breaking of Synergy tribo-layer which protected composite's surface, and d) Alert wear scar with reinforcement fibers out of the matrix promoting degradation of composites surface.

Table 5.2: Coefficient of friction (COF) for the pair's tooth-composite.

	Tooth-Composite		
Test designation (Normal load [N]; n. cycles)	**Alert**	**Synergy**	**Surefil**
J (8; 2,000)	0.81	0.56	0.29
K (5; 10,500)	0.89	0.53	0.21
L (6; 10,000)	0.97	0.62	0.18
M (3; 20,000)	0.84	0.60	0.21
N (8; 9,000)	0.84	0.51	0.42
O (8; 12,000)	0.84	0.55	0.58
P (6; 20,000)	0.87	0.58	0.58



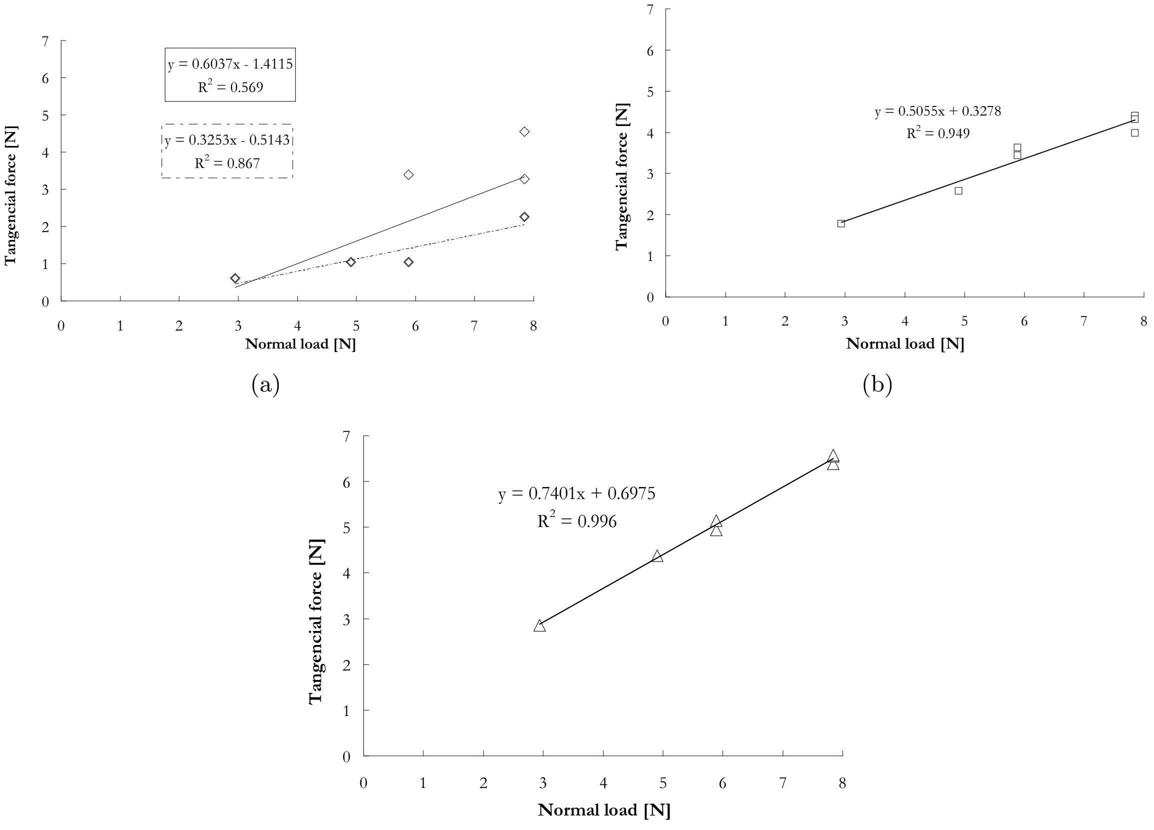
(a)

(b)

(c)

Fig. 5.10: Wear volumes of the restorative material and antagonist body, tooth, reciprocating test with distillate water; a) Surefil, b) Synergy, and c) Alert.

then 0.94 for both), as is confirmed by COF values in table 5.2. For tests J, K, L and M, Surefil presents similar COF values, but for more severe conditions N, O and P COF values are more than twice the other conditions. In fig. 5.11 a) are present two sets of values for Surefil under all tests conditions (◇) and a set for J, K, L and M test conditions (◈), for the first, COF is of 0.60 (R^2 =0.57) and only considering the second set 0.33 (R^2 =0.86) indicating two distinct behaviors for mild and more severe test conditions.



(a) (b)

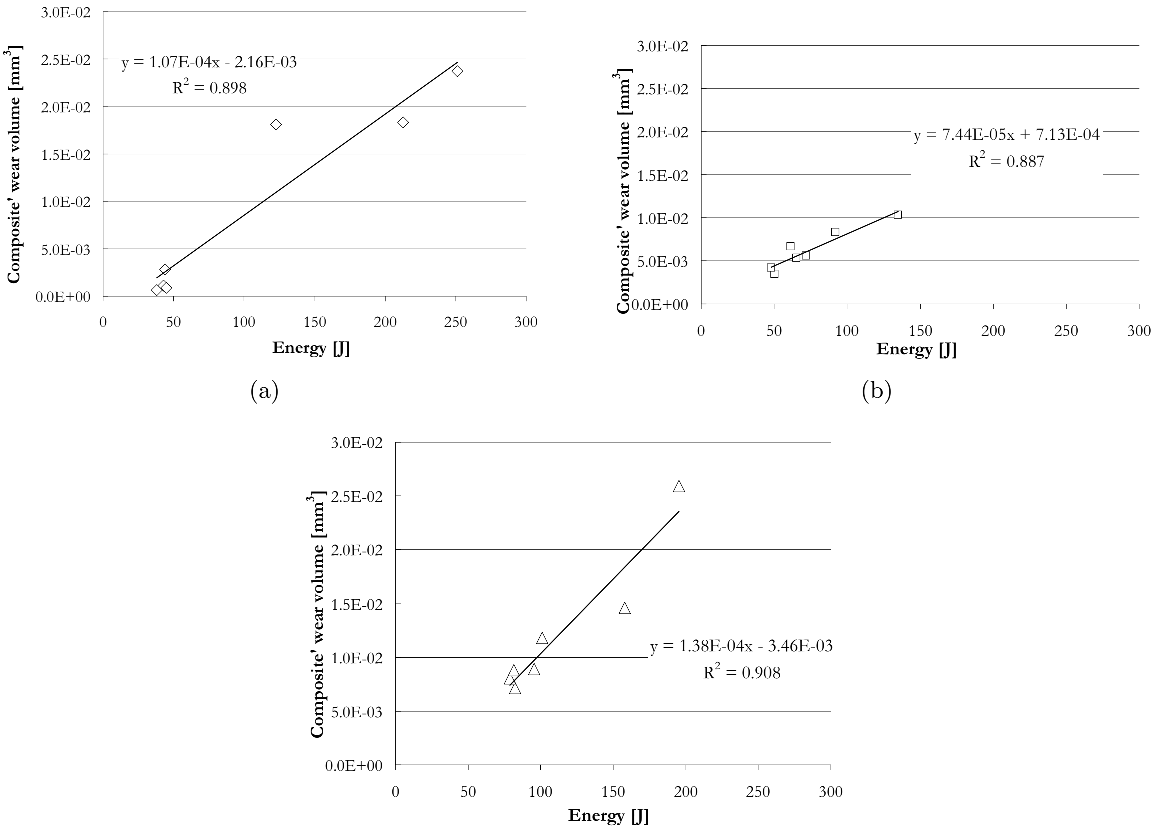
(c)

Fig. 5.11: Representation of COF for tooth-composite pair; a) Surefil, b) Synergy, and c) Alert.

Energy dissipated by friction, for the pair tooth-composite, was correlated to the material removed by wear, fig. 5.12. In spite of differences in COF values for the pair Surefil-tooth the relation between Surefil specimens and dissipated energy still fits a linear evolution with a VRE similar (same order of magnitude) to the one observed for the pair Surefil-glass, with identical slopes for tendency lines, 2.26×10^{-4} and 1.07×10^{-4} [mm^3/J] for the pair Surefil-glass and tooth-composite respectively. Regarding Synergy and Alert these restorative materials also have a linear relation between wear and dissipated energy within the entire test range.

Synergy-tooth presents a VRE with an order of magnitude smaller than that of Synergy-glass tests, 7.44×10^{-5} [mm^3/J] against 3.95×10^{-4} [mm^3/J]. As for Alert against tooth, correlation between wear and energy is high ~ 0.91. In spite of tests duration all VRE relations have the same magnitude of VRE relation, except for Synergy.

Fig. 5.13 shows the amount of antagonist material removed by wear as a function of the energy dissipated for the pairs tooth-composite. Concerning Surefil's antagonist teeth, the results reveal the same tendency as shown for the composite regarding energy dissipation, although with higher

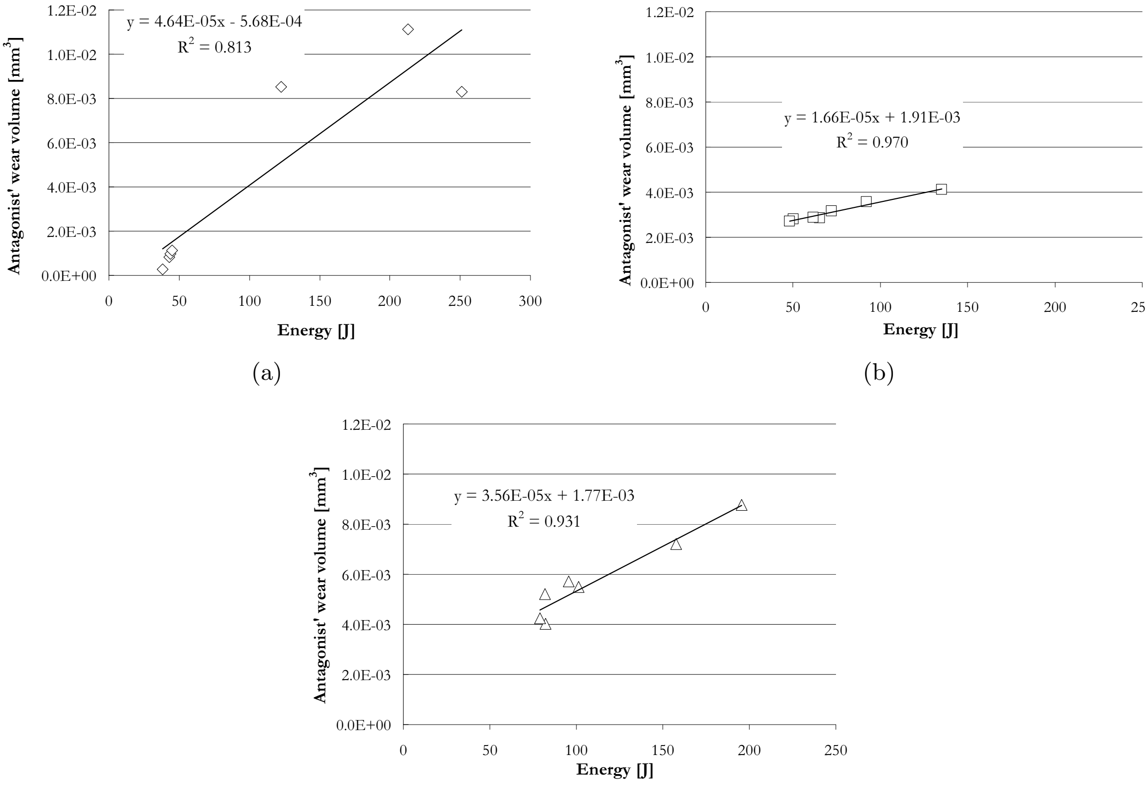


(a) (b)

(c)

Fig. 5.12: Representation of total energy and composite wear for the pair tooth-; a) Surefil; b) Synergy, and c) Alert.

dispersion in results, and, smaller correlation value, $R^2 \approx 0.81$. Wear volumes of teeth tested against Synergy and Alert are characterized by slopes of $1.66{\times}10^{-5}$ [mm^3/J] and $3.56{\times}10^{-5}$ [mm^3/J] respectively. As observed with glass, Alert has higher wear rates, which produce higher wear in the antagonist tooth.



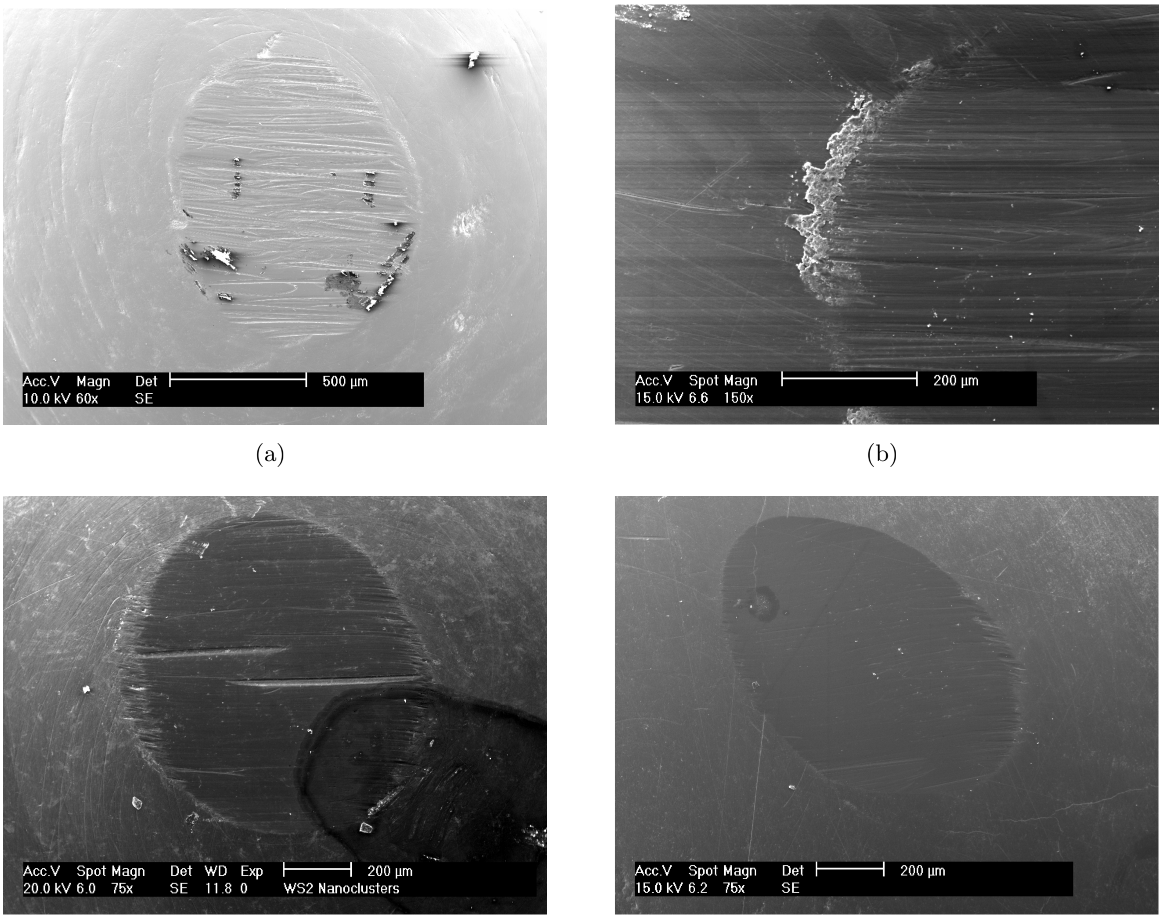
(a) (b)

(c)

Fig. 5.13: Representation of total energy and antagonist wear for pair's tooth-; a) Surefil; b) Synergy, and c) Alert.

Concerning the morphology of worn surfaces, the features observed on the wear surfaces, from a general point of view, agree with the results presented before. Fig. 5.14 shows three tooth surfaces, which resulted from different conditions. In all of them scratches appear; for the more severe conditions, the number of ridges is higher and in all teeth, adherent material from the composite can be found. Fig. 5.14 d) shows the wear mark of the tooth tested M (3 N and 20,000 cycles), its surface with fewer scratches explains that the wear volume of the composite is smaller than the condition 8 N and 9,000 cycles (N test). Teeth tested against Synergy presented very similar surface morphology.

Concerning composites' morphology tested against teeth, two types of surfaces have been found; one, where the particles are worn along with the matrix, showing a polished surface, fig. 5.15 c), and another, where the particles are prominent from the matrix, leading to a rougher surface, region A in fig. 5.15 a). Smooth surfaces with uniform wear of matrix and reinforcement particles were found more often in Surefil and Synergy, for some test conditions. The surface with rough appearance was probably started with scratches as is evident in fig. 5.15 b); this type of wear mark was also observed by Nagarajan *et al.* (2000). For the test M (3 N and 20,000 cycles), COF = 0.19, the wear mark presents almost no scratches and the most common damage is the

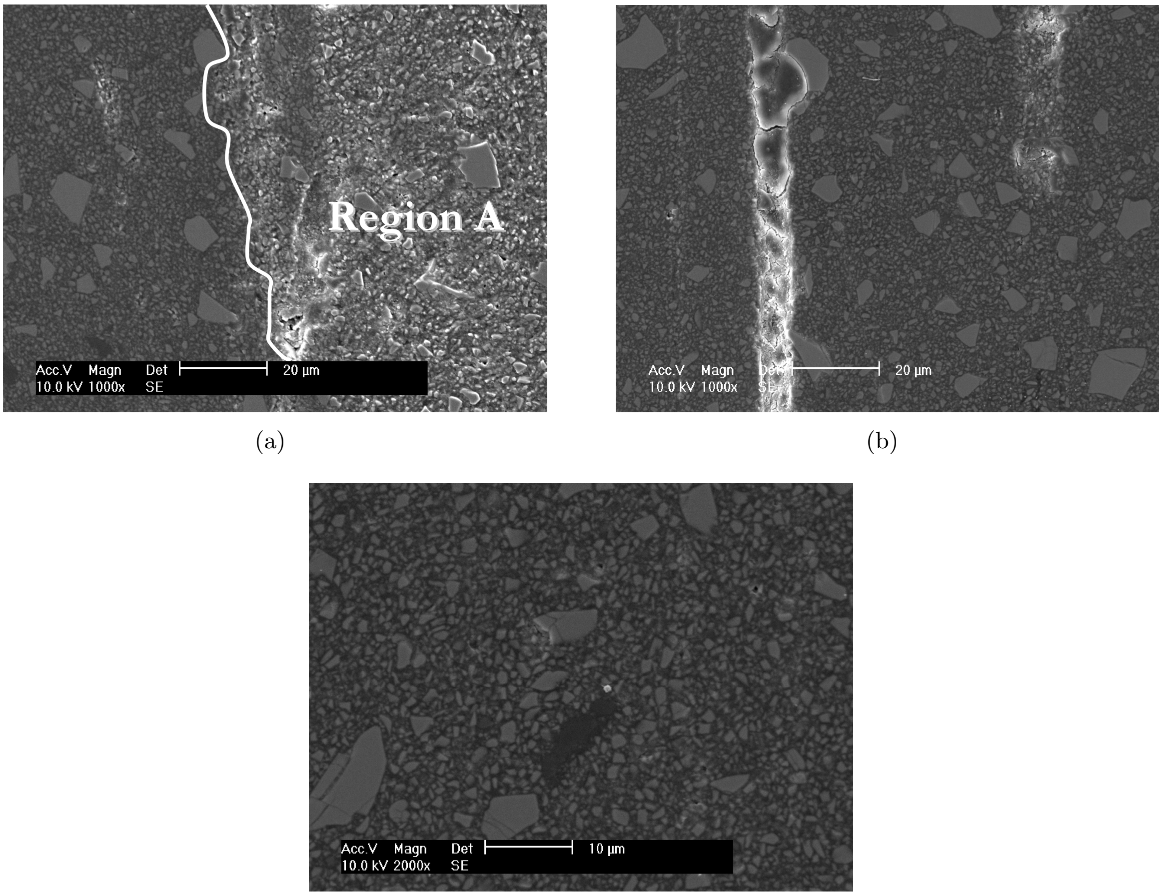


(a) (b)

(c) (d)

Fig. 5.14: Morphology of the teeth in the reciprocating tests against; a) Surefil, N (8 N; 9,000 cycles), b) Alert, O (8 N; 12,000 cycles), c) Alert, M (3 N; 20,000 cycles); and d) Synergy, M (3 N; 9,000 cycles).

breakage of reinforcement particles and their removal; otherwise, for more severe test conditions the regions with prominent particles correspond to a higher percentage of the scar area. Tests with smaller, normal loads tend to have more reduced removal of reinforcement particles, even if with higher test duration, fig. 5.15 d), the intensity of the load is a very important aspect as observed by other investigators (Nagarajan *et al.* 2000; Indrani *et al.*, 1995).



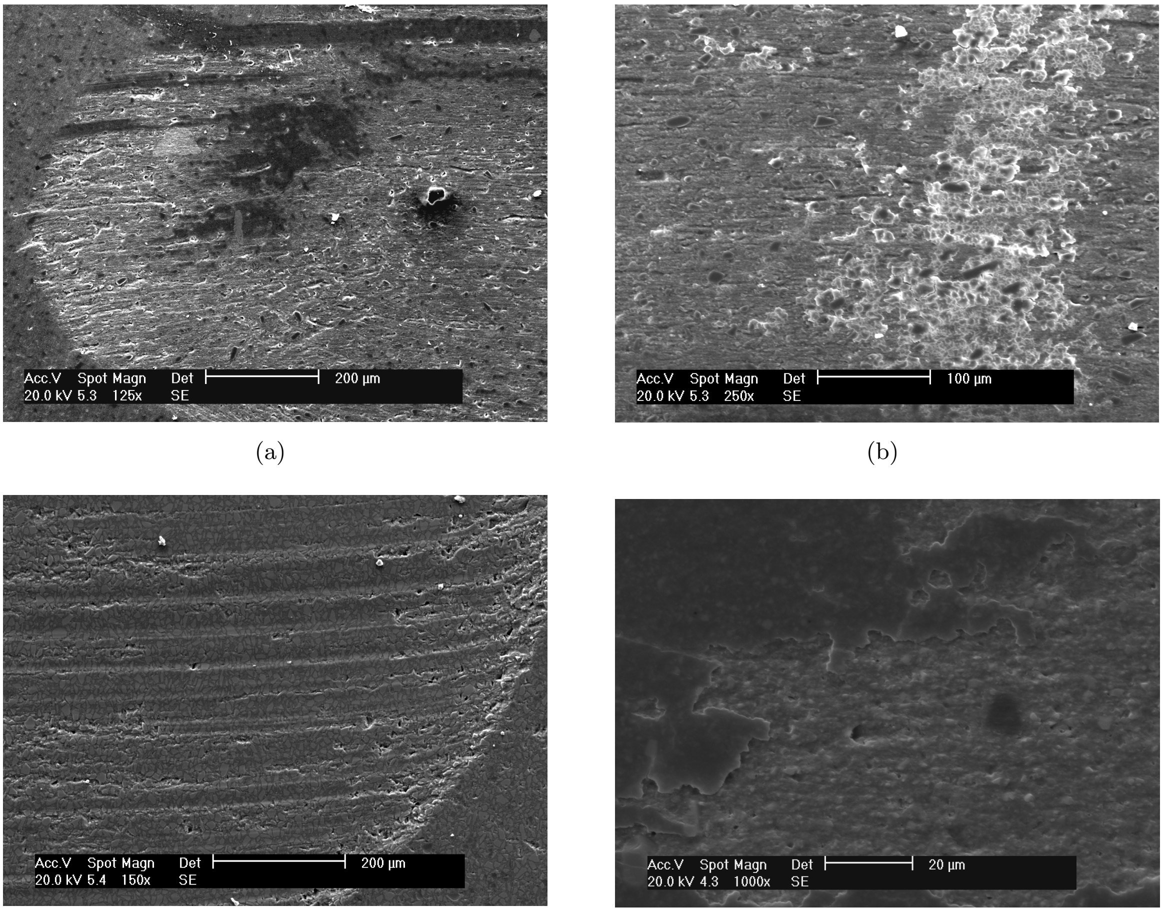
(a) (b)

(c)

Fig. 5.15: Morphology of Surefil in reciprocating tests against teeth for tests; a) N (8 N; 9,000 cycles), b) O (8 N; 12,000 cycles); and c) M (3 N; 20,000 cycles).

Regarding Alert and Synergy fig. 5.16 presents their typical wear surfaces. Alert presents a very rough wear surface, due to its' reinforcement with glass fibers, darker spots fig. 5.16 a) and fig. 5.16 b). Fibers were pulled out of the matrix and remained trapped in the contact. It is possible to observe that the limits of the contact fig. 5.16 a) correspond to the location were the damage is greater. Fig. 5.16 b) presents a small tribo-layer, which corresponds to the transferred material showed in tests of Alert against teeth, fig. 5.14 b). Synergy presents a more similar wear surface with Surefil, fig. 5.16 c) and fig. 5.16 d). In fig. 5.16 a) it is possible to observe a uniform wear of matrix and reinforcement particles, Synergy is characterized by a more homogeneous particle size distribution. Due to the smaller particle size, the tribo-layer formed in Synergy is more extensive than the one presented in Alert's surface, fig. 5.16 b), thus this layer serves as a protective element of the initial surface.

All studied composites reveal similar wear surfaces when tested against glass or human tooth.



(a) (b) (c) (d)

Fig. 5.16: Morphology of composite wear surfaces in reciprocating tests against teeth; a) Alert, P (6 N; 20,000 cycles), b) Alert, N (8 N; 9,000 cycles); c) Synergy, J (8 N; 6,000 cycles) and c) Synergy, L (6 N; 10,000 cycles).

For both pairs of materials there is a linear evolution between volume of material removed by wear and the dissipated energy. Surefil presents homogeneous material removal, particles are worn along with the matrix, although, when tested against human teeth this composite presents some regions with detached particles and rough surfaces, thus justifying the different values of COF for established conditions. For tests against glass, the morphology shows that reinforcement particles wore together the matrix generating smooth wear scars. Here the COF values are more similar. For this pair of materials the friction always remains low according to a linear model.

On the other hand, the pair tooth-composite displays a transition. For the lower values of normal load, especially with low duration tests, the coefficient of friction is low, the wear amount is small and the appearance of wear scars is smooth. However, for more severe test conditions, the friction coefficient is high, the volume of wear is great and the wear scars appear rough.

The behavior observed for the pair tooth-composite is very typical in ceramic materials. In ceramics, the transition from mild (smooth) to severe (rough) wear occurs through a micro-fracture process at the sliding contact. This change is associated to a drastic increase in wear at a critical load that depends on the material and test conditions, namely increases of load or the coefficient of friction, reported by Dong and Jahanmir (2002).

For Surefil against tooth, the transition in the wear behavior is associated to a marked change of friction. This fact allows us to explain the transition as a function of the local failure induced by friction. In cases where friction is low, the tangential force between the spherical surface and the composite surface is also very low compared to normal load. Thus in contact stress distribution, the hertzian component is predominant, inducing the occurrence of the maximum tangential stress underneath the surface. This stress distribution induces failure beneath the surface by a fatigue process that starts with the initiation of small cracks at the sub-surface and then propagates towards the surface. As this fatigue process requires a long number of cycles, the wear remains low. However, when the contact conditions are such that the friction between the spherical surface and the composite is high enough, the stress distribution varies significantly according to contact models with friction, as is the Hamilton's model (Hamilton, 1983). The major changes in the stress distribution are:

- Maximum tangential stress occurs on the surface ahead of the contact;
- Maximum tensile stress rises significantly and occurs on the surface behind the contact.

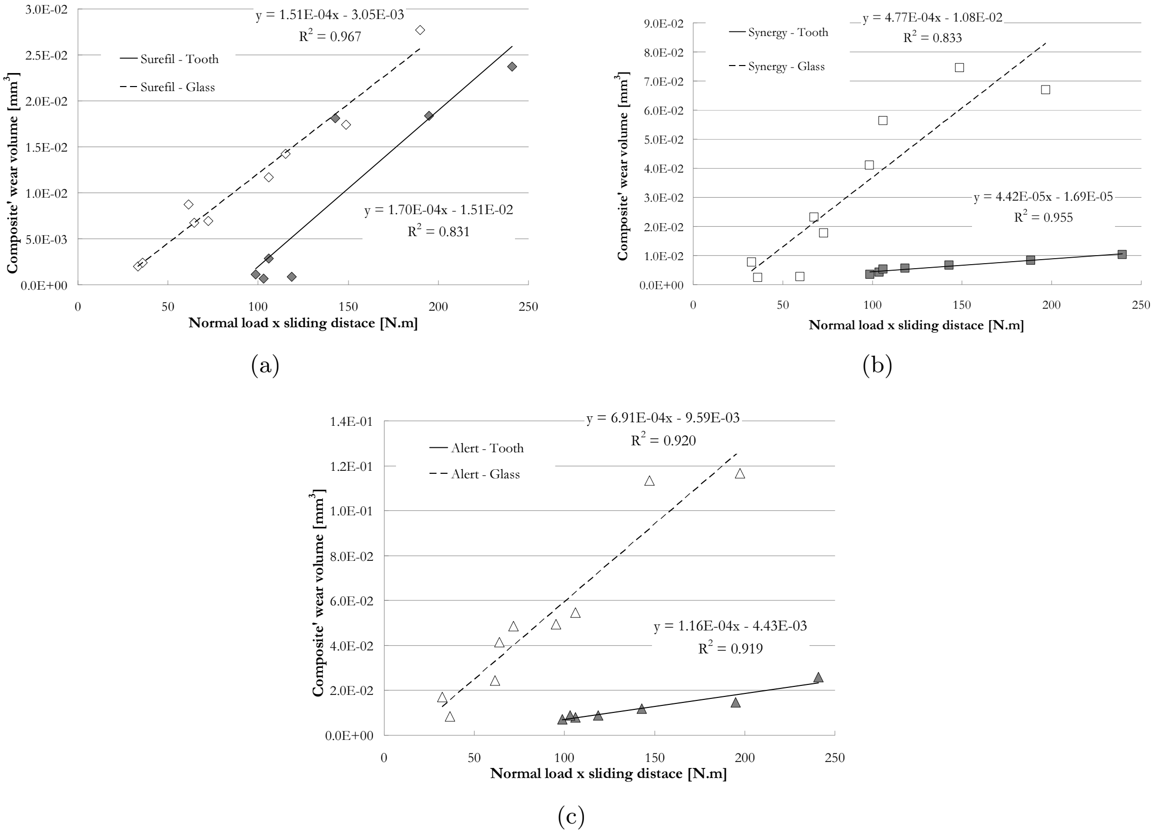
Both of these reasons justify the fact that for high coefficient of friction the failure occurs mainly in surface either by plastic deformation or by fracture. Johnson (1985) shows that for a coefficient of friction higher than 0.3 the location of first yield moves from beneath towards the surface. This transition value agrees very well with the obtained results. Test conditions: O, N and P, lead to coefficients of friction higher than 0.3 and revealed severe wear. For the other test conditions, which lead to coefficient of friction values lower than 0.3, the wear remains mild.

This explanation is emphasized by the fact that for the pair glass-composite, where COF remains always below 0.3, wear was mild for all tested conditions. The pair glass-composite, probably has a similar transition from mild to severe wear. Although a deeper study is needed, it seems that the test conditions, mainly test duration, were not enough to reach the transition (Brizmer *et al.*, 2006).

Synergy and Alert present similar wear mechanisms. In both pairs there is an emergence of a tribo-layer, composed by debris of matrix and reinforcement particles, as both materials are tested against glass or teeth. The difference of behavior between the two composites has to do with the reinforcement particles; Alerts' fibers are more aggressive due to shape and hardness than the small reinforcement particles of Synergy. Due to this difference and at less severe test conditions Synergy's tribo-layer acts like a protective surface and that is why Synergy presents small wear rates and wears less it's antagonist than Alert.

In any of these materials, and in spite of wear test conditions, natural teeth produced less wear in their antagonist materials and were less worn. This approach makes it possible to guarantee a direct correlation between wear results of composite-glass and an extrapolation to predict what might be the wear removed by a tooth when tested against that same composite. In spite of the dispersion of COF values it is still safe to use data from composite-tooth and determine/predict wear, due to the good correlation of data. Fig. 5.16 shows the equations plotted for composite wear volume versus normal load times sliding distance for each composite studied tested against glass and tooth.

From fig. 5.17 it is possible to understand how one can extrapolate wear results from a composite against glass spheres to an expected wear volume for the same composite against human tooth. Regarding the pairs composite-glass and composite-tooth it is clear from the graphics that for the same normal load sliding distance product the pair composite-tooth always has the best wear resistance. Synergy has the best performance considering both antagonists. Alert in spite of its morphology and a loose fiber performs better than Surefil when tested against teeth. Surefil which presented a more homogeneous wear shows slopes of composites' wear by test severity very similar to the ones obtained when Surefil was tested against glass spheres.



(a) (b)

(c)

Fig. 5.17: Morphology of composite wear surfaces in reciprocating tests against teeth; a) Alert, P (6 N; 20,000 cycles), b) Alert, N (8 N; 9,000 cycles); c) Synergy, J (8 N; 6,000 cycles) and d) Synergy, L (6 N; 10,000 cycles).

III. Partial conclusions

The wear of tooth enamel and glass spheres was investigated in reciprocating contacts against three dental restorative composites. Experimental study has been carried out with several normal loads and duration tests, *i.e.* representing several steps of severity conditions for materials in test.

This study has enabled to conclude that:

- The results of the pair glass-composites clearly fit a linear evolution for COF; 0.18, 0.76 and 1.15 for Surefil, Synergy and Alert, respectively. No wear mechanisms regime transition observed in any of the material pair;
- For the pair tooth-Surefil there is a transition from mild to severe. For the less severe tests (COF < 0.3) both pairs have identical behavior and similar values of COF and VRE, while for severe conditions (COF > 0.3) the values are very different;
- The results of Surefil-glass and Surefil-teeth are identical when the regime is mild; friction coefficient and VRE (for composite and antagonist) have similar values;
- It is possible and reliable to predict and extrapolate results of composite materials against teeth if composites are previously tested against glass; for the same test conditions.

5.3 Reciprocating wear tests

In the mouth physiological wear is caused by processes which involve; mastication without food between the contacting teeth (sliding wear), impact of teeth without sliding (contact wear) and during mastication when food is present during contact (abrasive wear). Fundamental research on this subject found that physiological wear is mainly due to sliding and abrasive wear which is produced at molar contact surfaces and temporomandibular joint position. Thus, in reciprocating tests the intention is to also evaluate the effect of a third body on the composite-antagonist material contact and how this affects wear behavior of the contacting surfaces. Therefore, two environmental conditions were used to elaborate the reciprocating wear tests: artificial saliva and abrasive slurry. Being that the second environmental condition is more severe to the contacting materials, time of exposure approximately 25% that of the artificial saliva duration tests. Table 3.10, summarizes test conditions concerning: duration, stroke, applied normal load, geometry and dimensions of antagonist body and the characterization of both abrasive solution and artificial saliva constitution. These conditions are valid not only for commercial composites but also for produced composites both tested against glass sphere as antagonist body.

5.3.1 Commercial composites

The study involved seven of all composites described previously in more detail in chapter 3. Commercial condensable composite materials tested were; Filtek P 60, Prodigy Condensable, Surefil, Synergy Compact, Alert, Pyramid Enamel and Pyramid Dentin. Besides the resin dental restorative commercial composites, Tytin amalgam was selected as the reference material.

As previously noted, with respect to the number of cycles, abrasive test duration is smaller due to the associated damage is terms of removed material. Abrasive test duration is of 2,600 cycles while wear tests under artificial saliva are of 10,500 cycles.

Reciprocating tests with artificial saliva against glass spheres presented very different amounts of material removed by wear from both pairs in test, amalgam and the seven restorative composites. Regarding glass sphere tests against amalgam, almost no wear material was generated in the respective antagonist and therefore it was impossible to quantify the volume of material worn. In crescent order of material volume removed by wear, amalgam was the restorative material that produced minimal wear in the antagonist body followed by composites; Surefil, Synergy, Pyramid Enamel, Prodigy, Pyramid Dentin, Alert and Filtek P60, in crescent order (fig. 5.18). Regarding wear volumes of restorative materials, Synergy registered smaller wear volumes followed by amalgam and Surefil, Pyramid Enamel, Pyramid Dentin, Alert, Filtek P60 and Prodigy.

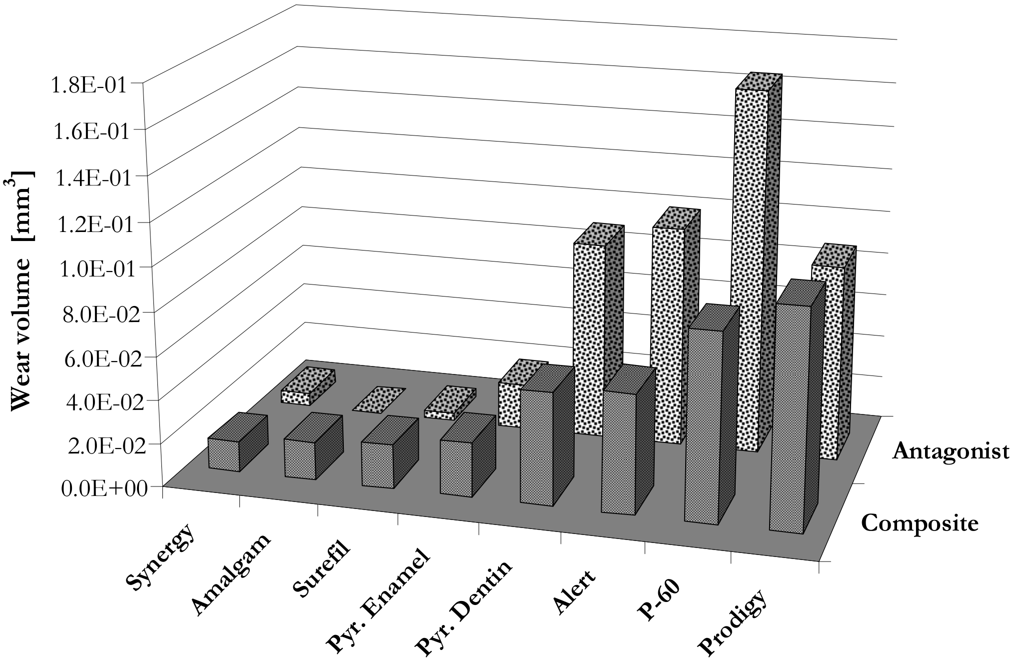


Fig. 5.18: Wear volumes of the restorative materials and antagonist body glass sphere, for reciprocating wear test with artificial saliva.

Regarding absolute values of material removed by wear from the two material pair the lowest absolute value was obtained for the amalgam/glass pair. Interestingly, Synergy manages a higher value of wear resistance, being characterized by average mechanical properties in this group of composites; but still is a remarkable difference in terms of sliding wear. In decreasing order of removed material volume the results were presented for the pairs; glass-: Filtek P60, Prodigy, Alert, Pyramid Dentin, Pyramid Enamel, -urefil, Synergy and amalgam.

Fig. 5.19 represents the same type of graph but for reciprocating wear tests done in an abrasive slurry environment. Wear volume value of amalgam, 2.95×10^{-4} mm^3, is very small when compared with composites wear values, which do not differ very much among them. Following amalgam, the wear volumes of the composites are in increasing order as follows: Surefil, Filtek P60, Alert, Pyramid Enamel, Pyramid Dentin, Synergy and Prodigy.

Although the number of cycles of this test is smaller than the test with saliva, wear volumes of the composites are greater due to the severity of the contact, where micro-glass hard particles are present. Fig. 5.20 compares the amounts of composites removed by wear for the pairs in study during reciprocating wear tests in artificial saliva and abrasive slurry.

Fig. represents wear volumes of the antagonist glass sphere. For all materials, wear volumes are much greater in the test with abrasive slurry except for Pyramid dentin, which showed similar wear volumes. Comparing the several composite materials, except Pyramid Dentin, when tested

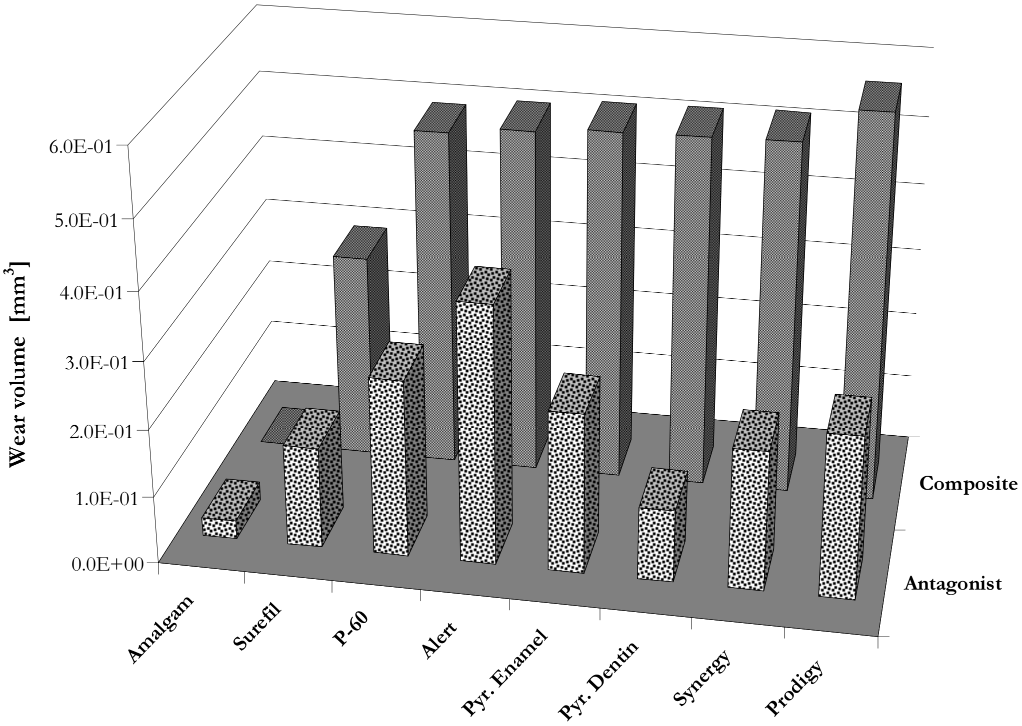


Fig. 5.19: Wear volumes of the restorative materials and antagonist body glass sphere, for the reciprocating wear test with abrasive slurry.

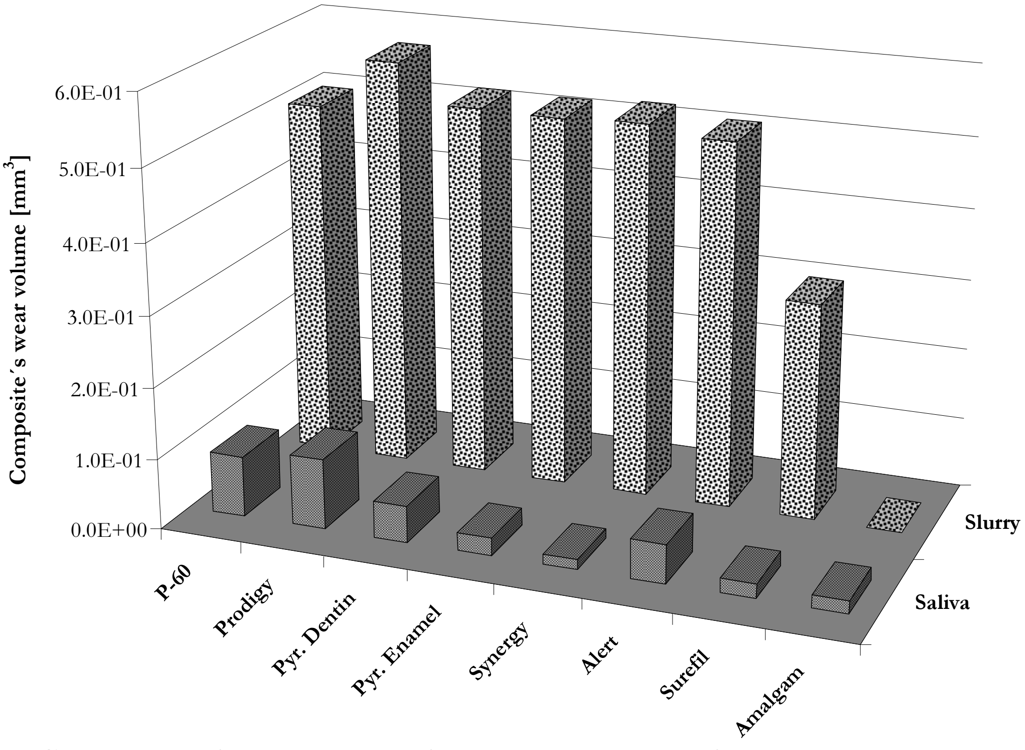


Fig. 5.20: Comparison of wear volumes of restorative materials for reciprocating test with abrasive slurry and artificial saliva.

with abrasive slurry, the difference in wear volume is small, except for Surefil which presented wear volumes approximately half the amount of other composites. However, for tests with saliva, composites Synergy, Surefil and Pyramid Enamel perform significantly better than the rest of the composites in the study.

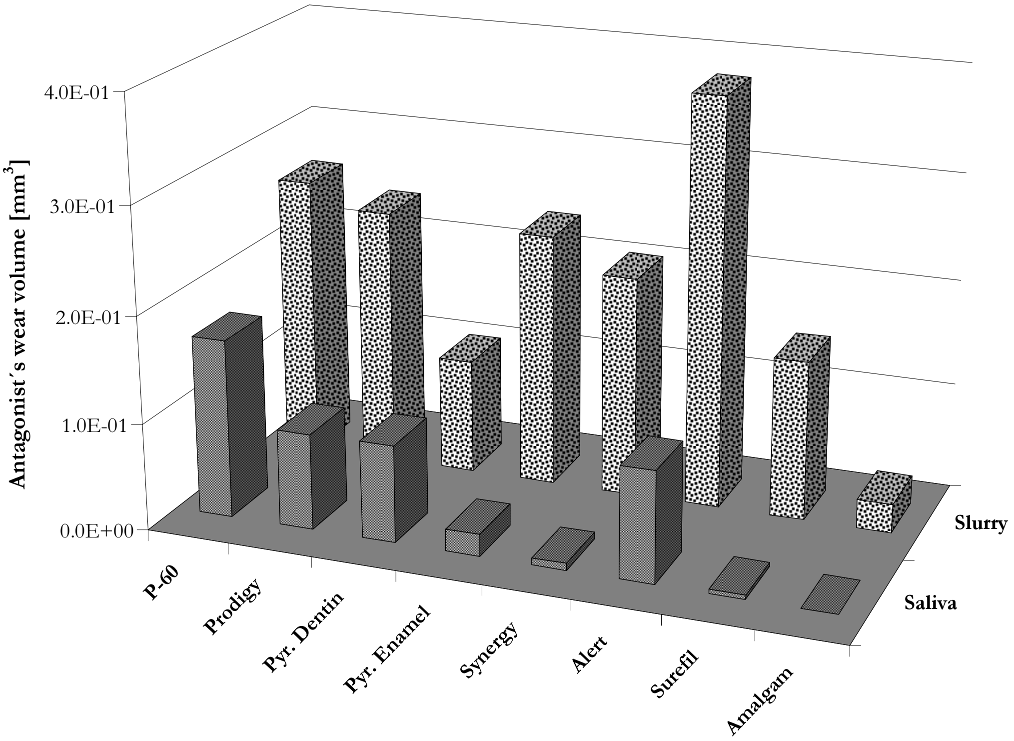


Fig. 5.21: Wear volumes of antagonist body for reciprocating wear test with abrasive slurry and with artificial saliva.

For abrasive tests a linear relation between the wear volume of restorative materials and their hardness fits the experimental results very well, fig. 5.22. Here the only composite that does not follow the tendency line is Surefil (◇). This may be due not directly to its hardness, but to the fact that its' microstructure is composed of sub-micrometric particles and also includes particles of around 40 μm, thus influencing its behavior, especially in abrasive tests. For the rest of the tested materials it shows that increasing values of hardness lead to smaller values of wear.

As observed in fig. 5.23 tests with saliva also roughly reveal the same tendency. However, Filtek P60 (△) and Synergy (◇) do not fit the same linear relation. When comparing the two wear tests, the influence of hardness in the wear resistance of the composites is much higher for sliding tests with saliva. This relation agrees with Archard equation (Archard, 1953). The slope of the tendency curves is 0.0808 for tests with saliva and only 0.0005 for the abrasive tests, thus hardness is more important to enhance wear resistance for contacts without abrasive particles.

Fig. 5.24 and fig. 5.25 represent wear resistance of composites plotted against wear resistance of antagonist material for reciprocating wear tests in abrasive slurry and artificial saliva environments respectively. Regarding tests with abrasive slurry no direct relationship could be established between the two values (fig. 5.24). However, when saliva is present, (fig. 5.25), there is a clear relation between wear resistances of composite and antagonist; a small value of composite wear corresponds to a small value of wear for the antagonist body. The different

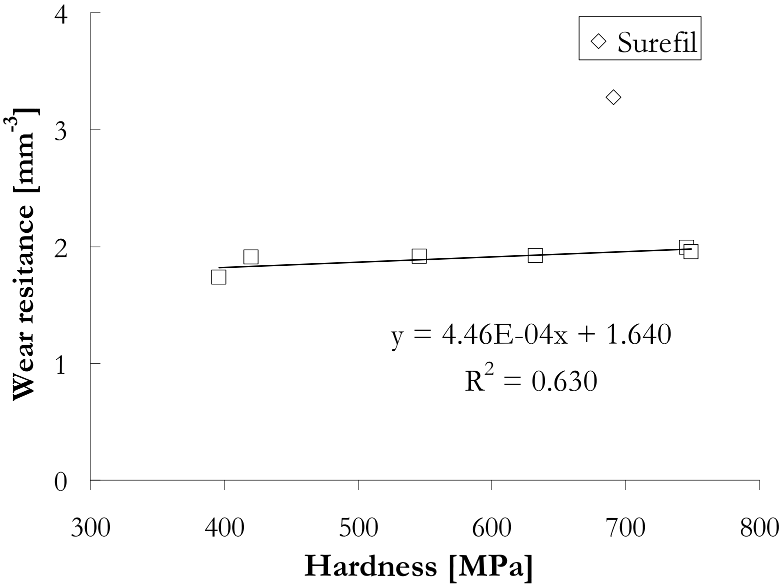


Fig. 5.22: Composites' hardness *vs.* wear resistance in reciprocating sliding tests for abrasive slurry environment.

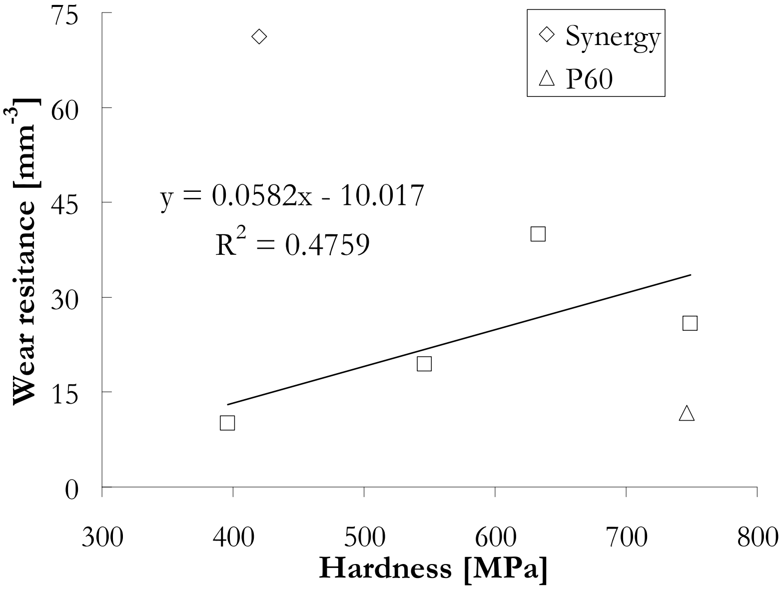


Fig. 5.23: Composites hardness *vs.* wear resistance of composites in reciprocating sliding tests for artificial saliva.

behavior observed in the two types of tests depends on the specific contact conditions. For the tests with artificial saliva the contact occurs without abrasive particles, so the area of contact was governed by the wear amount that arises in the softer material (composite). Nevertheless, when particles are introduced in the contact area the wear in the antagonist is more dependent on the way the abrasive particles are instantaneously incorporated by composite.

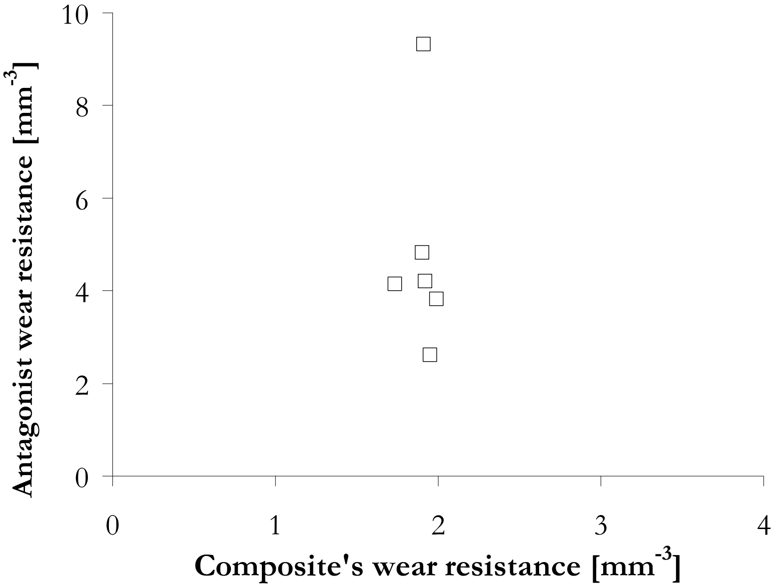


Fig. 5.24: Composite's wear resistance *vs.* antagonist's wear resistance in reciprocating sliding test in abrasive slurry environment.

Composite wear scar morphology was observed by SEM after each wear test. To improve the microscope observation the tested specimens were sputter-coated with gold.

For the test with abrasive slurry (fig. 5.26 a)) hard abrasive particles trapped between the contacting surfaces lead to large and deep scratches. In the wear tests with saliva the surfaces present fewer scratches and the particles are worn along with matrix (fig. 5.26 b)). For each type of test, and comparing composites and antagonist surfaces of different tested materials their typical morphologies did not vary very much.

I. Partial conclusions

The wear of dental restorative composites was investigated on reciprocating contacts against glass spheres. This experimental study was carried out with two different environmental solutions: artificial saliva and aqueous abrasive slurry. This study made it possible to conclude that:

- On both restorative materials and antagonist glass, the wear volumes are greater for the tests with abrasive slurry than saliva;
- In tests with abrasive slurry, amalgam performs better than any of the tested composites. However, in the tests with artificial saliva one composite showed better wear resistance than amalgam;
- Most composite materials reveal a linear relation between wear volume of restorative material and their hardness. This behavior was observed on both performed tests. However,

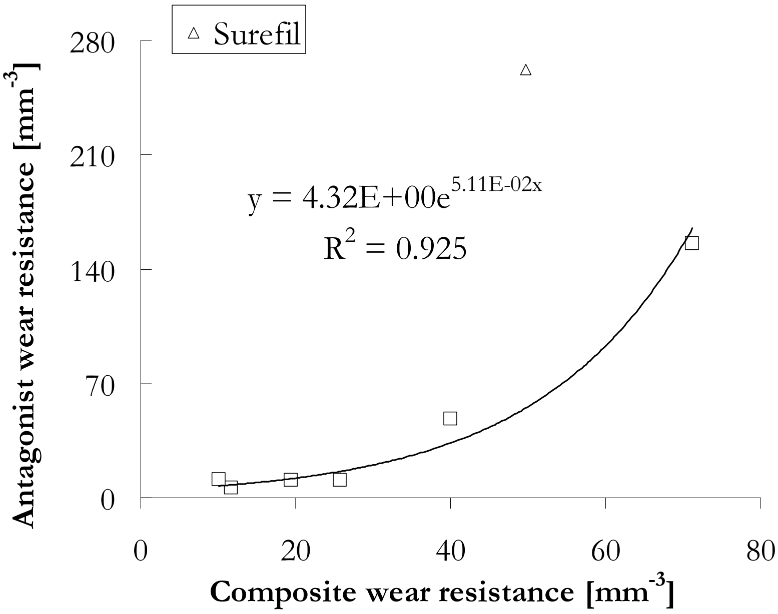
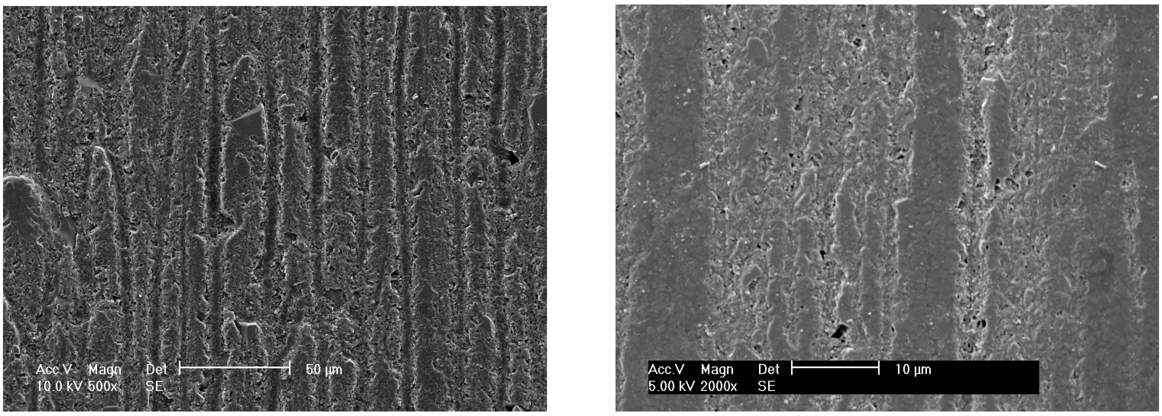


Fig. 5.25: Composite's wear resistance *vs.* antagonist's wear resistance in reciprocating sliding test in artificial saliva environment.



(a) (b)

Fig. 5.26: Typical composite morphology of specimens in reciprocating sliding test with; a) abrasive slurry, (Surefil), and b) saliva, (Prodigy).

hardness effect on improvement of wear resistance is more marked in tests with saliva;

- For mild contact condition, which occurs for tests with artificial saliva, a big difference exists in the wear resistance of various composite materials. However, for severe contact the wear volume of amalgam is very small, when compared with composites, which do not differ very much. Identical behavior was observed for the antagonist material;
- For tests with abrasive slurry, hard abrasive particles are trapped between the contacting surfaces leading to large and deep scratches. In the wear tests with saliva the surfaces present less scratches and the particles are worn along with matrix.

This study allowed several important conclusions to be made but did not fully permit an understanding of how each one of the composites components influence their performance. Thus, the next study is intended to understand how filler fraction, average particle dimension and matrix influence the overall wear behavior of composites.

5.3.2 Produced composites

After the performance evaluation of commercial composites it was not possible to determine precisely how composites' components influence wear behavior of composites in sliding and abrasive wear. Again the use of produced composites was decided to understand sliding wear behavior under two and three body abrasion tests. Therefore as done previously for mechanical properties assessment for tribological test with artificial saliva and abrasive slurry the same variation in components; filler content variation (filler volume fraction and average size particle dimension) and matrix variation was used.

Specimens reinforced with silica microparticles average particle dimension of 6 μm and volume fraction range between 0% and 46%. Afterwards the study was focused in a two fix filler fraction values (30% and 10% in volume filler fraction) and in each, average particle dimension was range from 0.13 μm to 22 μm. As previously for mechanical properties, evaluation matrix variation was also used to understand its influence on tribological behavior of composites.

I. Filler volume fraction variation

Reciprocating tests were done considering two environments: artificial saliva and abrasive slurry. For tests with artificial saliva, different amounts of wear were generated upon glass sphere by the various composites tested. Fig. 5.27 a) and fig. 5.27 b), show values of wear volume obtained for composites with different volume filler fraction, ranging from 0% (PR) to 46% (PR 46). Wear volumes for composites with 37% and 46% particle content are enormous, respectively 0.38 mm^3 and 1.48 mm^3 (fig. 5.27 b)) when compared with the rest. Wear volume for the PR 46 is: 16 times the value obtained for the resin, 0%, 3 times the value of wear volume of the composite with 37% and 400 times the value of the composite with 24% content. Composite with 24% particle content was the one that registered least material removed by wear.

Regarding antagonist's wear, namely glass sphere, tested against the various composite materials, the range in wear volume is not as high as that registered for composite wear volumes. Again, values of antagonist wear tested against composites with 37% and 46% particle content is higher than the rest even though the difference between 46% and resin is "only" 10 times, while, for the antagonist with less volume the value is of about 30 times. The glass sphere with less wear volume was the one tested against composite with 12% particle content, however, the difference registered between the antagonists tested against composites of: 12%, 16%, 24% and 30% is very small, fig. 5.28.

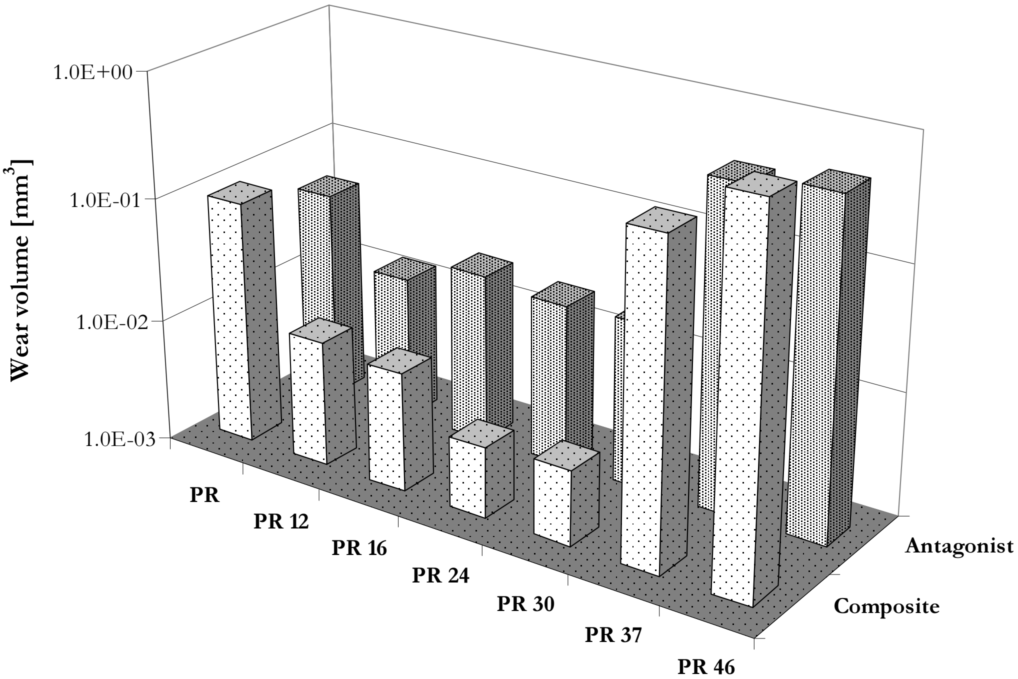


Fig. 5.27: Wear volumes of composite materials and their antagonists in an artificial saliva environment for reciprocating test.

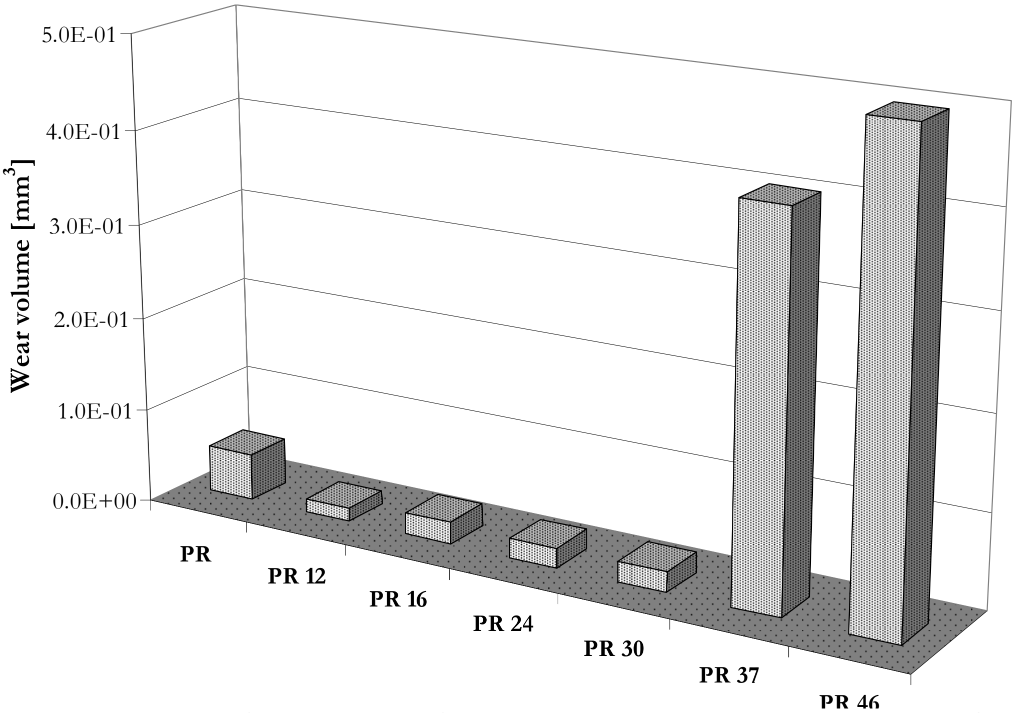


Fig. 5.28: Wear volumes of glass spheres for reciprocating wear tests in a with artificial saliva environment.

Fig. 5.29 presents wear results for reciprocating tests done in an abrasive slurry environment, for composites and their antagonist materials. For composite materials, generally, a rise of wear volumes occurred for increasing particle content, although wear volume values of composites with 37% and 46% particle content are very similar. For composite specimens with lower filler fractions smaller wear volume values were measured. Comparing wear values for different environments, saliva and abrasive slurry, and for specimens with particle content of 12%, 16%, 24% and 30%, specimens tested in the abrasive solution present higher wear volume values. Analyzing antagonist body wear volumes one can say that there is a gradual increase in wear volumes for increasing particle content. The smallest value registered was against resin specimen.

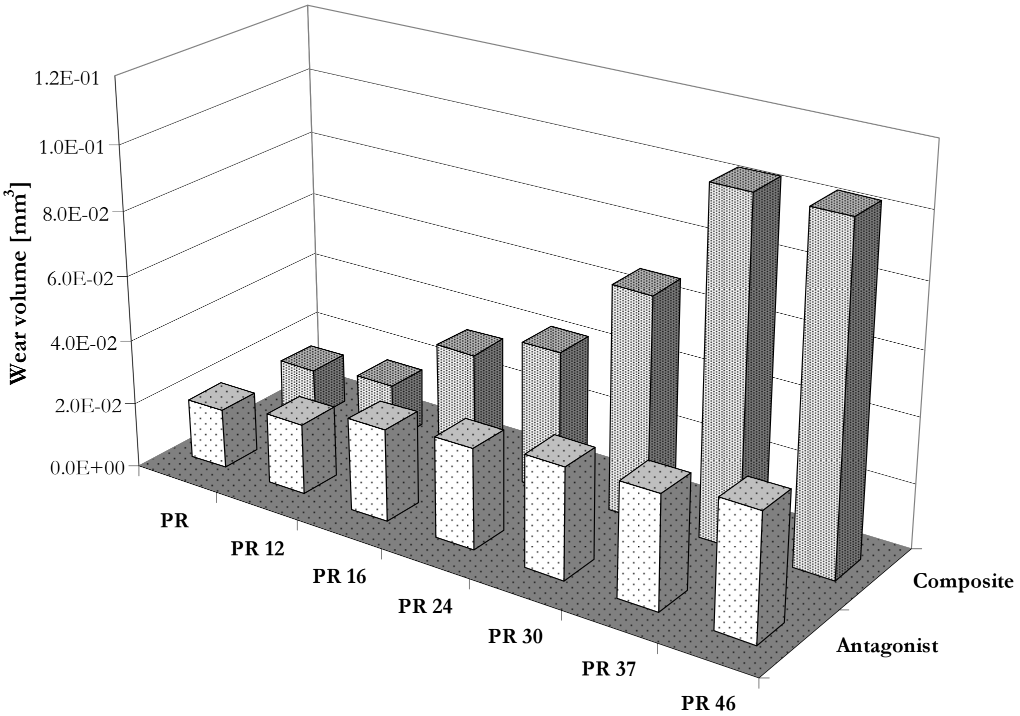


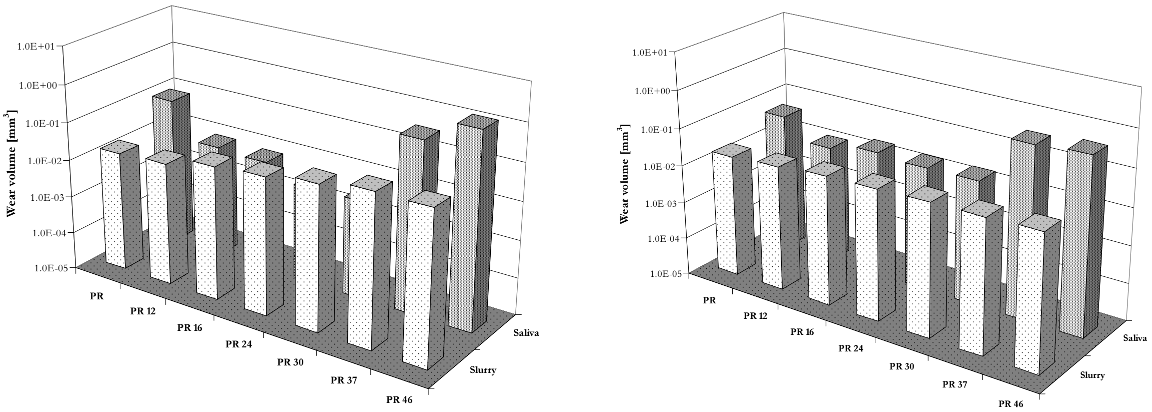
Fig. 5.29: Wear volumes of composite materials and their antagonists in an abrasive slurry environment for a reciprocating test.

Fig. 5.30 presents wear volume values, in logarithmic scale, for a) composite materials and b) antagonists for all filler content tested in both saliva and slurry environment. Comparing wear volumes of composites and antagonists tested in both environments for 12%, 16%, 24% and 30% filler content, slurry solution tests register higher wear volumes, for composites and antagonist materials. For saliva environment, specimens PR, PR 37, PR 46 and respective antagonists show higher wear volumes relatively to slurry environment with the same filler content.

Composites wear scars of reciprocating tests in slurry, observed by SEM, revealed larger wear marks. Fig. 5.31 shows two abraded surfaces of composites with 0% and 12% particle content, where some abrasive particles and micro-glass spheres attached to the composites surface may be observed.

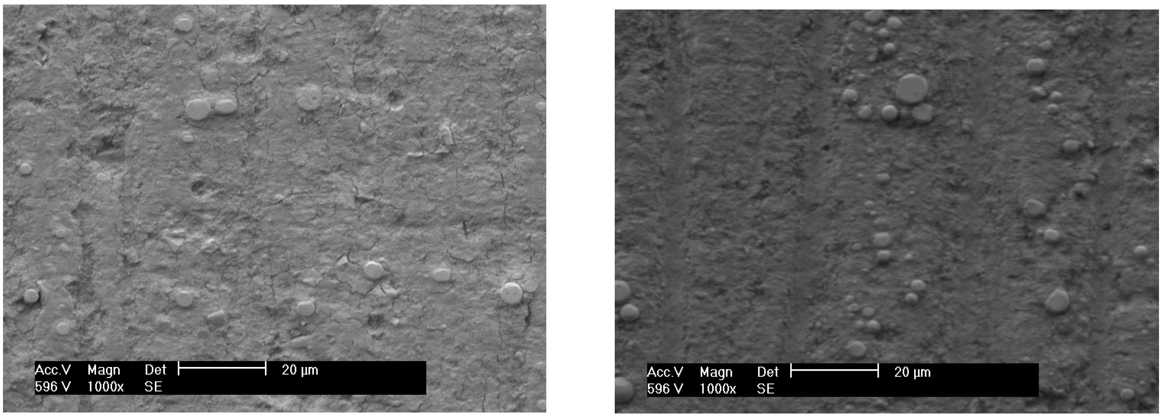
For reciprocating wear tests, fig. 5.32, scratches abrade particles and matrix. Also, in several specimens tested with saliva there is a thin layer formation which agglomerates resin debris, noticed especially in the specimens without particles, fig. 5.32 b).

The main difference, in terms of surface morphology for the two types of environment, is



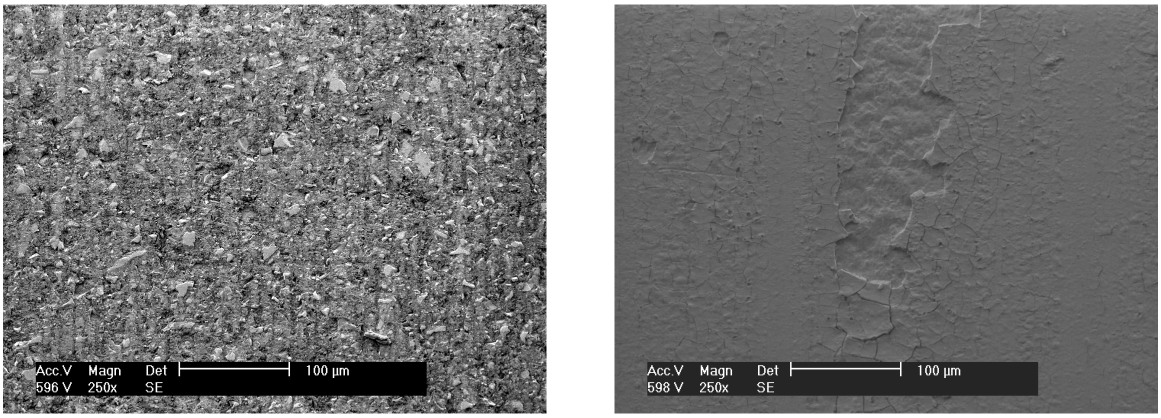
(a) (b)

Fig. 5.30: Wear volumes of tested materials in saliva and slurry environment for; a) composite materials and b) antagonists, in reciprocating test.



(a) (b)

Fig. 5.31: SEM observations for reciprocating tests with abrasive slurry: a) resin specimen (PR); b) composite specimen with 12% particle content (PR12).



(a) (b)

Fig. 5.32: Reciprocating tests with saliva: a) 46% particle content, abrasion of the particles along with the matrix; b) 0% particle content, with an adherent thin layer.

the existence, or not, of the resin layer. In reciprocating tests with abrasive slurry this layer is destroyed, and removed by the particles at contact. In fig. 5.32 a) it is possible to see this compact and homogeneous layer with cracks in the sliding direction.

II. Partial conclusions

Wear of resin composites was investigated on reciprocating contact against glass spheres with two environmental solutions: artificial saliva and aqueous abrasive slurry. This study made it possible to conclude that:

- Reciprocating wear tests with artificial saliva show lower composite wear values for 24% and 30% filler content, while antagonist wear shows less wear when tested against filler contents of 12%, 16%, 24% and 30%. Wear values for 0%, 37% and 46% particle content are the most significant. Therefore, there is a minimum composite volume filler percentage to produce less wear;

- For abrasive slurry environment and analyzing wear volumes of antagonist body and composite specimens, one can say that there is a gradual increase in wear volumes for increasing particle content of composites. In this environment the best performing composites are the ones with less filler particle content;

- Reciprocating tests, with specimens of 12%, 16%, 24% and 30% particle content concluded that wear volumes for the specimens and the antagonist, are higher for the abrasive slurry environment. For other conditions, namely saliva, specimens of 0%, 37% and 46% particle content register higher values of wear.

III. Average filler size particle dimension

After the evaluation of volume filler fraction effect we chose to analyze while maintaining filler volume fraction, the effects of filler average particle size dimension. Initially the intent was to study only one percentage of volume filler fraction (30% in volume), but as nanoparticles are now a trend it was decided to include them, and due to its characteristic, very high values of particle surface area, the initial volume fraction was impossible to attain using the same mixing method. Therefore in order maintain the same variables constant, *i.e.*, resin, particle material and mixing procedure the volume filler fraction corresponding to the maximum capacity of resin and silica nanoparticles was of 10% in volume.

a. 30% volume fraction

From the observation of fig. 5.33, for reciprocating wear tests in artificial saliva environment, for 30% filler volume fraction with resin specimens serving as reference, results obtained show high values of composite wear for resin specimens and for specimens with 30% filler volume and average particle dimension of 22 μm. Specimens PR 30/6 and PR 30/16 have very similar wear volumes, 4.03×10^{-3} and 4.11×10^{-3} [mm^3], respectively. PR 30/3 is about 50% higher than the previous. Resin obtained the highest wear values, 9.21×10^{-2} mm^3.

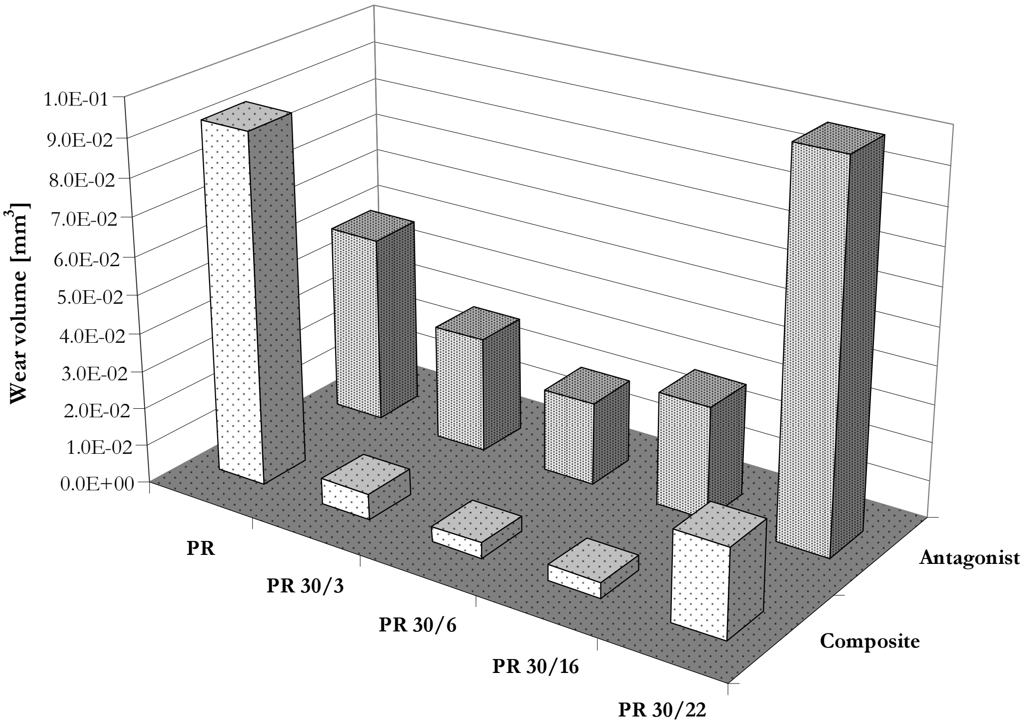


Fig. 5.33: 30% volume filler fraction composites and antagonist material wear volumes for reciprocating test in an artificial saliva environment.

Regarding antagonist wear volumes for artificial saliva environment the minimum value was registered for glass sphere specimens tested against PR 30/6 composites specimens. As found for composite materials, PR 30/3, PR 30/6 and PR 30/16 have similar wear volume amounts. Antagonist materials tested against resin and PR 30/22 are characterized by the highest values of removed material.

Analyzing results of reciprocating wear test with abrasive particles, shows that the value of resin is the smallest. Composite wear resistance increases with increasing average particle size dimension. In abrasive sliding tests, composite specimens with larger particle dimension tend to have smaller wear, fig. 5.34.

Regarding antagonist body, these show more wear when in sliding contact with composite specimens containing large particles. Glass sphere wear volumes do not show very different volume of removed material when tested against PR 30/3, PR 30/6 and PR 30/16. Again, as for composite wear analysis, antagonist bodies in contact with polyester resin specimens tend to cause less material removal.

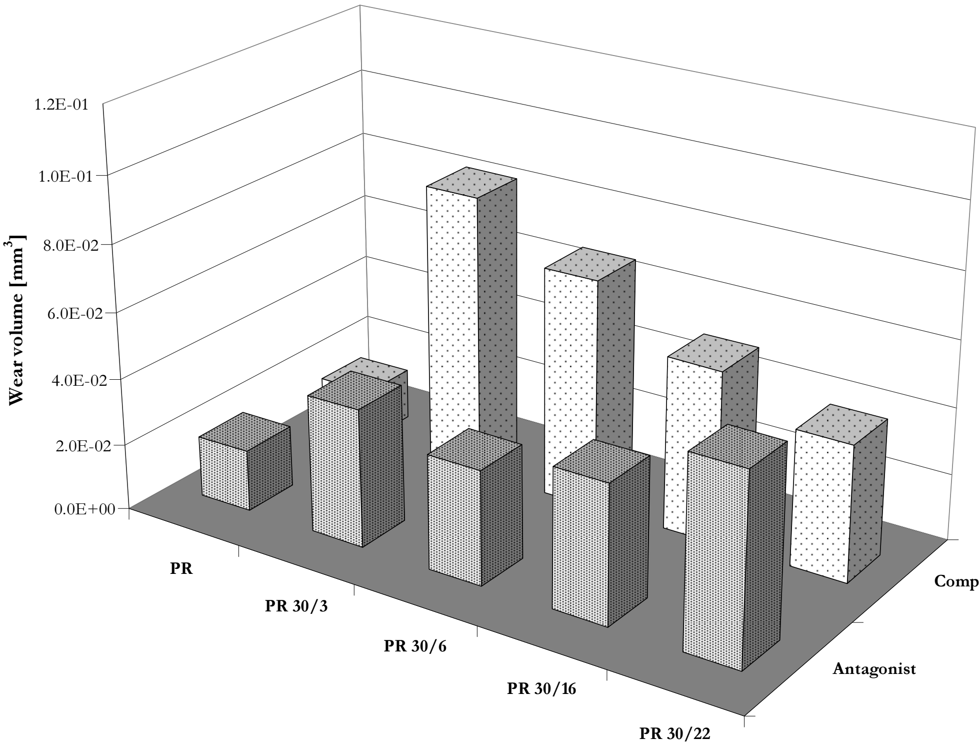


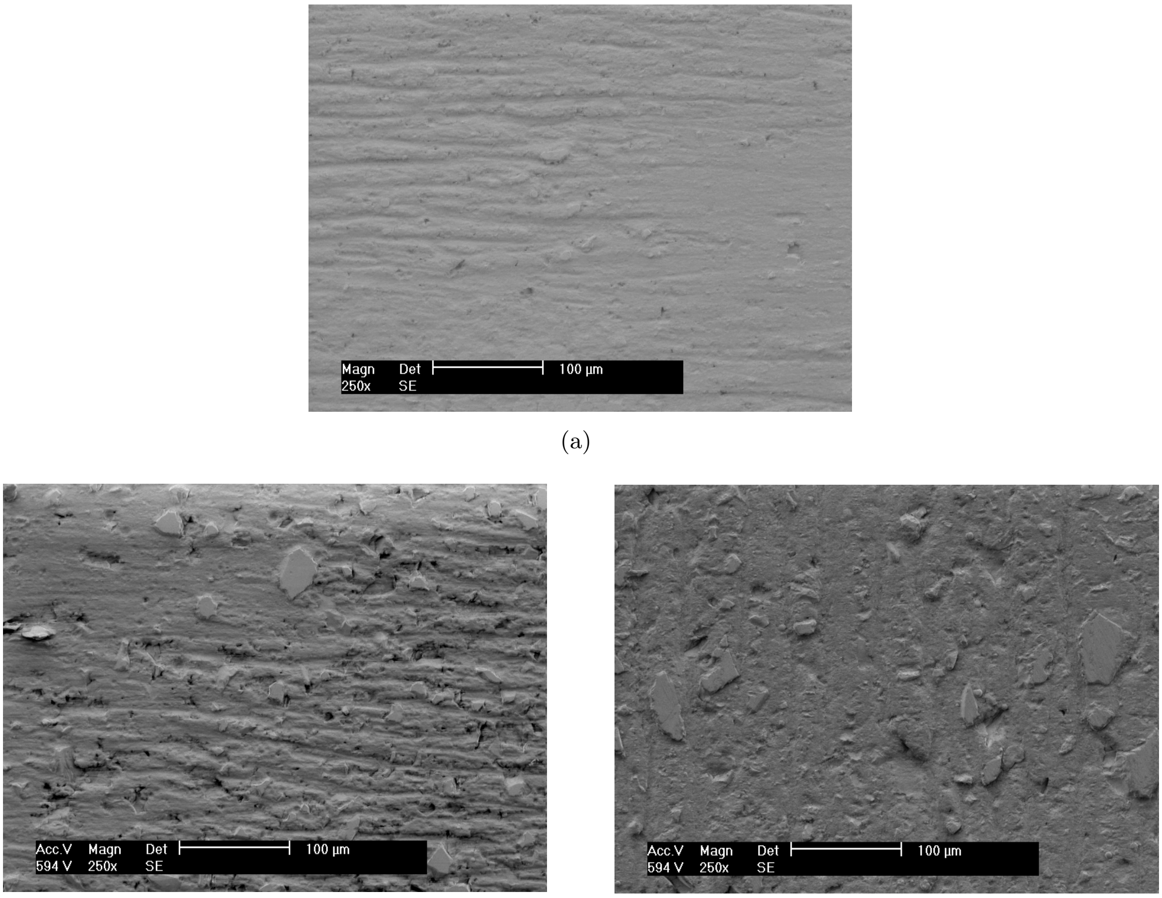
Fig. 5.34: 30% volume filler fraction composites and antagonist material wear volumes for reciprocating test in abrasive slurry environment.

There is a clear tendency to diminish wear volume of composites when average particle size increases, while on the other hand, an increase in antagonist wear is observed. Under tested conditions, resin against glass sphere is the material pair which shows smaller volumes of material removed by wear.

As reinforcement particle distribution in terms of particle dimension has a wider range, spaces between the larger particles are occupied by smaller particles, thus decreasing the interparticle spacing and wear reduction, allowing for reduction in abrasion through the "protection-hypothesis" (Jorgensen and Asmussen, 1978; Jorgensen *et al.*, 1979; Bayne *et al.*, 1992). Attrition is reduced through increased fracture toughness. Good stress-transfer at the resin/filler interface, improves the bond between filler and matrix by increasing the filler surface area (Jorgensen et al, 1979).

On the other hand bigger reinforcement particles in composite manage to produce greater damage in the antagonist body, causing an increase in wear.

This evolution could also be clarified by observing the wear surfaces under SEM (fig. 5.35). No fractures are present at the abrasion surface. Composite with smaller particle dimension presents smooth surface and reinforcement particles are not detached from matrix (fig. 5.35 a)). In fig. 5.35 b) and fig. 5.35 c) composites with larger particles, present deeper grooves while particles still remain attached to matrix.



(a)

(b)

(c)

Fig. 5.35: Composites morphology taken in wear scar for specimens with average particle dimension of; a) 3 μm; b) 16 μm, and c) 22 μm.

b. 10% volume filler fraction

As explained before, due to the nature of nanoparticles, with very high values of contact area, another batch of specimens had to be manufactured to study produced composites that included these varieties of particles, namely 10% filler volume fraction.

Regarding reciprocating sliding tests, the same environmental conditions were applied as for volume filler percentage and average particle dimension.

As occurred for 30% filler content, polyester resin and its antagonist registered the highest wear volumes of the pairs in study (fig. 5.36). The best performing pair was PR 10/3 and PR 10/6. Composite wear of nanofilled composite was higher than any microfilled composite or any of the specimens produced with 30% and 70% precipitated silica E (PR 10/1 and PR 10/2 respectively) and micro silica particles (3 μm). Although nanofilled composites have the worst results, following polyester resin, antagonists performed very well but with wear volumes larger than the ones tested against PR 10/3 and PR 10/6. Comparing both composites with particle mixture of silica; precipitated silica E with average particle dimension of 0.13 μm and 3 μm, composite with 70% nanoparticles had better results. Specimens of this composite presented similar result regarding wear volumes, to the ones showed for PR 10/16 and PR 10/22. Concerning antagonist's wear the results match wear volumes of composites except specimen PR 10/0.1. This nanofilled composite produces a very small amount of material removal from its antagonist.

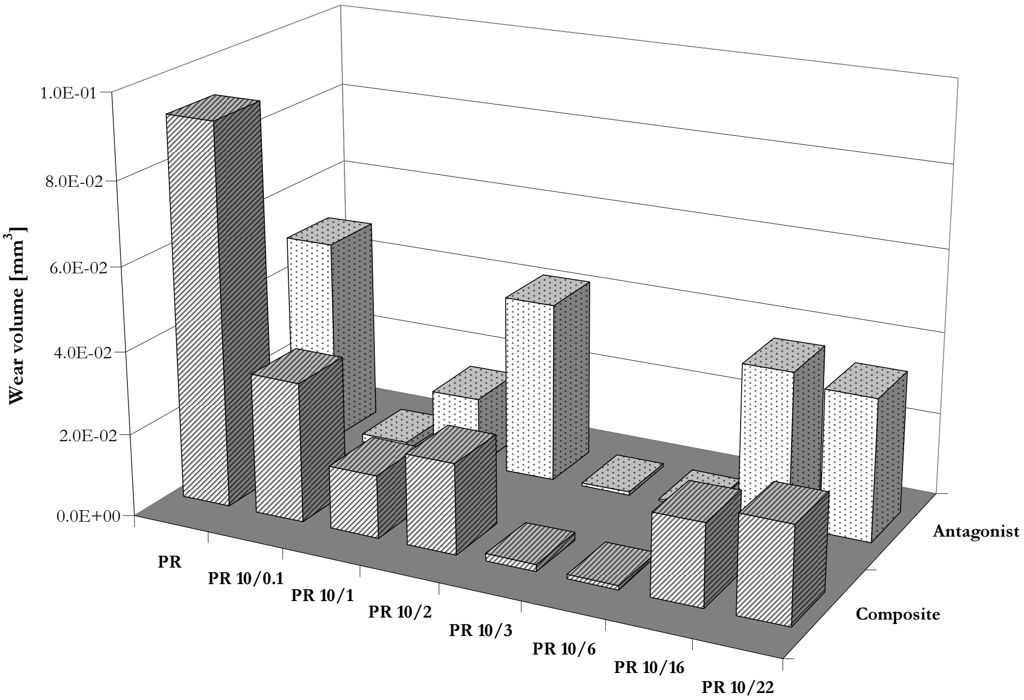


Fig. 5.36: Glass spheres tested against 30% volume filler fraction composites material in reciprocating wear tests in an environment with abrasive slurry.

Comparing the wear performance of composites with 30% filler volume to the results obtained with 10% filler volume for the same particle dimension in sliding wear tests with saliva, PR 10/22 and PR 30/22 presented the same wear for composites tested while specimens with 10% in volume and average particles dimension of 3 μm and 6 μm had much smaller wear volumes then specimens of 30% filler content with the same particle dimension (fig. 5.37). Regarding tests with 10% filler content, PR 10/16 presents very high values of wear when compared with PR 30/16. For both distinct filler content, composites PR10/6 and PR 30/6 are the ones with lowest wear volumes as observed in the graph of fig. 5.37.

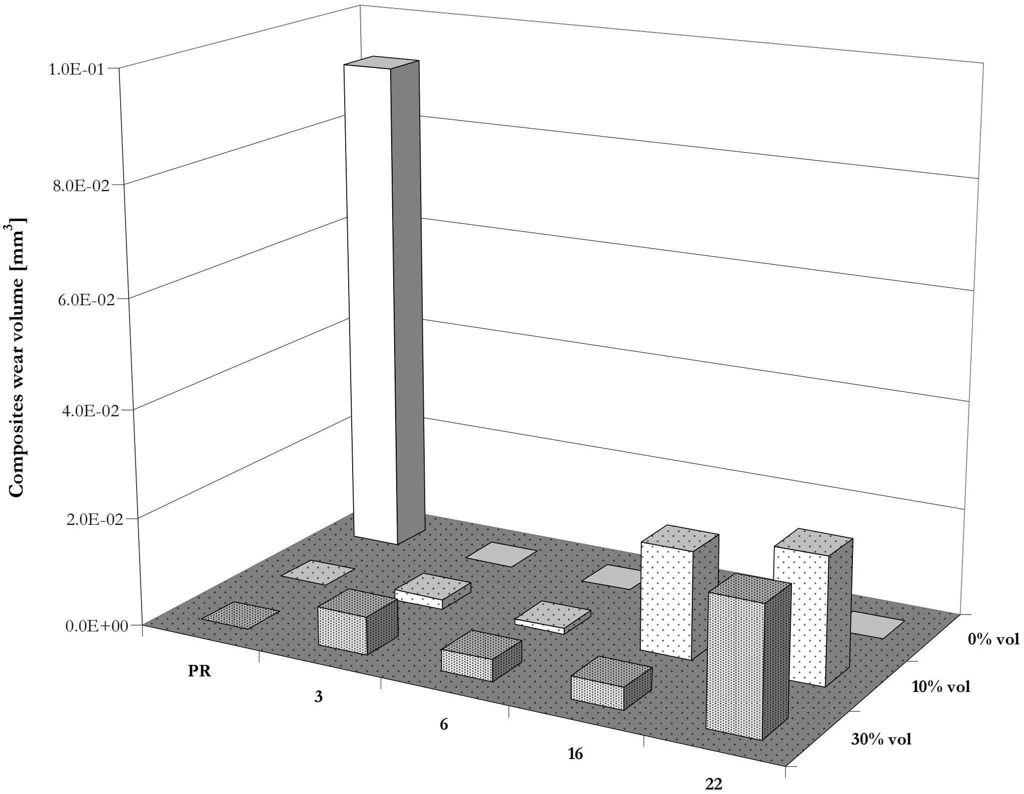


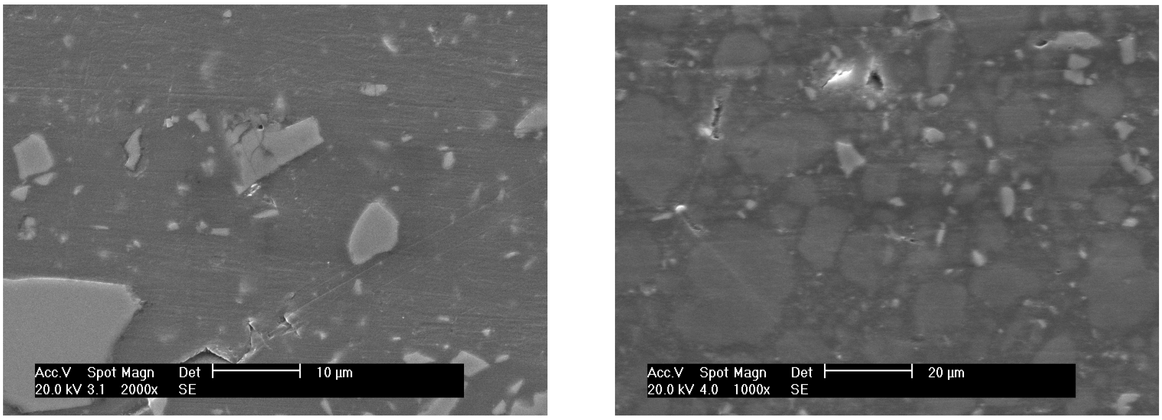
Fig. 5.37: Composites wear volume against glass spheres in reciprocating wear tests in saliva environment with specimens of: 10% filler volume fraction and 30% filler volume fraction for average particle dimensions of 3 μm, 6 μm, 16 μm and 22μm and polyester resin specimens PR without inorganic filler particles.

Surface morphology for reciprocating wear tests in artificial saliva environment was very similar to specimens with 30% filler content as there was also a uniform removal of resin and reinforcement particles (fig. 5.38). Due to the lower filler volume content, the resin layer observed for specimens with 10% filler was not as expressive, yet still noticeable.

For composites specimens with larger filler particles in the contact area some spots show greater degradation (fig. 5.39 a)). When observed more closely it is possible to understand that the damage is produced in the sub-surface and thus fracture of this area occurs (fig. 5.39 b)). Similar situations occur in reciprocating contacts for 30% filler content. Regarding 10% filler, this phenomenon is evidenced only for specimens with average particles sizes of 16 μm and 22 μm. For specimens with nanoparticles, and mixture of nano- and microparticles, a homogeneous wear is noticed.

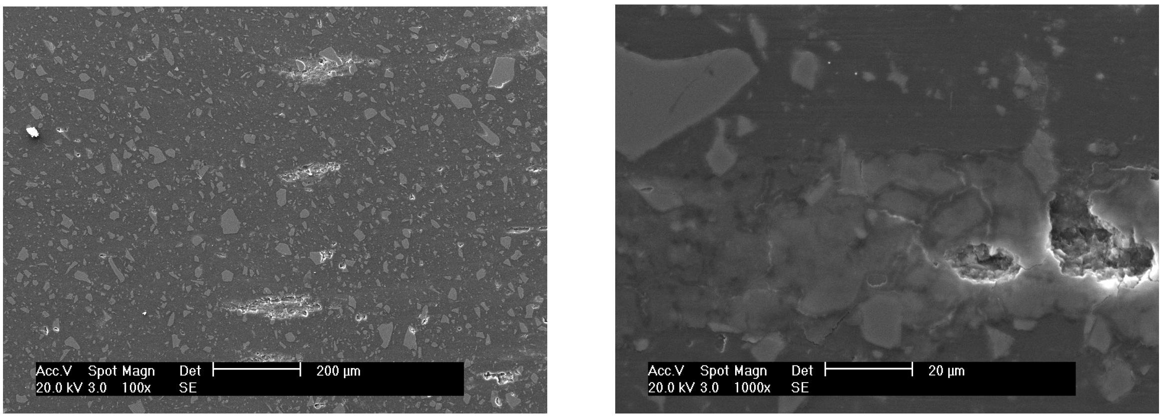
IV. Partial conclusions

After the analysis of wear behavior in reciprocating wear contact concerning filler content in produced composites and for filler volume fraction variation (0%, 10%, 12%, 16%, 24%, 30%, 37% and 46%) and average filler particle dimension in saliva environment test it can be concluded



(a) (b)

Fig. 5.38: Composites morphology taken in wear contact area for specimens with 10% filler content in reciprocating saliva environment, for specimens; a) PR 10/16; and b) PR 10/1.



(a) (b)

Fig. 5.39: Composites morphology taken in wear contact area for specimens with 10% filler content in reciprocating saliva environment, for specimens PR 10/16; a) 100×, and b) 1000×, magnifications.

that, concerning filler volume content variation, fig. 5.40:

- Up to 30% filler content, composite wear is smaller than only matrix composition. 37% and 46% inorganic filling has more wear;
- The smallest composite wear value was obtained for 10% filling (1.02×10^{-2} mm^3) followed by 24% and 30% with 3.72×10^{-2} and 4.03×10^{-2} mm^3 of removed material.
- Regarding average filler dimension and considering the two filler volume percentages, smaller wear values are obtained by specimens with 6 μm particle dimension.
- Nanoparticles did not show any noticeable advantages regarding composite wear when compared with other particle dimension specimens, whether isolated or in mixture (30% and 70%) of silica microparticles.
- Nanoparticle composite specimens produce low wear in the antagonist body, and even though these did not represent the best wear values, for 10% particle filled composites, specimens with particles of 3 μm and 6 μm performed better. Obviously the introduction of inorganic fillers in composites also has mechanical related property variation as previously shown.

Fig. 5.41 presents all values of material removed by wear in an abrasive slurry environment. As noticed for 30% filler fraction specimens studied for this same condition presented smaller amounts of wear when compared with saliva test environments. For this filler fraction content the same trend happens.

Through the analysis of the graph it is possible to see that, generally, an increase in wear resistance occurs for increasing average particle dimension. Clearly the smallest wear average value occurs for specimens with 22 μm reinforcement particles. Condon and Ferracane (1997) highlighted that the effect of filler volume on wear resistance follows a linear relationship, with high filler volumes decreasing wear rates due to the lower expanse of resin unprotected by filler particles, which is supported by other researchers (Heintze *et al.*, 2007; Manhart *et al.*, 2000b).

Specimens produced only with nanoparticles and mixture of nano and microparticles obtained the highest wear volumes, especially PR 10/0.1 and PR 10/2. Curiously specimens with only 70% nanoparticles (of 10% in volume fraction of particles) present smaller wear relatively to specimens with only nanoparticles, Yesil *et al.* (2008) compared wear test results of commercial restorative materials which incorporate nanofillers and these did not significantly improve composites' performance when compared with microfilled commercial composites. When considering the same filler volume fraction and with increasing filler particle dimension the number of particles is reduced significantly and therefore average particle distances increase. The shorter the distance between the particles, the more the matrix will be protected against the erosive activity from the hard particles and/or fibers in the contacting surfaces (Jørgensen and Asmussen 1978; Bayne *et al.*, 1992; Venhoven *et al.*, 1996).

In these tests, the presence of reinforcement particles is negative to the overall performance. Polyester resin specimens register better wear resistance than composites, which is the opposite of what happens in sliding contacts in artificial saliva situations. The presence of the abrasive particles of the slurry in contact allows them to adjust the sliding velocity of the surfaces of resin and antagonist. Due to the softer nature of the resin specimen the slurry particles "polished" the glass surface and produced a small wear value in the resin specimen. Regarding composite wear, the material removed is smaller for increasing reinforcement particle dimension (when filler fraction is kept constant) increase in filler size prevents the formation of deep, wide and

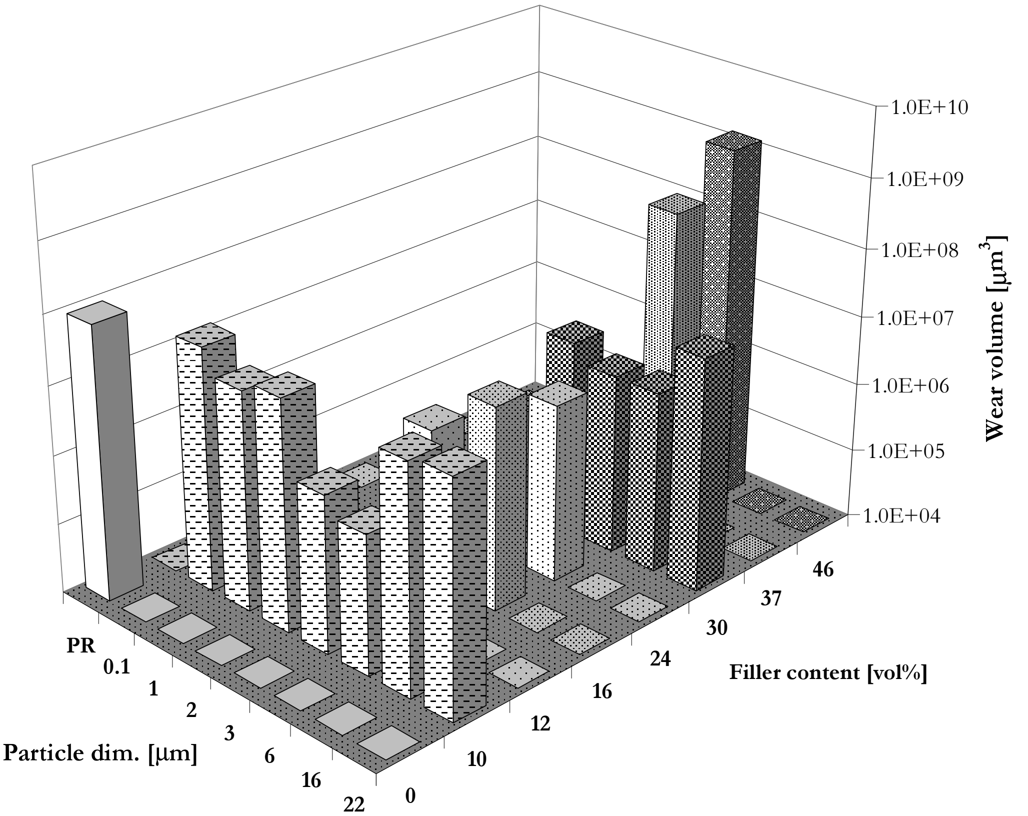


Fig. 5.40: Reciprocating wear results for polyester and silica composites in saliva environment for filler vol. fraction ranging from 12% to 46% (average particle dimension of 6 μm) and 10% and 30% filler content for particles dimension from 0.1 μm to 22 μm against glass sphere antagonist. Wear volume of composites with 37% and 46% are not fully represented due to their wear magnitude. Polyester specimens are also represented in the graph to serve as reference.

continuous grooves, and enhancement of the surface hardness. These factors combine to improve the ploughing and cutting resistance (Liu *et al.*, 1999).

Harsha *et al.*, (2003) reported three-body abrasive wear studies were carried out using a rubber wheel abrasion test with polyaryletherketone matrix specimens which presented less wear and abrasion when compared with reinforced polyaryletherketone ones. Through micrographs he observed matrix damage and subsequent matrix removal due to the formation and propagation of microcracks as well as macrocracks at the surfaces. He also reported the absence of any plastic deformation or grooves formation due to the brittle nature of matrix with wear debris detached from the surface in the form of thin layers, similar to a delamination process.

In spite of having less number of cycles, abrasive slurry tests produced higher wear volumes. Artificial saliva tests are less aggressive than slurry environment ones which promoted a higher wear rate for both materials in contact. The formation of a tribo-layer has previously been identified under two body wear conditions, but not in relation to slurry environment (Dwyer-Joyce *et al.*, 1994) which also helps to better explain wear results for tests without abrasive slurry.

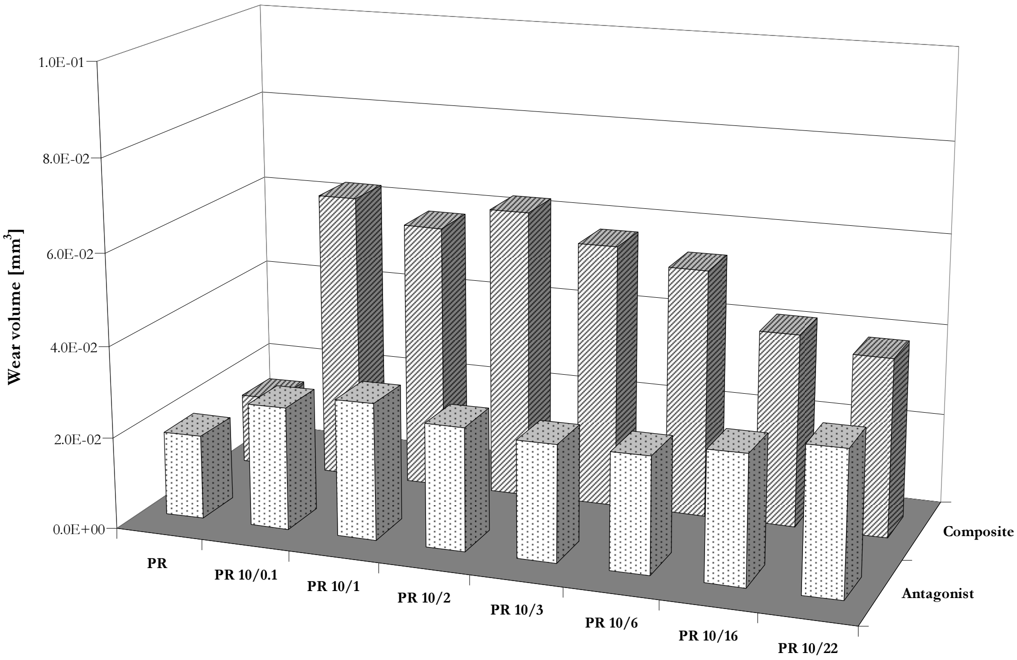


Fig. 5.41: Glass spheres tested against 10% volume filler fraction composite material for several average particle dimensions for reciprocating wear tests in an abrasive slurry environment.

Concerning wear values of antagonist materials, specimen with the best wear resistance was PR (0% filler volume fraction). The rest of glass spheres present in all tests against particle reinforced composites presented very similar wear values; the difference between the lowest and highest was 19% which is insignificant if to saliva wear results. Again nanoparticle reinforced materials tend to wear less their antagonist as seen before in tests with saliva environment.

In fig. 5.42 it is possible to observe in more detail what was stated previously for abrasive slurry tests for 10% and 30% particle filled composites. An obvious reduction of wear in specimens when reinforcement particles increase in dimension, but even when compared with the 22 μm particles unreinforced specimens present higher wear resistance tested under abrasive environment.

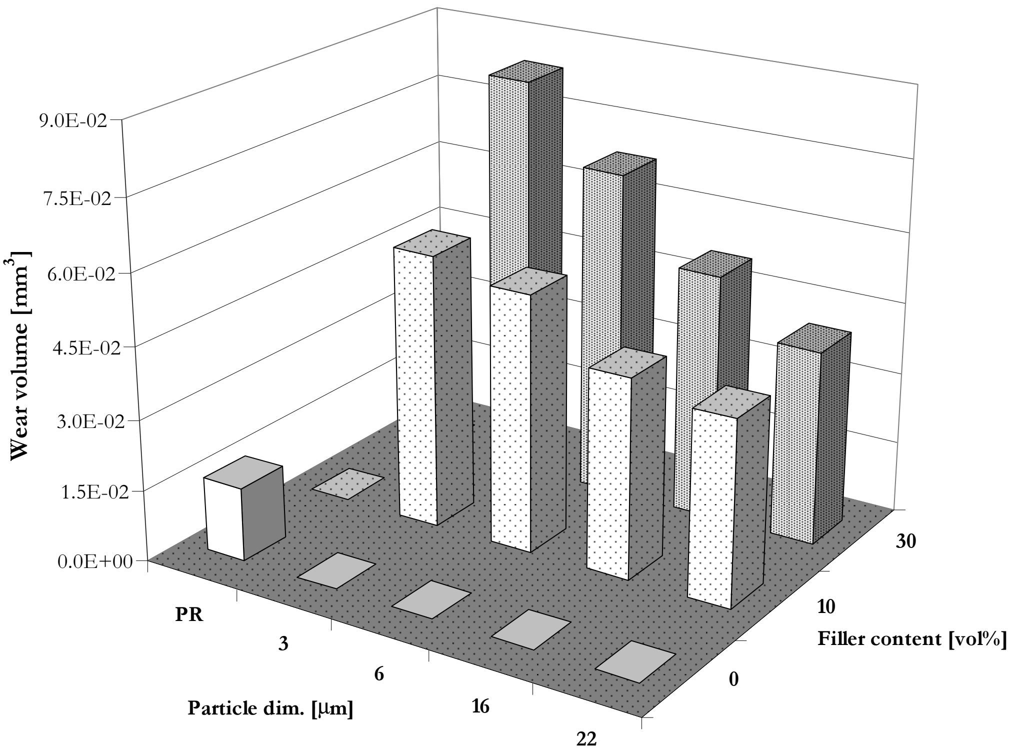


Fig. 5.42: Composites wear volume against glass spheres in reciprocating wear tests in slurry environment with specimens of: 10% filler voloume fraction and 30% filler voloume fraction for average particle dimensions of 3, 6, 16 and 22 μm and PR unreinforced polyester resin specimens.

In the graph of fig. 5.43 it is possible to observe how environment conditions, saliva and abrasive slurry, affect composite wear with reinforced particle dimension from 0.1 μm to 22 μm. Bear in mind that slurry environment produces a lot of material removal for the same contact conditions, frequency, number of cycles and normal load, but comparing the wear distribution for these two distinct environment conditions it is possible to observe that particle dimension is more important when there is no abrasive third-body in the middle of composite and glass surfaces and there are particle dimensions more favorable than others. Another important conclusion is that nanoparticles on their own, as reinforcement do not present better wear resistance and limit reinforcement filling percentage of composites and therefore do not allow for enhancing of some mechanical properties.

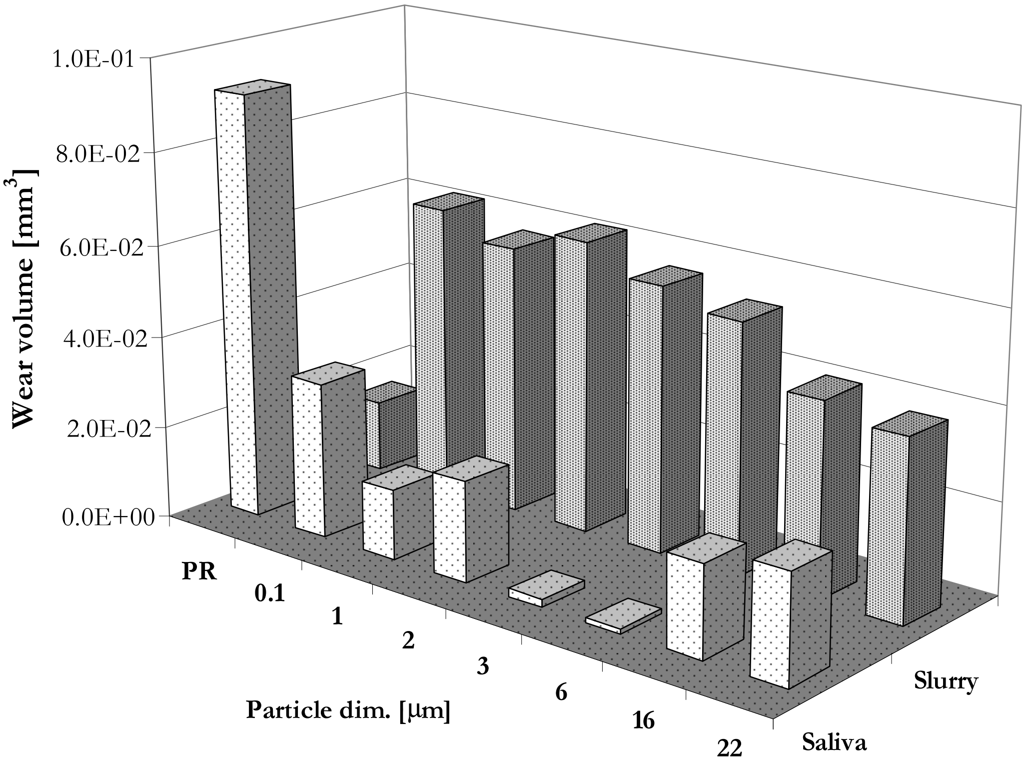
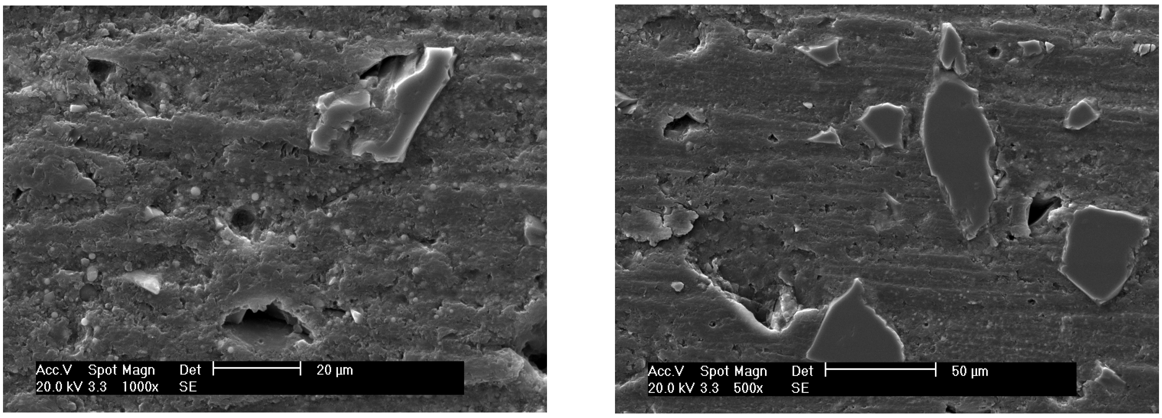


Fig. 5.43: Composites wear volume against glass spheres in reciprocating wear tests in slurry and saliva environments for 10% filler volume fraction specimens for seven average particle dimensions and polyester resin specimens PR without reinforcement particles.

Concerning contact morphology of the tested specimens in abrasive slurry medium, the mechanisms observed are basically the same. Hard particles of slurry solution initiated sharp surfaces, thus removing matrix and releasing small particles and subsequently larger particles. Fig. 5.44 a) shows holes due to reinforcement particle removal which rest trapped between contacting surfaces producing large grooves in the contact area. This explains high values of wear generated in both the composite material and the antagonist.

A common feature in all contact surfaces was the encrustation of glass micro-spheres (~ ϕ 4 μm) in the composite surfaces. Contact surfaces presented a superficial well compacted layer constituted by matrix, abrasive particles and reinforcement particles, fig. 5.45 a) and fig. 5.45 b). In fig. 5.45 c) it is possible to see this superficial layer and the grooves due to reinforcement particles which after being removed from the matrix rest trapped in the contact. Fig. 5.45



(a) (b)

Fig. 5.44: Wear scars from reciprocating wear contact for slurry solutions medium for resin composites with 10% filler volume (average particle dimension of 22 μm) content against glass spheres.

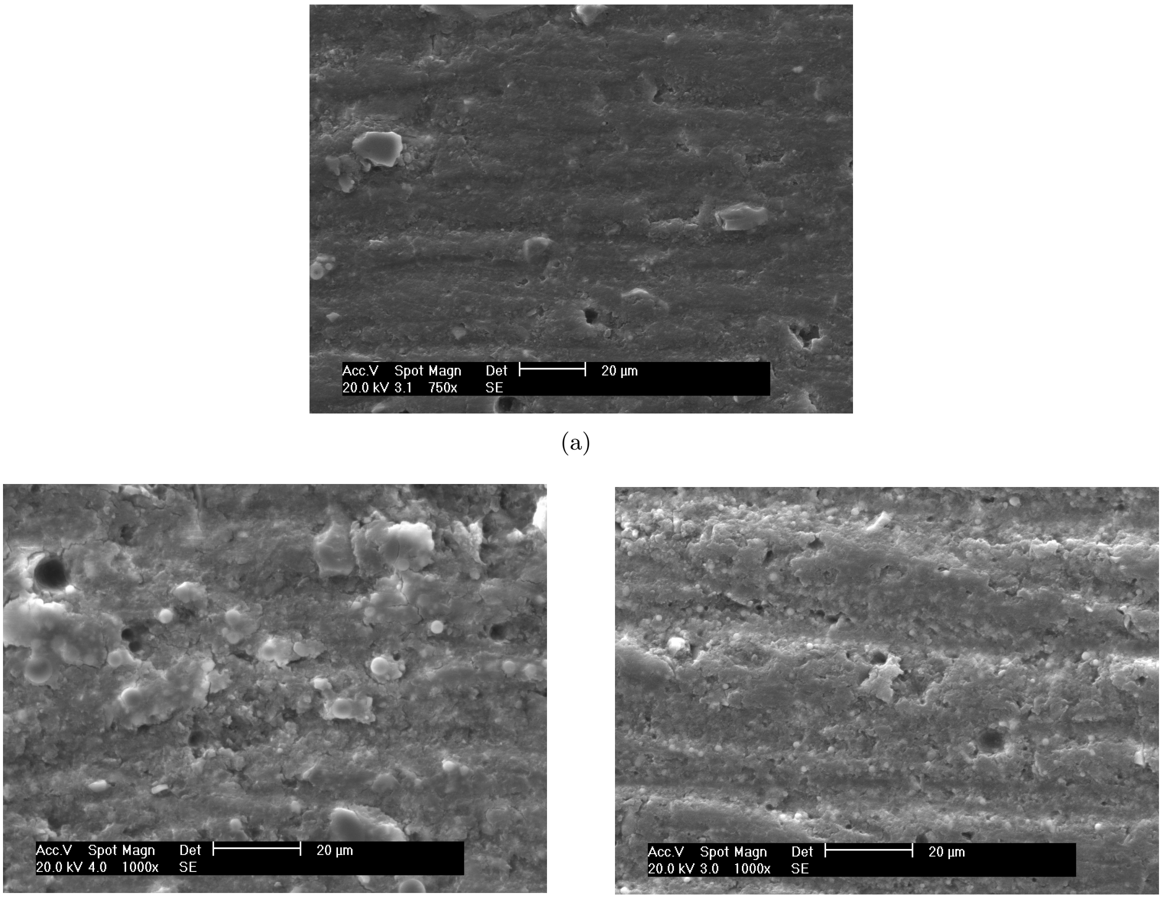
c) corresponds to a PR 10/3 composite specimen, with small particles compared to composite pictures shown in fig. 5.44 and, the referred layer, due to smaller reinforcement particles seems be more dense and compact. In the latter case, reinforcement particles are not so noticeable, fig. 5.45, and these composite materials present better wear resistance.

Fig. 5.46 presents composite surfaces for PR 10/1 specimens and it is possible to observe good adhesion of abrasive particles from the abrasive slurry to the matrix. As seen before, with other contacting surfaces and different inorganic filler dimensions, some holes are due to removal of particles and, again, some grooves are due detached reinforcement particles.

After the analysis of the results of reciprocating wear tests done under abrasive slurry solutions, observing the graph from fig. 5.47 and taking into account the filler content, it is possible to conclude that, regarding filler volume fraction; there is an increase in composite material removal for 12%, 16%, 24%, 30%, 37% and 46% volume filler fraction. Surprisingly, 10% (filler volume fraction) has higher wear values when compared to 12%. However, for the 12% condition only a series of composites have been processed and a small variation to the nominal composition could be expected. When filler fraction was kept constant (at 10% and 30% filler volume fraction) there is a general decrease in wear when average particle dimension increases. Therefore, for abrasive slurry conditions, wear resistance increases for small filler fraction content and large reinforcement particles. Reinforcing composites only with nanoparticles does not invert the tendency of increasing wear of small particles. For reciprocating wear tests in this medium unreinforced condition is the best solution, as proved for polyester resin specimens (PR).

V. Matrix variation

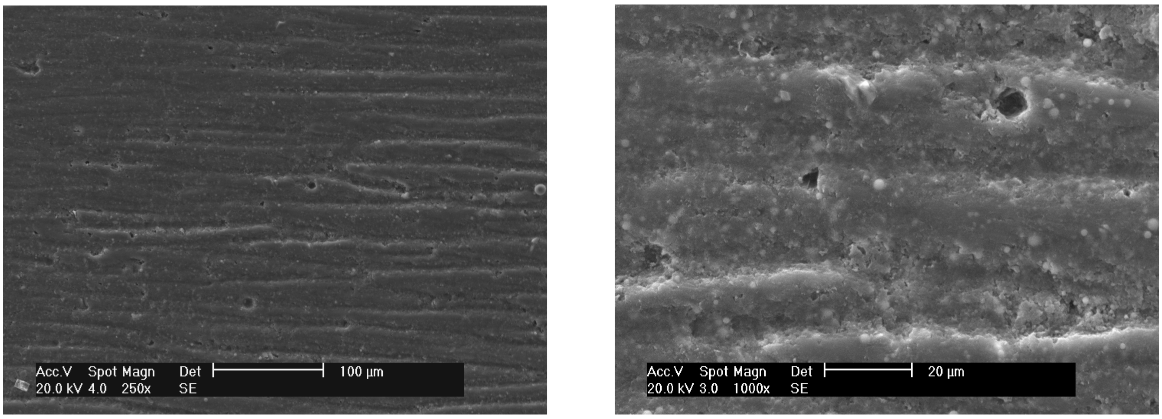
The effect of the matrix in wear was a small part of the present study and regarding the investigation of matrix influence, reciprocating wear tests under artificial saliva environment with 10,500 cycles and 5 newton normal loads were executed. As previously done for other variables, first resin specimens were evaluated and afterwards, composite specimens with the same matrix, but reinforced with 24% volume of 6 μm silica microparticles, were tested. The idea was to determine how much of an influence could be expected with a variation in urethane dimethacrylate (UDMA) percentage in the matrix. Three percentages were considered 0%, 10%



(a)

(b) (c)

Fig. 5.45: Wear scars from reciprocating wear contact for slurry solutions medium for glass spheres against resin composites with 10% filler volume content and average particle dimension of; a), b) 16 μm, specimens PR 10/16, and c) 3 μm, specimens PR 10/3.



(a) (b)

Fig. 5.46: Wear scars from reciprocating wear contact for slurry solutions medium for resin composites with 10% volume filler content and average particle dimension of 1 μm against glass spheres.

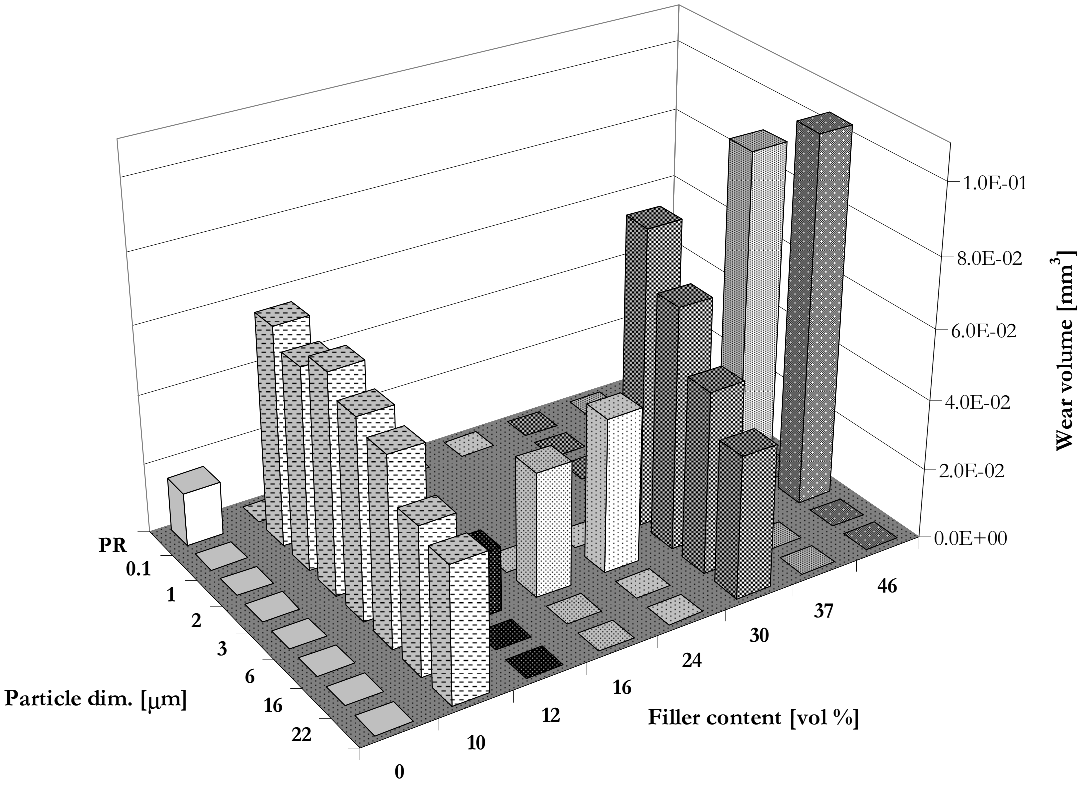


Fig. 5.47: Reciprocating wear results for polyester and silica composites in slurry environment for filler vol. fraction ranging from 12% to 46% (average particle dimension of 6 μm) and 10% and 30% filler content for particles dimension from 0.1 μm to 22 μm against glass sphere antagonist. Polyester specimens are also represented in the graph to serve as reference.

and 20% mol of UDMA. These three percentages were also considered in the composite material and their influence was assessed. The wear test results are shown in the fig. 5.48.

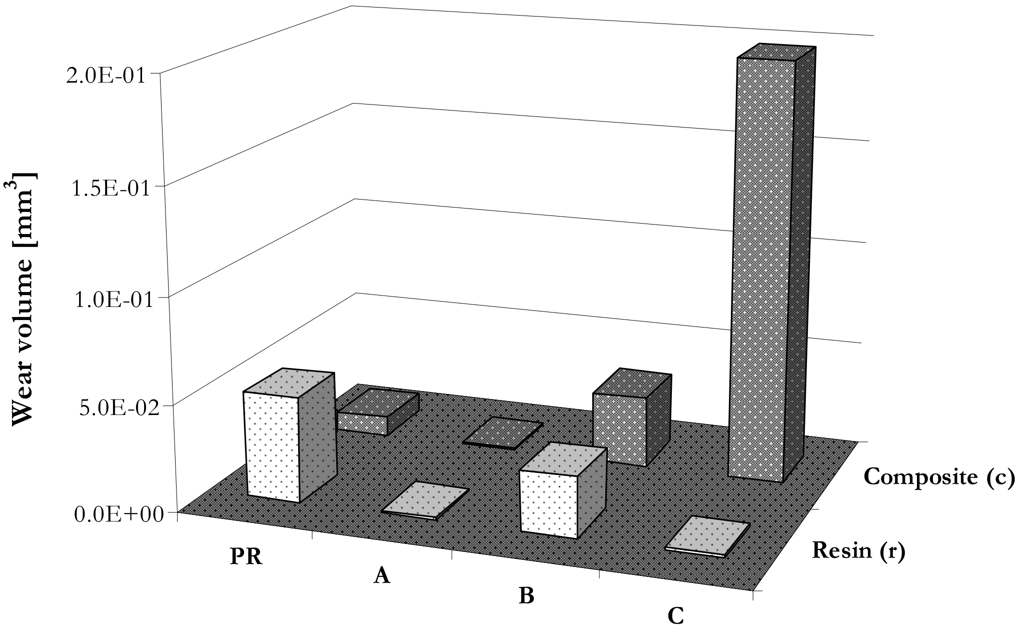


Fig. 5.48: Reciprocating wear results for resin and composites specimens PR, rA, rB and rC. Composite specimens have 24% volume filler content and four matrices are present, polypropylene and three similar matrices with 3 different UDMA mol percentages tested against glass spheres in artificial saliva.

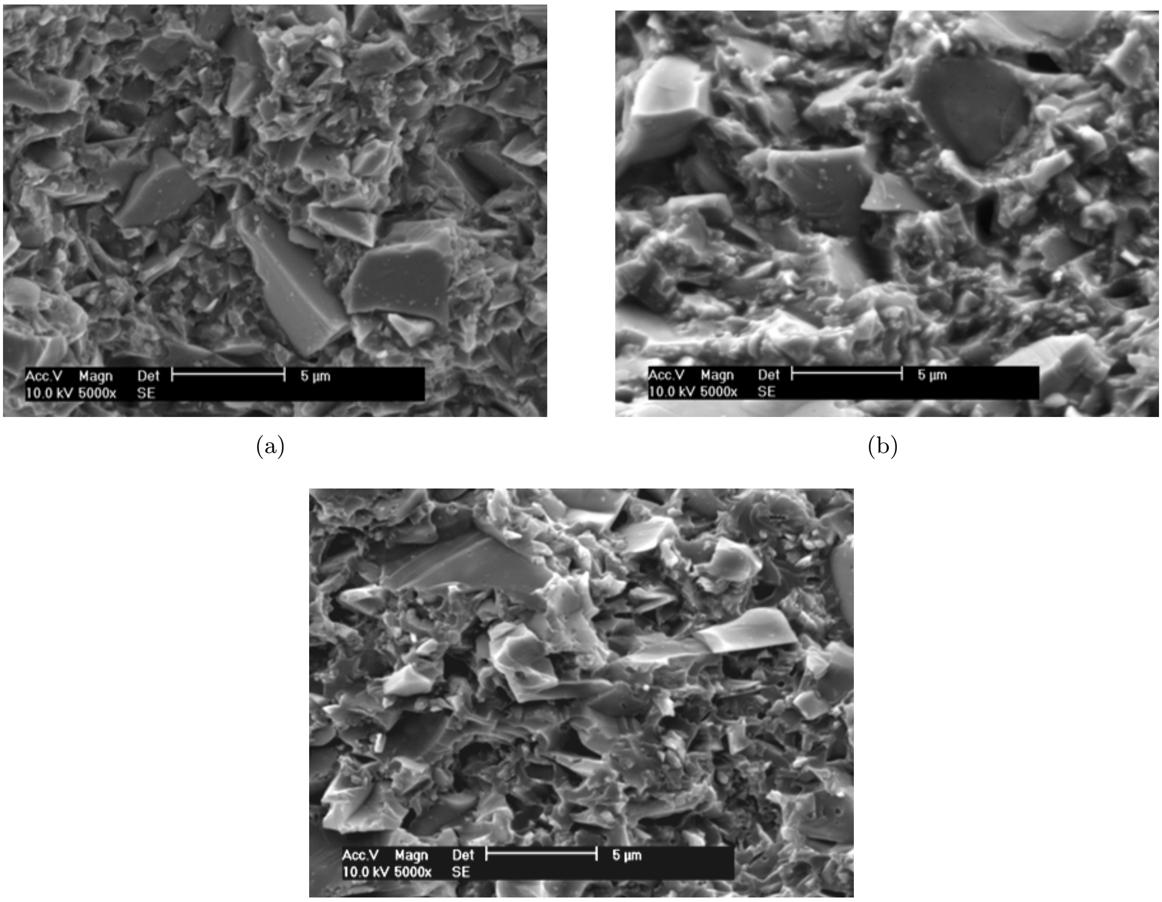
When analyzing composite wear results of unreinforced resins, polypropylene is the resin with less wear resistance. For the resin specimens with Bis-GMA, TEGMA; MMA and UDMA resin specimen with the 10% mol of UDMA is the one with the second highest wear. 0% and 10% mol UDMA content performs very similarly, although 0% mol UDMA has the lowest wear value.

Comparing wear results of composites with the ones obtained in unreinforced conditions, the most significant differences occur for propylene (PR) where reinforcement particles induce a reduction of one order of magnitude in wear volume. For matrix composition C, with 20% mol UDMA, a large increase in wear was registered, $1.72{\times}10^{-3}$ [mm^3] to $1.99{\times}10^{-1}$ [mm^3] specimens rC and cC, respectively. matrices with 10% mol UDMA, for resin and composite did not reveal significative wear volume difference.

This result confirms what was observed for every mechanical property analysed; all tested specimens cC always presented poorer results then cB specimens with only 10%. There seems to exist weak bonding between the organic and inorganic components of composite cC. This is also revealed by the comparison between wear volume of rC and rB, when analyzing material removed by wear rC has much better results then rB, but when reinforcement is present the composites behave oppositely.

When observing SEM photographs there are no apparent morphological differences between the composites which have matrices with different chemical formulation, fig. 5.49.

Another important conclusion regarding this evaluation is that when comparing these three matrices formulations which are very different from the polypropylene matrix (which use is not specific for dental applications), resin performance is much better than polypropylene, but when



(a)

(b)

(c)

Fig. 5.49: SEM photographs at 5000x of fracture surfaces for composites containing a) 0 mol %. UDMA cA; b) 10 mol % UDMA, cB, and c) 20 mol % UDMA cC.

added reinforcement particles, the percentage of UDMA decreases the wear resistance capabilities of the composite, probably due to characteristics of urethane dimethacrylate which when applied to matrices creates a more flexible polymer of reduced strength upon curing. Notice that the matrices used to evaluate the effect of matrix have similar formulations to some commercialized dental composites. Both base monomers UDMA and Bis-GMA are relatively large molecular structures compared to the flexible TEGDMA structure and undergo hydrogen bonding (Floyd and Dickens, 2006), which may affect crosslink density and therefore its mechanical and tribological properties.

5.4 Study of degradation modes of dental composite material in friction by point contact

The aim of this study is to evaluate degradation modes of dental composite material in friction by point contact. Three condensable posterior restorative dental materials, Synergy, Surefil and Alert, were selected to be tested against steel spheres. Geometrical contact was sphere/plane with a unidirectional motion and increasing normal load. The objective of this test is to produce different contact conditions which lead to different failure modes. For the same material pair the roughness of the steel sphere was altered in order to produce different relations between normal and tangential stresses, $0.2\ \mu\text{m} < \text{Ra} < 8.6\ \mu\text{m}$.

In terms of Ra values of the spheres they were of 0.21 μm, 0.66 μm and 8.66 μm, for the smooth, medium and rough sphere respectively. Fig. 5.50 shows the plotted values of normal and tangential loads versus sliding distance's for load-scanning tests, from left to right for; small, medium and high values of spheres roughness and for materials; a) Synergy, b) Surefil and c) Alert.

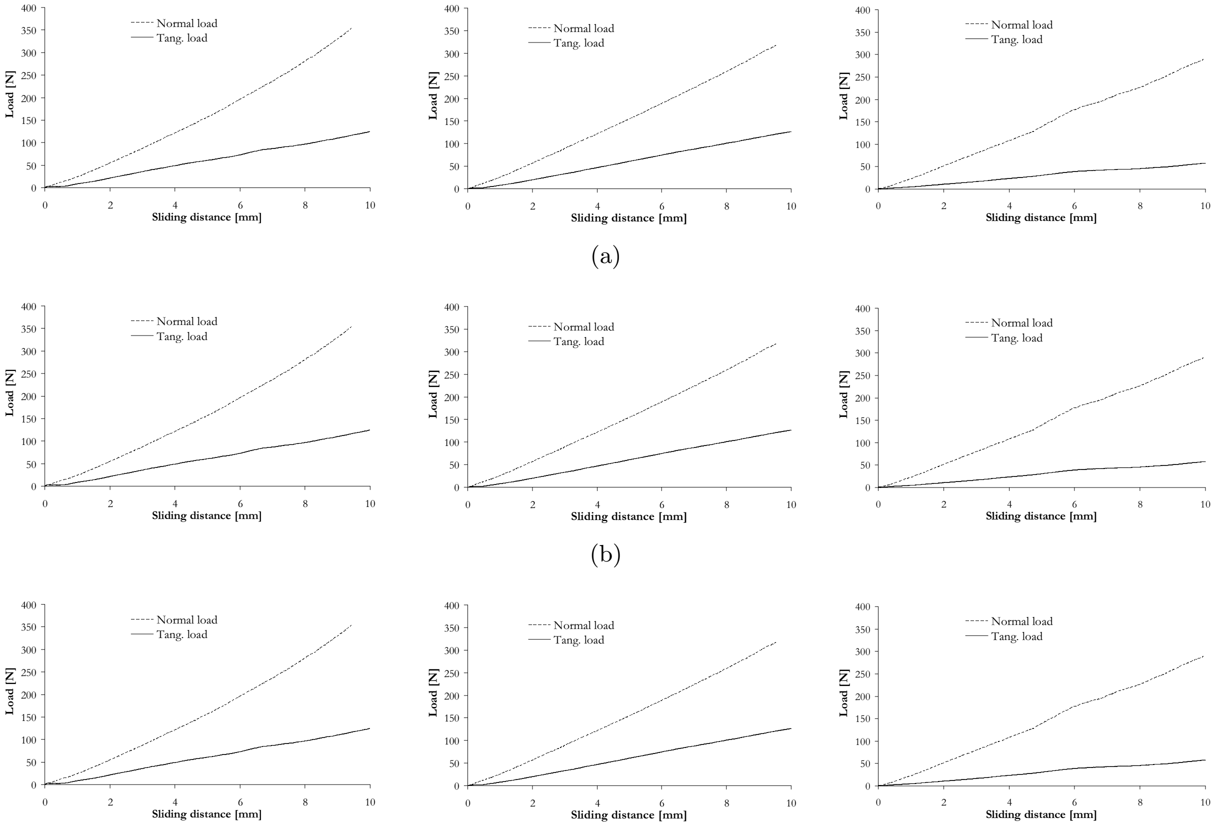
Considering Amontons-Coulomb friction model, which established a linear evolution between friction force and normal applied load, plotting tangential force against normal force should lead to a linear evolution, being the coefficient of friction the slope. Fig. 5.51 a), fig. 5.51 b) and fig. 5.51 c) plot linear regression curves for the coefficient of friction of the three studied degrees of roughness, using the entire normal load domain for Synergy, Surefil and Alert respectively, for each material tested and sphere roughness.

In fig. 5.51 b) and fig. 5.51 c) for Surefil and Alert, it is possible to observe a clear slope for the different values of sphere roughness: 0.2 μm, 0.66 μm and 8.66 μm, while Synergy shows a similar slope (COF) for medium and high sphere roughness.

The acquired data allows for the representation of normal and tangential loads along the displacement of the sphere. Relating these graphics with the wear scar produced by each sphere on the dental composite allows us to establish a relationship between the observed morphological features and the values of the loads that occurred at those specific places. The present case serves to identify the exact location of the fractures produced by increased loading for the three different spheres with distinct roughness.

Fig. 5.52 shows the load-scanning wear scars for all materials. Fig. 5.52 a), fig. 5.52 b) and fig. 5.52 c) represents the wear scars for Synergy against spheres of 0.2 μm, 0.7 μm and 9 μm roughness. Surefil Synergy and Alert present similar wear scars for the smaller values of 0.2 μm sphere roughness.

For the pairs Synergy, Surefil and Alert against smooth sphere, no cracks or fractures were observed. For this sphere roughness and considering the previous materials, average COF values were respectively 0.2, 0.06 and 0.04, and no cracks were observed in the composites scar. For the pairs Synergy, Surefil and Alert-medium and rough sphere, Surefil and Alert did not present



(a)

(b)

(c)

Fig. 5.50: Evolution of normal and tangential loads versus sliding distance in load scanning test for spheres with roughness values of 0.2 μm; 0.7 μm and 9.0 μm, represented from left to right for commercial restorative composites: a) Synergy, b) Surefil, and c) Alert.

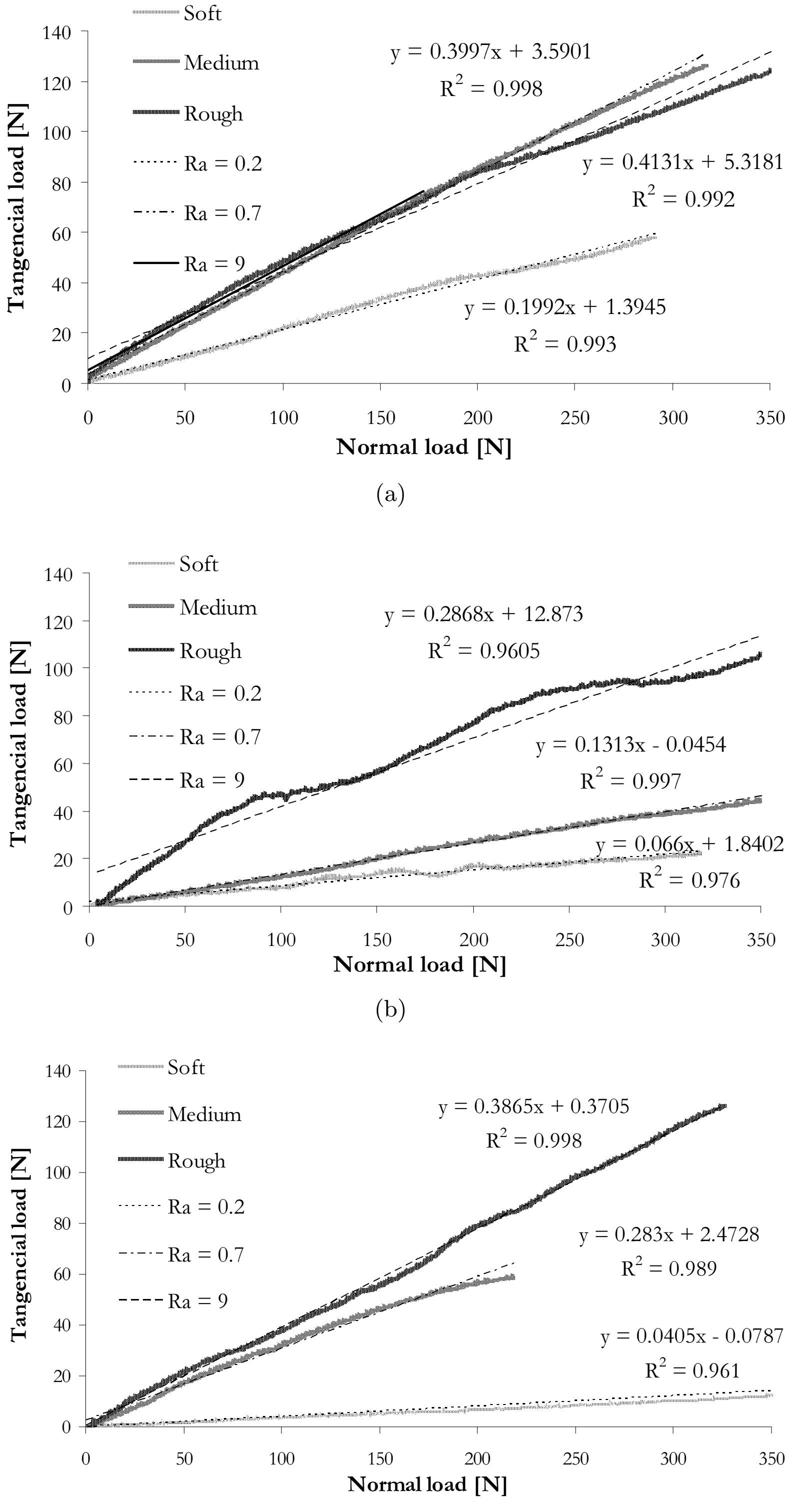
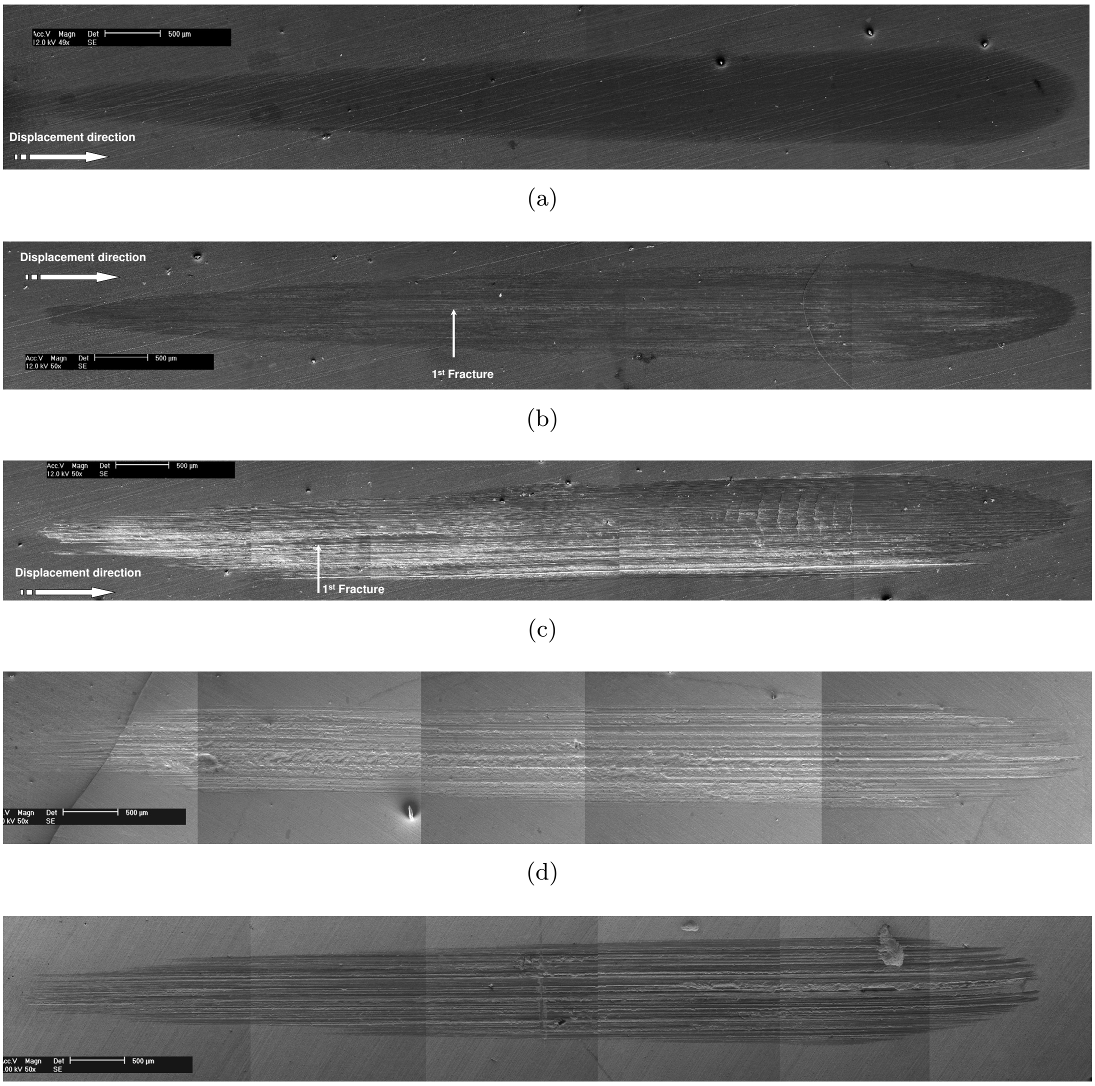


Fig. 5.51: Evolution of normal load plotted against tangential load for 0.2 μm, 0.7 μm and 9.0 μm sphere roughen for composite materials: a) Synergy, b) Surefil, and c) Alert.

any cracks while for Synergy the scar reveals a transition of failure mechanism. For small loads, the Synergy scar appears smoother without cracks; however, after reaching a specific contact condition, the surface reveals some cracks. The direction of the curvature of these cracks allows us to conclude that these fractures occurred behind the contact when the surface tensile stress was at maximum value. The first damage site is observed at approximately 3.8 mm of displacement from the beginning of the load cycle with corresponding loads of 124 N and 52 N for the normal and tangential directions, respectively. These values of load are taken directly from the data acquired by the load cell.

Regarding spheres with higher roughness (9 μm), again, only Synergy (fig. 5.52 c)) presented fractures in the wear scars, Surefil (fig. 5.52 d)) and Alert (fig. 5.52 e)), in spite of their visible plastic deformation due to spheres asperities do not reveal any superficial cracks, fig. 5.52 d) and fig. 5.52 e), respectively.



(a)

(b)

(c)

(d)

(e)

Fig. 5.52: SEM Wear scars images of load-scanning for Synergy against spheres with Ra values of: a) 0.2 μm, b) 0.7 μm, c) 9.0 μm; d) Surefil, and e) Alert against sphere with 9.0 μm roughness.

For Synergy against rough sphere in load-scanning test, the first damage site was observed at 2.65 mm from the beginning of the load cycle (fig. 5.52 c)). This location corresponds to the values of 75 N and 36 N respectively for normal and tangential directions.

Therefore, knowing the applied loads in the contact, and assuming that the geometry of the contact is constant (constant radii of the sphere) it is possible to determine the stress distribution, through the use of Hamilton's equations (Ramalho, 2004). Thus, the method applied to understand the cause of damage appearance was comparing the stress distribution for two situations: first situation, considering that there was no damage (pair composite-smooth sphere) and the second situation, considering that a fracture was verified (pair composite-medium rough sphere). The two studied conditions were compared for the specific value of normal load, at which the first crack appears, in the pair composite-medium rough sphere.

After observing graphics from fig. 5.50, and relating them to SEM images it was possible to determine normal and tangential force values and their correspondence to the location of the first superficial damages. Due to the fact that fracture appeared only for load-scanning tests involving Synergy composite material all of the following analysis is related to this composite material. For Synergy-medium roughness sphere values of 124 N and 52 N were obtained for the pair, normal and tangential loads, respectively, 75 N and 36 N, for the pair Synergy-rough sphere, also for normal and tangential loads, table 5.3.

Values used for this study correspond to contact condition where the first crack appears in the pair composite-sphere with medium roughness. Afterwards these distributions were compared to the stress distribution of composite-smooth sphere, for the same value of normal force. Composite behavior is considered elastic and calculations of the normal and tangential forces applied in the centre of contact were determined based on this premise. For the calculations were computed the normal and tangential forces applied in the centre of contact, the material behavior is considered as elastic. These only allow for a qualitative approach of the problem, once plasticity occurs in the contact, but is none the less a powerful method to evaluate the differences in stress distribution. Fig. 5.53 shows axis and load directions applied to the contact.

Table 5.3: Contact conditions corresponding to the location of the first superficial crack.

Sphere surface roughness	**Normal load** [N]	**Tangential load** [N]
Smooth	No cracks	No cracks
Medium	124	52
Rough	75	36

In terms of stress fig. 5.54 presents the distribution in the composite' depth for σ_{Tresca}, σ_{x} and σ_1 for the pair composite-medium roughness fig. 5.53 a), fig. 5.53 b) and fig. 5.53 c) and composite-smooth sphere; fig. 5.53 d), fig. 5.53 e) and fig. 5.53 f), respectively. These representations correspond to the plane $y = 0$. Both values and distribution of stresses are significantly different, namely for what concerns: distribution of Tresca stress (fig. 5.54 a) and 5.54 d)), contact against medium rough sphere presents higher values than the second pair. While composite-smooth sphere (fig. 5.54 d)) presents the higher values of stress, 200 MPa – 225 MPa, at 217 μm below the surface, *i.e.*, in the sub-surface, the pair composite-medium roughness sphere presents the higher values of 480 MPa – 520 MPa at the surface.

Normal stress distribution in OX axis, σ_{x}, values for composite-smooth sphere are also much smaller (-600 MPa to -500 MPa, fig. 5.54 e)) then for the other pair (-1,200 MPa to -1,000 MPa, fig. 5.54 b)).

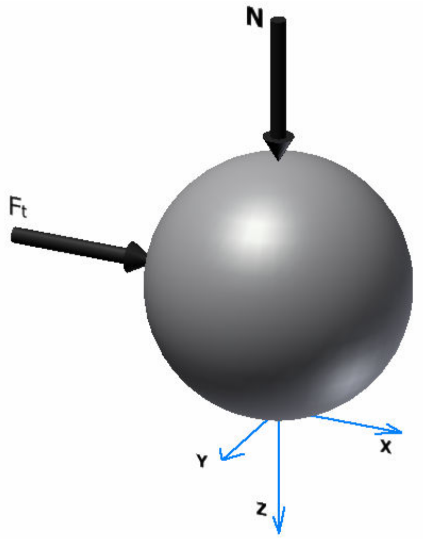


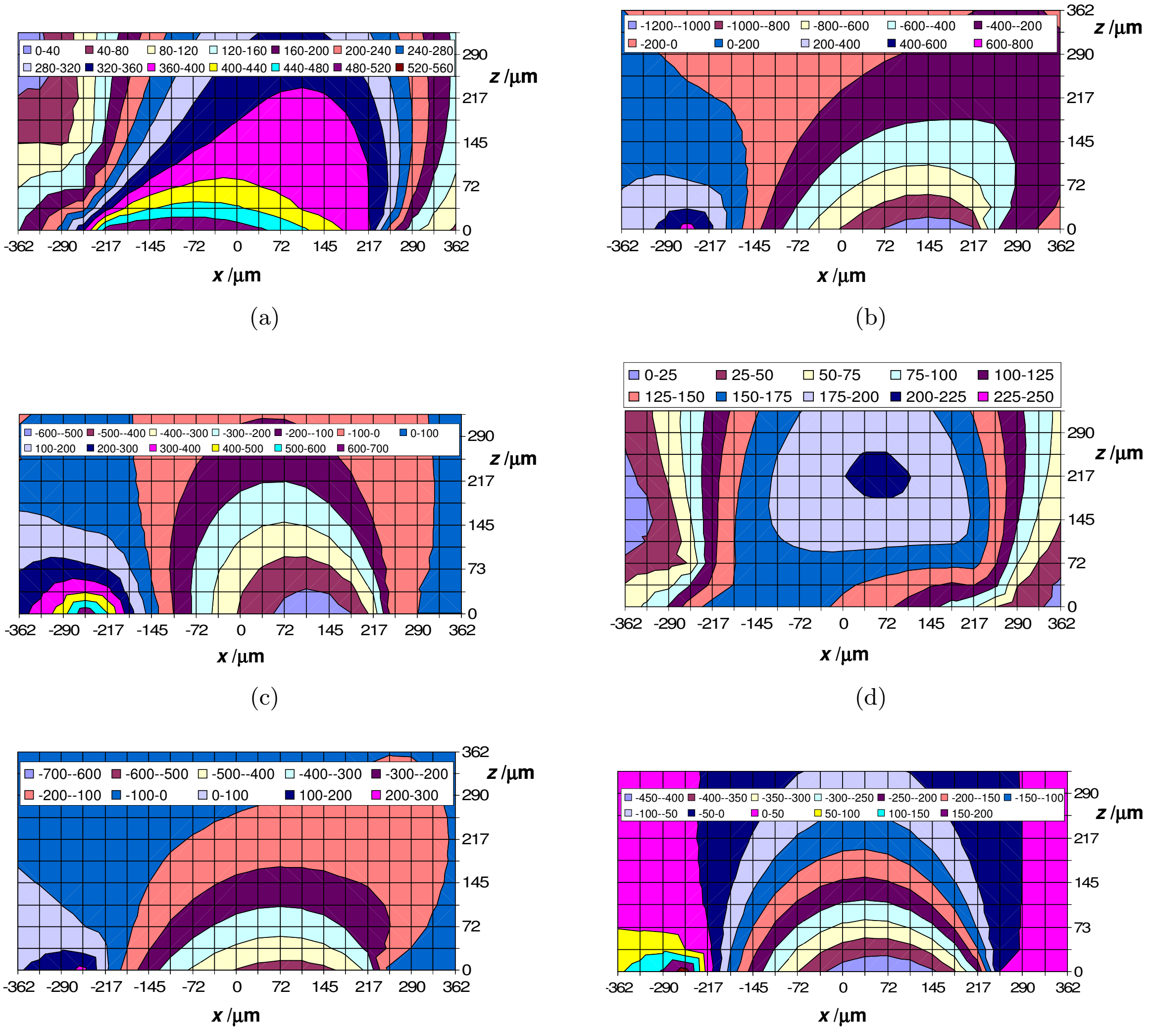
Fig. 5.53: Axis directions and applied loads to the contact.

Maximum normal stress distribution, σ_1, these two pairs have very distinct stress distributions. For composite against smooth sphere the maximum values range from 150 MPa to 200 MPa, while for the other pair, the range is from 600 MPa to 700 MPa, in a location behind the contact center. These traction stresses cause hemi-circular cracks present in fig. 5.52 b) and fig. 5.52 c), and presented in more detail in fig. 5.55 a) and 5.55 b) (Lawn *et al.*, 1993). Fig. 5.56 shows maximum normal stress distribution along composite's surface and for the x direction for low and medium roughness sphere, and again values for composite medium rough sphere pair are almost 4 times those obtained for composite-smooth sphere at the surface of the composite behind the contact.

As observed in fig.5.54 a) for composite-medium rough sphere pair values of Tresca stress distribution are very high at the surface, therefore, surface plastic deformation occurs. The value of σ_1 is also high, which allows for the arise of cracks in only one passage and therefore high values of wear; on the other hand if σ_1 has a small value, cracks do not arise in one single passage. Due to this fact we can conclude that, if friction is very high there is a change in the stress distribution leading to high values of σ_1 behind the contact, therefore propagating cracks in mode I, associated to high values of wear. If friction has a small value, as is the case with the pair composite-smooth sphere, then σ_1 is low, fig. 5.55 e), and its value is not enough to induce instantaneous cracks. However, a slow process of crack initiation by fatigue should be initiated underneath or in front of contact surface. This analysis enables the deduction of the most probable location of crack occurrence and therefore a high or small quantity of wear that may be associated to the process.

I. Partial conclusions: Load-scanning

In case under study, transition in wear behavior is associated to a marked change of coefficient of friction. This fact may explain the transition as a function of local failure induced by coefficient of friction. In cases of low friction values, tangential force between spherical surface and composite surface is very low compared to the normal load. Thus in the contact stress distribution, the hertzian component is predominant, inducing occurrence of maximum tangential stress underneath the surface. This stress distribution induces failure beneath the surface by a



(a)

(b)

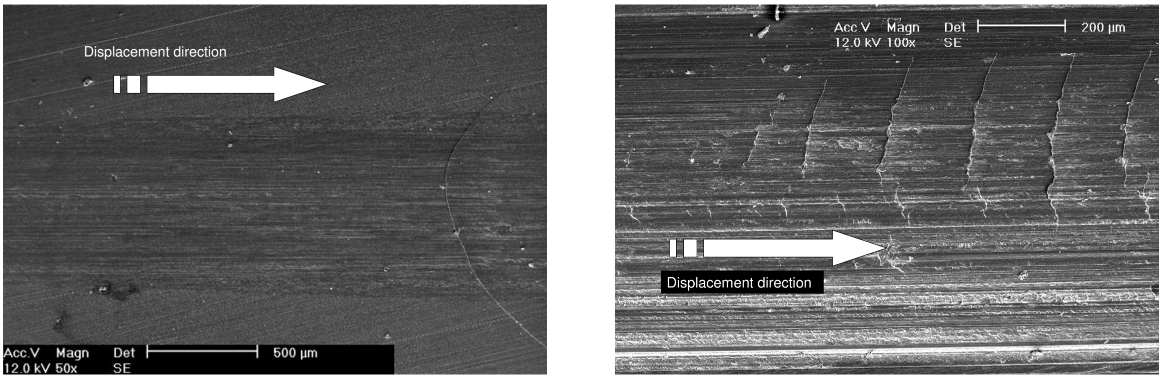
(c)

(d)

(e)

(f)

Fig. 5.54: Stress distribution along the composite's depth, σ_{Tresca}, σ_{x} and σ_1, for; composite-medium roughness a), b) and c) and composite-smooth sphere; d), e) and f) pairs respectively.



(a) (b)

Fig. 5.55: Detail of fracture cracks after the sphere passage due to high values of traction stress behind the contact, for the pair: a) composite-medium rough sphere and b) composite-rough sphere.

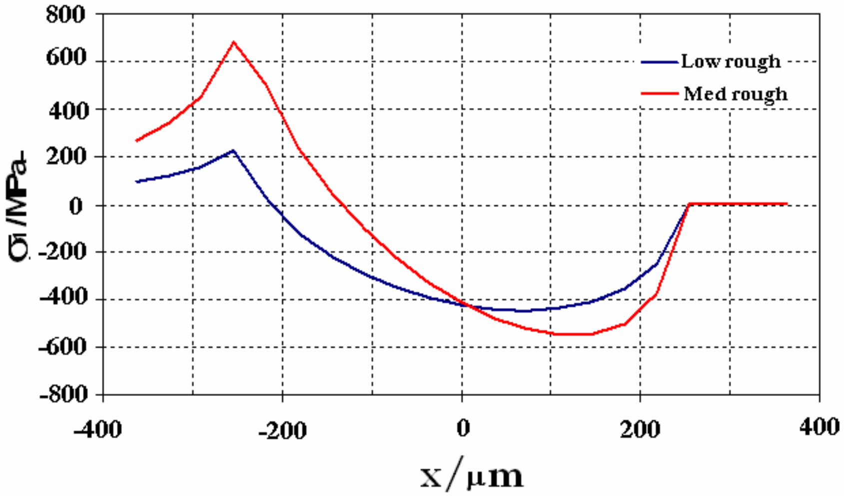


Fig. 5.56: Stress distribution of maximum normal at the surface along the composites surface, for low and medium rough sphere.

fatigue process that starts with the initiation of small cracks at the sub-surface with consequent propagation up to the surface.

Nevertheless, wear occurs via the breaking of atomic bonds and the removal of material, which is related to, among other factors, the strength and toughness of the material. Previous studies have observed that the resistance to material removal is dependent on, among other factors, the fracture toughness of the material (Xu et al., 2003b).

Regarding Synergy tests, multiple cracks inside the composite wear scars were consistent with the known brittleness of the composite. A linear correlation between wear and flexural strength was reported by Peutzfeldt and Asmussen (1992). A similar relationship was found for whisker composites (Xu *et al.*, 2004), between wear and flexural strength from an earlier study (Xu *et al.*, 2000). Wear involves micro-fracture; hence, it is also expected to depend on fracture toughness. However, besides correlating fracture toughness with surface chipping and bulk fracture, little evidence was available on the relationship between fracture toughness and wear of dental composites (Tyas, 1990).

Neither Alert, nor Surefil presented any cracks and/or fractures for any of the sphere roughness values.

Nevertheless when contact conditions are such that friction between spherical surface and composite is high enough, stress distribution varies significantly according to contact models with friction, as is the Hamilton's model (Hamilton, 1983).

With load scanning test it was possible to observe the change in the morphology of composite's surface (Synergy). The appearance of cracks in a single passage test with variation of coefficient of friction and with the analysis of stress distribution with the help of Hamilton's equation indicates high values of plastic deformation in the front of the contact and cracks behind the contact which is due to the high values of traction at the surface, leading to semi-circular cracks. The comparison of stress distribution for the pair of material without cracks allows us to understand that the maximum values of stress occur, that these values are much higher and their location is at the contact surface instead of the sub-surface leading to a slower process with propagation of cracks from the sub-surface to the surface.

Both of these reasons justify that for high coefficient of friction, failure occurs mainly in surface either by plastic deformation or by fracture, and thus lead to the variation of the wear volume in reciprocating wear tests.

5.5 Wear methodology application: pH and aging influence on tribological behaviour

After establishing all the methodology and experimental procedures, verification was necessary. Teeth, in the oral cavity, are subjected to very specific service conditions; wide-ranging temperatures, contact loading, loading rates, sliding conditions and pH variation. Several studies have established that an exposure of resin composites in aqueous environments lowers their mechanical properties. Due to changes in the structure of these materials, softening of the resin matrix and/or bond failure in the outer layer of the filler and in the filler-matrix interface region reduces the mechanical and tribological performance. During the day the mouth presents different values of pH, and thus it is important to determine the effect of pH on the composites tribological behavior. The objective was to determine the nature of dependence between tribological behavior of commercial composites and the influence of pH values and aging time. This evaluation was done for seven commercial composites and each was aged during periods of 3, 6 and 22 months at a stabilized temperature of 37°C (± 1°C) in baths of three pH values – 3, 7 and 9. The commercial composites studied were; Filtek P60, Prodigy Condensable, Surefil, Synergy Compact, Quixfil, CeramX and Alert.

For the tribological evaluation, reciprocating contact against glass spheres was done, as described previously. At the conclusion of the tests the wear was assessed on the composite and also on the counterface. An energetic approach was also used to relate the wear/energy of the pair composite-glass. Morphological analyses of contacting surfaces were also done.

Bearing in mind the large number of variables; seven resin composite materials, three pH buffer solutions and four aging periods, the most succinct way to show effects of aging time and pH influence should be to represent wear variation relatively to wear reference values, for composite and glass sphere antagonist. Therefore, each specimen tested for a specific pH and aging period is targeted in percentage relatively to its reference value, which corresponded to same specimen material tested right after being processed and without influence of aging or pH solutions baths. All reference specimens were processed with material of the same commercial batch as aged specimens. 0 month aging period represents specimens wear results reference, which were not stored in any buffer solution for any period of time.

Thus, for each composite a graph with three series will be presented, corresponding to buffer solutions of pH 3, 7 and 9, and where the percentage of increase or decrease of material removed by wear of each specimen relatively to their reference material is represented against the aging time in months.

In order to fully understand the tribological behavior of the glass-composite material pairs, a table summarizes the obtained results for all tested conditions; including the reference tests wear values. Besides the average coefficient of friction and wear values of both composite material and antagonist, each table also includes the percentage of variation in wear volume for each studied condition (aging time and pH solution).

In general, all studied materials suffered the greatest variation for the longest aging period – 22 months. Exception was Prodigy aged in pH 3 buffer solutions. Specimens aged 6 months presented higher wear variation and a 55.8% decrease, and the ones aged during 22 months a 48% decrease. Surefil showed similar behavior, also for pH 3: the 22 months old specimens presented a decrease in wear volume of 27.5% and the 6 months aging specimen a decrease of 34% relatively to the reference material.

Generally, the buffer solution which least affects the tribological behavior of composites is pH 7 buffer solution. However, Quixfil, Prodigy and Surefil composite materials were less affected when aged in pH 3 buffer solutions.

Observing graphs from fig. 5.57 to 5.63, and tables 5.4 to 5.10 it is possible to notice that the 3 month period is, generally, the one with the smaller variation, with the exceptions of Synergy and Quixfil, which present the lowest variations for the 6 month aging period (tables 5.9 and 5.10).

In general, the evolution of antagonist wear is coherent with the variation of the composite wear. However, variations in glass sphere wear volumes are, commonly, much higher than the ones observed for composites (table 5.4 to table 5.10).

After analyzing the obtained results it was possible to notice that, at the end of the first aging period, three months, the majority of composites presented a wear amount which did not vary much relatively to reference for any of the studied buffer solutions.

In terms of volume material removed by wear the most affected material was Quixfil, with a big decrease in wear volume for pH 3 (62.5%) and an increase of 165% for pH 9. For Surefil, Ceramx and Filtek variations in volume material removed by wear was negligible. Prodigy aged in buffer solution pH 9, increased wear volume about 44.5% while Synergy aged in pH buffer solution 7 at 3 month period decreased 4%.

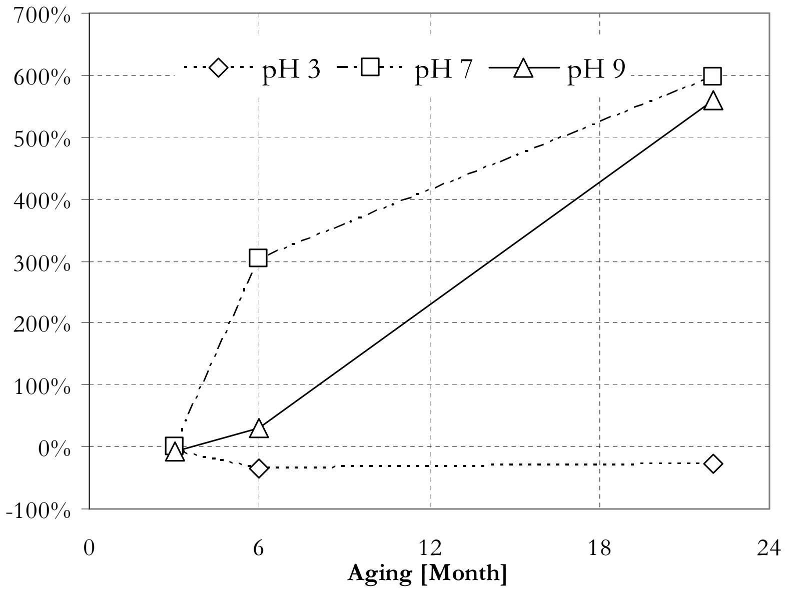


Fig. 5.57: Variation, in %, of Surefil wear volume relatively to reference in pH buffer solutions of 3, 7 and 9 for 3, 6 and 22 months aging time.

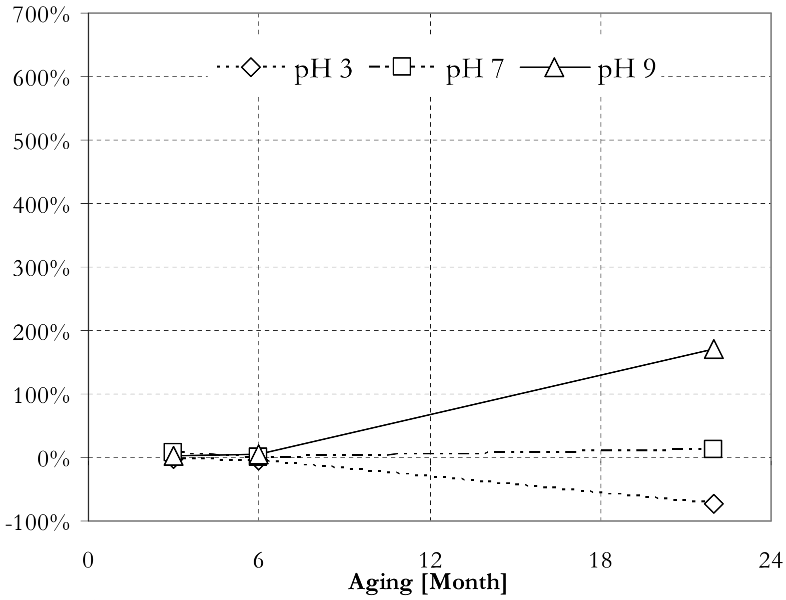


Fig. 5.58: Variation, in %, of Ceramx wear volume relatively to reference in pH buffer solutions of 3, 7 and 9 for 3, 6 and 22 months aging time.

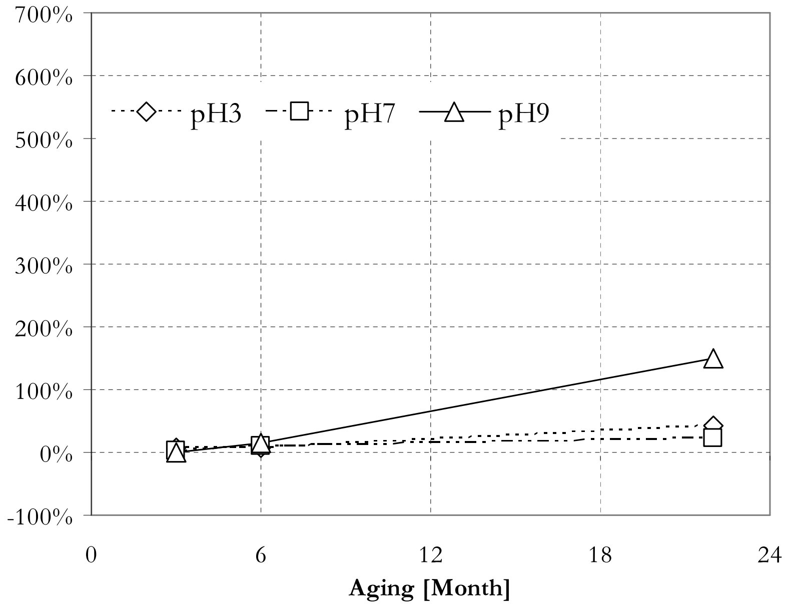


Fig. 5.59: Variation, in %, of Filtek wear volume relatively to reference in pH buffer solutions of 3, 7 and 9 for 3, 6 and 22 months aging time.

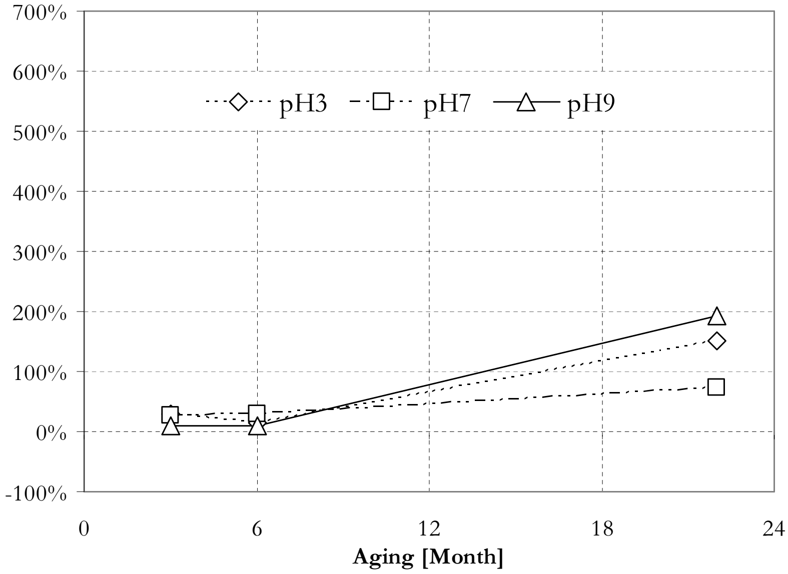


Fig. 5.60: Variation, in %, of Alert wear volume relatively to reference in pH buffer solutions of 3, 7 and 9 for 3, 6 and 22 months aging time.

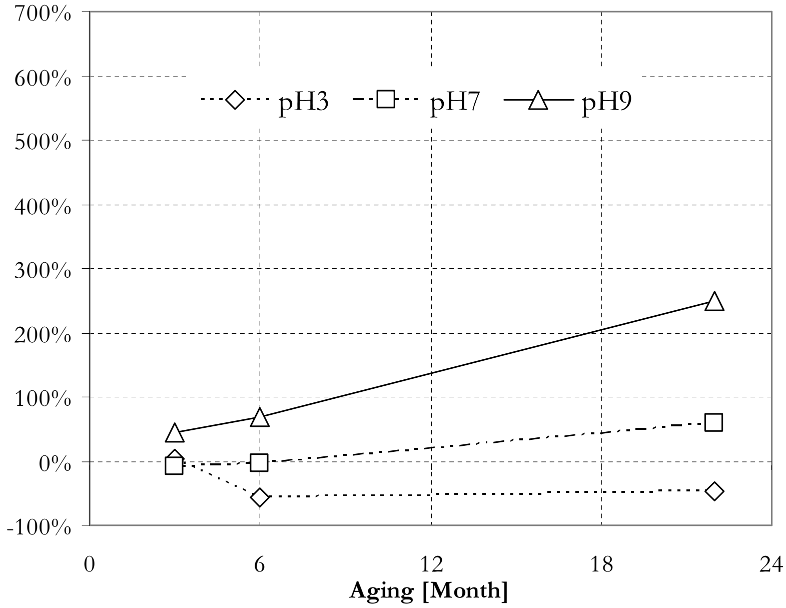


Fig. 5.61: Variation, in %, of Prodigy wear volume relatively to reference in pH buffer solutions of 3, 7 and 9 for 3, 6 and 22 months aging time.

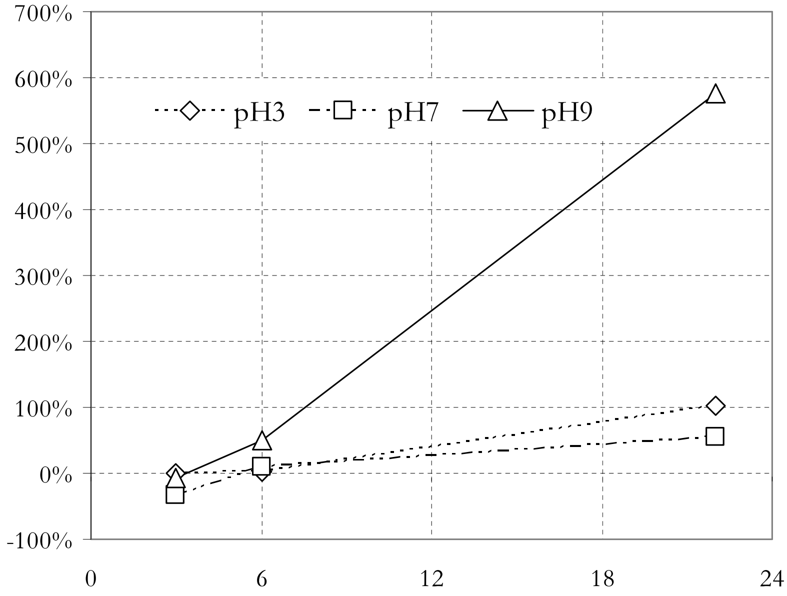


Fig. 5.62: Variation, in %, of Synergy wear volume relatively to reference in pH buffer solutions of 3, 7 and 9 for 3, 6 and 22 months aging time.

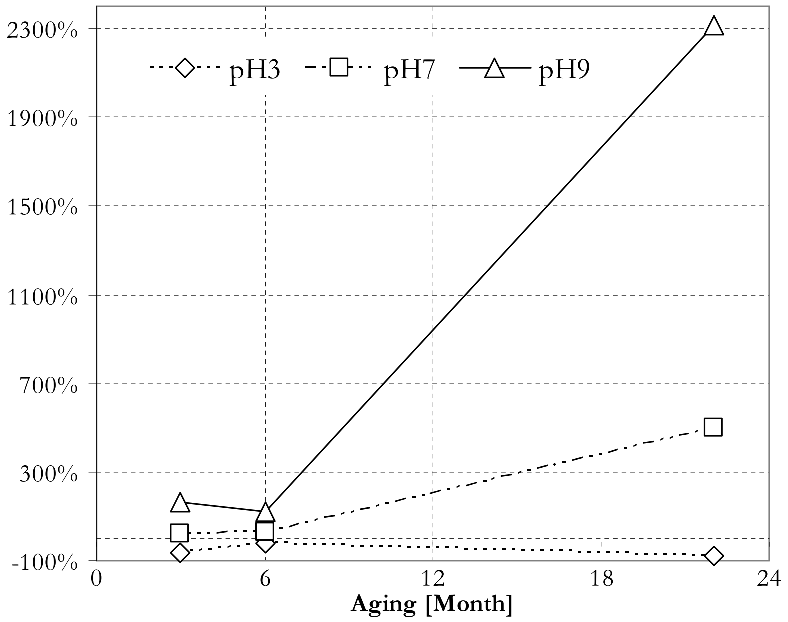


Fig. 5.63: Variation, in %, of Quixfil wear volume relatively to reference in pH buffer solutions of 3, 7 and 9 for 3, 6 and 22 months aging time.

Table 5.4: Vc and Va represent wear volume of Surefil composite and its antagonist respectively in [mm^3] for reference period and conditions.

0 months		**Aging** [Months]					
Vc= 0.011	COF=0.29	**3**		**6**		**22**	
Va= 0.0044		**Wear vol.**	**COF**	**Wear vol.**	**COF**	**Wear vol.**	**COF**
pH 3	Composite Antagonist	−6.3% −87.4%	0.24	−34.7% −36.7%	0.38	−27.5% −56.9%	0.20
pH 7	Composite Antagonist	+0.6% −64.3%	0.28	+304.7% +956.5%	0.56	+596.3% +1278.1%	0.64
pH 9	Composite Antagonist	−8.0% −80.9%	0.29	+31.0% −79.1%	0.28	+560.2% +1080.9%	0.62

Table 5.5: Vc and Va represent wear volume of CeramX composite and its antagonist respectively in [mm^3] for reference period and conditions.

0 months		**Aging** [Months]					
Vc= 0.038	COF=0.33	**3**		**6**		**22**	
Va= 0.070		**Wear vol.**	**COF**	**Wear vol.**	**COF**	**Wear vol.**	**COF**
pH 3	Composite Antagonist	−1.8% −19.9%	0.58	−4.6% −1.1%	0.67	−72.6% −97.3%	0.22
pH 7	Composite Antagonist	+6.4% +4.5%	0.69	+0.7% −18.9%	0.67	+11.3% +14.9%	0.75
pH 9	Composite Antagonist	+1.8% +1.9%	0.70	+5.3% −20.2%	0.62	+171.7% +28.8%	0.74

For 6 month aging period results were very similar to the ones registered for 3 month: instead of three materials less affected only two seemed to have fewer differences relatively to the reference, CeramX and Filtek.

Table 5.6: Vc and Va represent wear volume of Alert composite and its antagonist respectively in [mm^3] for reference period and conditions.

0 months		**Aging** [Months]					
Vc= 0.031	COF=0.51	**3**		**6**		**22**	
Va= 0.064		**Wear vol.**	**COF**	**Wear vol.**	**COF**	**Wear vol.**	**COF**
pH 3	Composite Antagonist	+29.2% +25.7%	0.70	+13.9% −27.4%	0.59	+151.2% +42.8%	0.69
pH 7	Composite Antagonist	+27.5% +6.8%	0.60	+29.4% −17.0%	0.55	+74.2% +106.2%	0.79
pH 9	Composite Antagonist	+9.8% +0.4%	0.62	+10.1% −31.5%	0.53	+192.0% +78.4%	0.77

Observing aging results after 22 months, differences between references and aged materials are the widest of all three aging periods considered. Contrary to what happened in the other periods, all materials were significantly affected by buffer solutions. As before, the relative positions of the antagonist body in what concerns material removed by wear was maintained.

For acid buffer solution, composite materials can be generally divided in two groups considering how aging time affects wear behavior. Surefil, Ceramx, Prodigy and Quixfil tend to decrease their wear with an increase of the aging time while Filtek, Alert and Synergy tend to increase wear with increasing aging time. Quixfil had a peculiar behavior for 6 month aging period as it revealed an especially high value of wear compared with the value for 3 and 22 months.

Twenty two months is the aging period with greatest influence on wear. Through the comparison with the reference materials it was possible to register variations of -28%, -73%, 151%, 43%, 102%, -81% and -48% respectively for Surefil, Ceramx, Alert, Filtek, Synergy, Quixfil and

Table 5.7: Vc and Va represent wear volume of Filtek P60 composite and its antagonist respectively in [mm^3] for reference period and conditions.

0 months		**Aging** [Months]					
Vc= 0.057	COF=0.76	**3**		**6**		**22**	
Va= 0.150		**Wear vol.**	**COF**	**Wear vol.**	**COF**	**Wear vol.**	**COF**
pH 3	Composite Antagonist	+7.5% −5.0%	0.77	+8.3% +2.5%	0.75	+43.3% −10.9%	0.78
pH 7	Composite Antagonist	+1.4% +20.0%	0.85	+10.5% −17.1%	0.72	+23.6% −4.1%	0.74
pH 9	Composite Antagonist	+1.2% −16.0%	0.76	+16.0% −3.4%	0.75	+150.9% +10.9%	0.82

Table 5.8: Vc and Va represent wear volume of Synergy Compact composite and its antagonist respectively in [mm^3] for reference period and conditions.

0 months		**Aging** [Months]					
Vc= 0.012	COF=0.34	**3**		**6**		**22**	
Va= 0.0085		**Wear vol.**	**COF**	**Wear vol.**	**COF**	**Wear vol.**	**COF**
pH 3	Composite Antagonist	+1.1% +87.9%	0.44	+1.8% +1.3%	0.41	+102.3% −27.8%	0.41
pH 7	Composite Antagonist	−32.2% −33.2%	0.40	+10.3% +43.5%	0.40	+53.6% −48.0%	0.49
pH 9	Composite Antagonist	−7.1% +8.6%	0.39	+50.5% +123.2%	0.42	+575.7% +634.5%	0.82

Table 5.9: Vc and Va represent wear volume of Quixfil composite and its antagonist respectively in [mm^3] for reference period and conditions.

0 months		**Aging** [Months]					
Vc= 0.092	COF=0.88	**3**		**6**		**22**	
Va= 0.102		**Wear vol.**	**COF**	**Wear vol.**	**COF**	**Wear vol.**	**COF**
pH 3	Composite Antagonist	−62.5% −80.2%	0.46	−21.4% +2.3%	0.84	−81.3% −95.7%	0.37
pH 7	Composite Antagonist	+22.2% +3.2%	0.89	+26.6% +21.3%	0.92	+496.5% +129.2%	0.94
pH 9	Composite Antagonist	+165.0% +17.7%	0.92	+120.6% +6.9%	0.80	+2317.1% +597.6%	1.02

Table 5.10: Vc and Va represent wear volume of Prodigy composite and its antagonist respectively in [mm^3] for reference period and conditions.

0 months		**Aging** [Months]					
Vc= 0.036	COF=0.53	**3**		**6**		**22**	
Va= 0.046		**Wear vol.**	**COF**	**Wear vol.**	**COF**	**Wear vol.**	**COF**
pH 3	Composite Antagonist	+4.0% +15.3%	0.57	−55.8% −38.5%	0.44	−48.0% −24.8%	0.57
pH 7	Composite Antagonist	−8.3% −3.5%	0.61	−3.6% −23.4%	0.48	+59.2% +29.1%	0.63
pH 9	Composite Antagonist	+44.5% +49.5%	0.51	+69.3% −15.2%	0.67	+250.2% +87.5%	0.64

Prodigy.

Analyzing graphs of fig. 5.57 to fig.5.63 one can conclude: for pH 7 buffer solution, all composites studied had a decrease in wear resistance with time. Ceramx is less sensible to aging period, especially regarding neutral buffer solution. Prodigy, Synergy and QuixFil present more wear resistance at 3 months aging than the reference materials.

Wear performance is more affected at 22 months aging. When comparing with the reference materials, composites have an increase in volume material removed by wear of 596%, 11%, 74%, 24%, 54%, 496% and 59% for Surefil, Ceramx, Alert, Filtek, Synergy, Quixfil and Prodigy, respectively.

Observing wear performance of composites one can conclude, that for pH 9 buffer solution, all materials tend to decrease their wear resistance with increasing aging time. Comparing with other buffer solutions analyzed, one can conclude that increase in wear is more important when 22 months results are considered, in terms of wear performance, than that results obtained with 3 and 6 months aging period. After 22 months aging increases of 560%, 172%, 192%, 151%, 576%, 2317% and 250% were registered for Surefil, Ceramx, Alert, Filtek, Synergy, Quixfil and Prodigy, respectively.

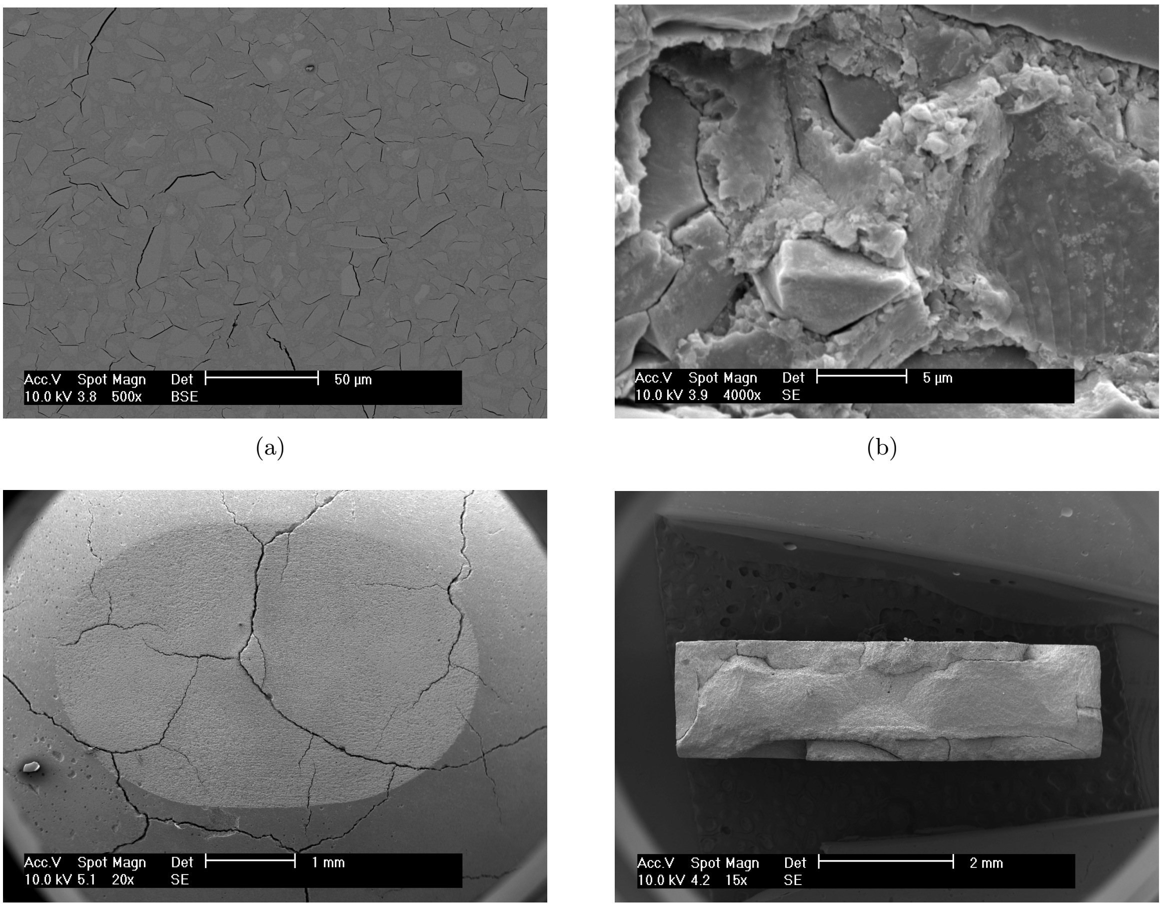
Analyzing COF average values, it is possible to see that materials that increase their wear resistance present lower values of wear, corresponding to smaller COF values than the ones of reference materials.

Wear values of composite and antagonist generally increase with larger aging period, especially for the pH 9 buffer solutions. After removing each specimen from the respective baths, changes in specimen's appearance could be observed. Considering surface features, specimens aged in pH 3 solutions were more affected than the ones aged in pH 7 and pH 9 bath solutions. Quixfil was largely affected by aging period in the basic solution, its surface presented many cracks, and its cross-section presented a very large part of its thickness affected by basic solution. This pH and time condition was the one that registered simultaneously not only the highest increase but also highest absolute value of material removed by wear, compared with its reference.

Morphology of composite wear scars was observed by SEM after the wear tests. To improve microscope observation, the tested specimens were sputter-coated with gold.

From the batches of materials tested, Quixfil was the most affected in terms of morphology in every pH condition. Quixfil presented fractures for all tested pH conditions; fig. 5.64 a), pH 3.

The same composite also displayed poor bonding at the interfacial region between matrix and reinforcement particles. Besides that, it was also visible that some particles, in the wear scar, broke and were removed from the matrix; fig. 5.64 b), pH 7. For pH 9 along with fractures in the interface matrix/particles it was possible to observe many porous cracks in the specimen's surfaces, fig. 5.64 c). The same picture allows for the understanding of to what extent specimens were affected by aging time, with specimens presenting large cracks along specimen surface. Fig. 5.64 d) shows specimen cross-section and reveals the extent of aging effect on its thickness, which is justified by the especially poor composite wear resistance when aged in this pH buffer solution.



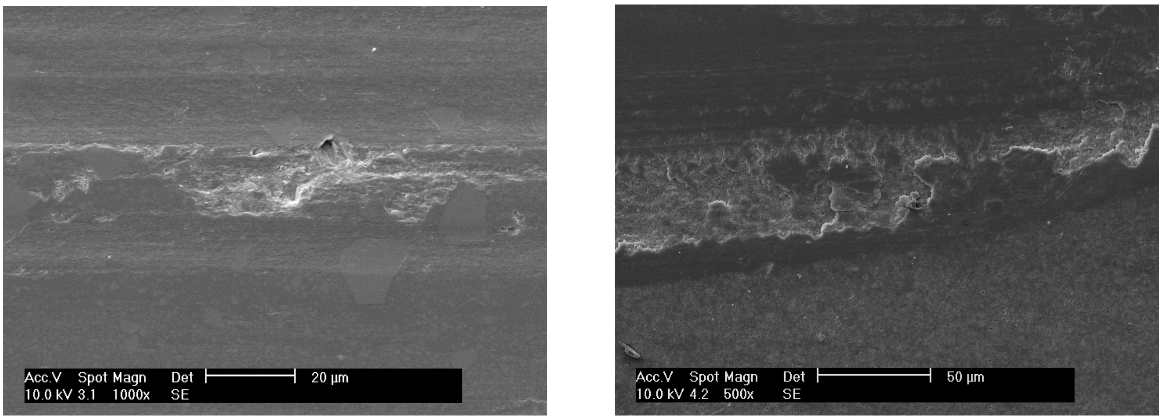
(a) (b)

(c) (d)

Fig. 5.64: Quixfil specimens for buffer solutions; a) pH 3, wear scar; b) pH 7; c) pH 9, presenting the wear mark, and d) pH 9, specimen cross-section.

In terms of the wear mark morphology, Synergy and Surefil present very similar characteristics: they both have uniform tribo-layer. These layers are constituted by a mixture of matrix and particles and a consistent and homogeneous wear of matrix and particles. Few particles broke or were removed from the matrix (fig. 5.65). Similar wear characterization was observed by Jorgensen and Asmussen (1978).

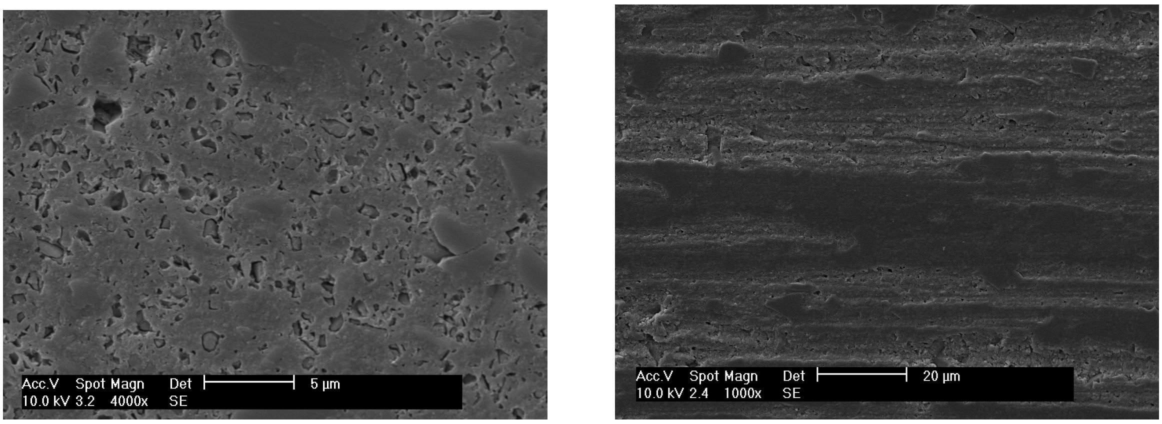
Alert was also affected by aging, revealing gaps in the interface of particles and fibers with the matrix, fig. 5.66 a). Wear mark of this composite also presented a tribo-layer, but in a smaller portion of the contact. This layer was "broken" by the detached particles and fibers



(a) (b)

Fig. 5.65: Typical wear scars with homogeneous removal of matrix and particles for; a) Surefil, pH 9, and b) Synergy, specimen aged in pH 3 buffer solution.

from the matrix which remained in the contact ploughing the specimen's surface (fig. 5.66 b)); this behavior is similar for pH solutions of 3 and 9.



(a) (b)

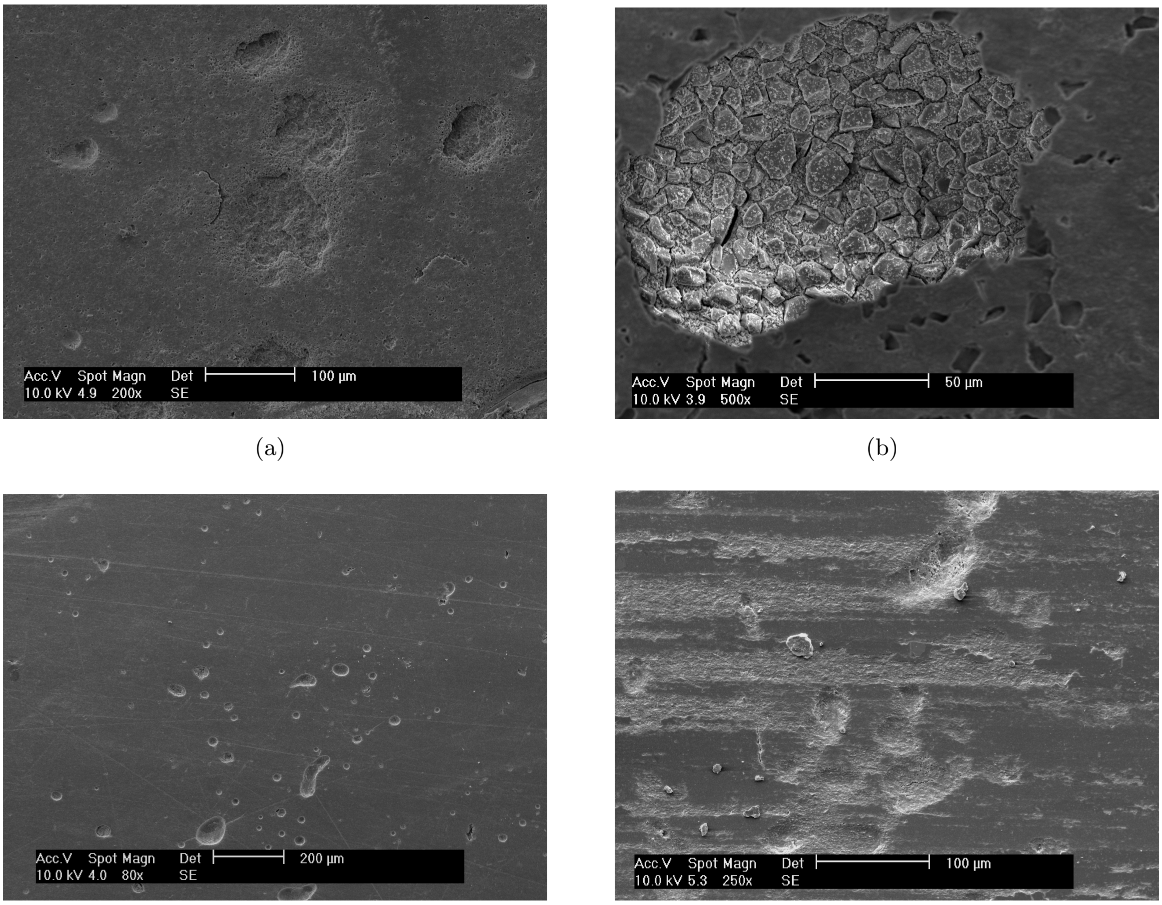
Fig. 5.66: Alert specimens; a) polished surface for pH 3 aging; b) wear mark with tribo-layer aged in a pH 9 buffer solution.

Prodigy, Ceramx, Quixfil and Synergy all presented surface damage due to aging. Damage started with detachment of large particles and consequent spreading to a larger circular area, similar to porous, and is noticeable through outstanding particles without matrix involving them, fig. 5.67.

I. Partial conclusions

Condensable resin posterior composites were investigated in order to understand effects of aging time and pH influence on their tribological wear behavior.

Reciprocating tests were done against soft glass spheres in distilled water environment, allowing the following conclusions:



(a) (b)

(c) (d)

Fig. 5.67: Surface defects due to aging for; a) Ceramx, pH 3, b) Quixfil, pH 9; c) Synergy, pH 3, and d) Prodigy, pH 3.

- All composites presented the widest variations, increase or decrease, in wear volume for the longest aging period: 22 months;
- For buffer solution with pH 3, Surefil, Ceramx, Prodigy and Quixfil registered an increase in wear resistance, while Filtek showed a moderated decrease. Alert and Synergy showed considerable increase (more than a 100% variation relatively to their reference) in wear volumes, especially for 22 months;
- pH 7 buffer solution had the least effect on materials in question. Materials aged in neutral solutions presented smaller variations relatively to reference materials, except for Surefil, which presented the worst wear resistance for this buffer solution; Quixfil presented the smallest variation for pH 3;
- Specimens aged in alkaline solution pH 9, combined with long aging time, were more affected than in other solutions demonstrating higher variations in wear volumes; for this buffer solution variations from reference were not significant for 3 and 6 months aging periods;
- Materials most affected by pH and aging time were, *i.e.* with greater variation in wear: Quixfil (variations in wear volumes ranged from -100% to 2300%), Synergy (from 0% to 600%) and Surefil (-100% to 600%); on the other hand Ceramx (-100% to 200%), Filtek (23% to 200%), Alert (50% to 200%) and Prodigy (-50% to 250%) were listed with smaller range variations;
- Evolution of antagonist wear was coherent with the variation of the composites wear and their relative position was maintained, although variations in glass sphere wear volumes were, in general, much higher than the ones observed for composites;
- Increase in wear relatively to reference followed, in general, a COF increase;
- Morphologically, aging, independent of the value of pH tends to degrade the interface between matrix and reinforcement particles.

Chapter 6

Conclusions and future work

6.1 Analysis structure

In order to summarize the results presented in this work it is necessary to recognize the main areas of study here present. The initial scope of the work was the mechanical and tribological behavior of commercial direct restorative filling materials. Due to the evolution of the work process it became increasingly clear that this was a multi-variable system with innumerous variables. Hence, and due to the fact that commercial composites were closed systems a new route had to be traveled. A systematic approach using composites produced in the laboratory was also considered to assess and determine the influence of the composite's intrinsic factors.

Fig. 6.1 presents a chart which illustrates the systematic approach guidance in the study regarding the evaluation of the mechanical and tribological behavior of commercial composites, studying mainly the influence of external factors on its tribological behavior and the determination of mechanical properties.

The composites produced in laboratory allowed a vaster evaluation and understanding of their behavior, tribological and mechanical wise, and the influence of intrinsic and internal parameters on their global performance.

Due to the significative number of parameters and variables assessed, resume charts were prepared in order to systematize the more relevant information. As previously stated the composite categories of tested materials were commercial composites and produced composites. In each of these the study focused on the tribological and mechanical properties.

Table 6.1 and fig. 6.2 to fig. 6.4 summarize the tribological characteristics and mechanical properties for commercial composites. Due to the number of composites and to the variety of studies, only a few composites were presented in all studies. Synergy was selected as the commercial composite which served as reference for the presentation of the wear and mechanical performance, not only because this composite was present in all studies but because it is characterized by average values in almost all properties. Therefore, charts only display the highest and lowest values of the property and/factor in study, corresponding to the best and worst commercial composites, represented as a percentage of Synergy's behavior.

Table 6.1 presents the values of Synergy for mechanical and tribological tests which were used as reference values in charts from fig. 6.2 to fig. 6.4. For a clear and faster comprehension of the graphs some symbols are added to the side. When a parameter in scrutiny registers an increase in the property in analysis an arrow of increase ($\Uparrow$) is placed beside. On the other hand, when a decrease of the property is observed a decreasing arrow ($\Downarrow$) is used. When no variation

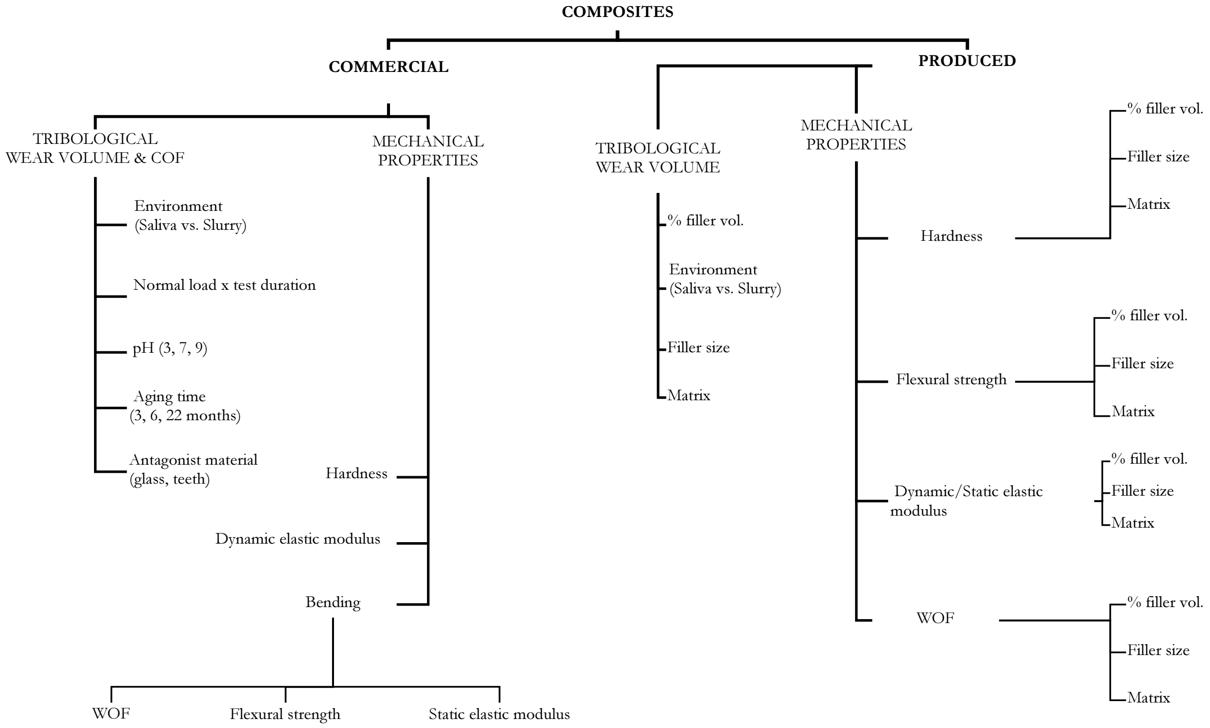


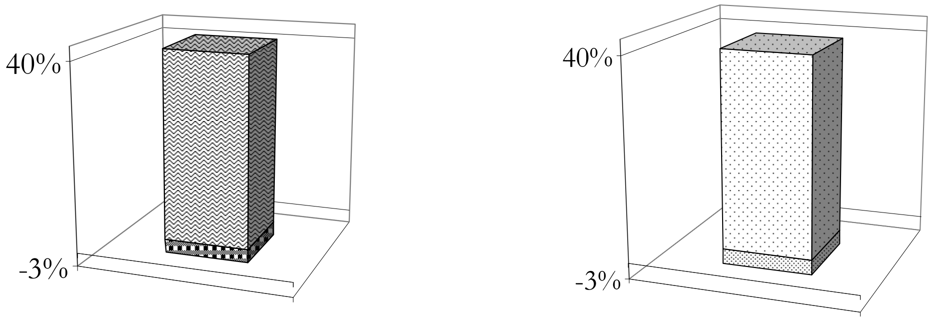
Fig. 6.1: Chart with schematic approach guidance in the study regarding the evaluation of the mechanical and tribological behavior of commercial and produced composites.

is reported the symbol (⇔) indicates no variation. But if the property has an inflection with a maximum (∩) or a minimum (∪) the respective symbols are associated with the variation, and the maximum and/or minimum values are added. Finally, when a parameter registers an increase relatively to the reference material after stabilization in the property values, the symbols associated are: ⇑ ⇔.

Table 6.1: Values of Synergy assessed properties for mechanical and tribological tests, (STD).

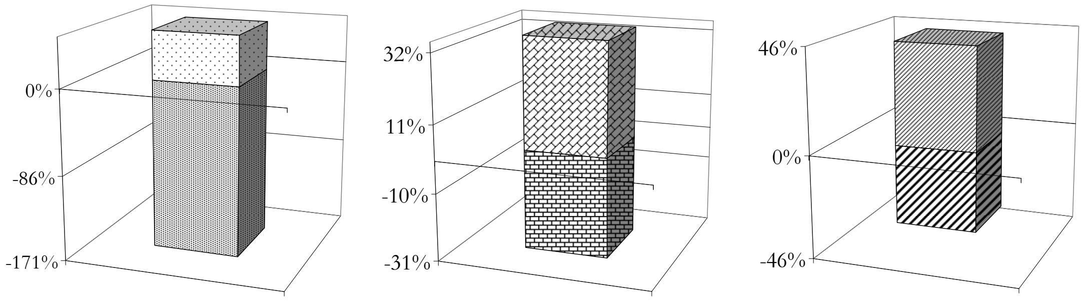
Composite wear [mm^3]		**Vickers hardness values** [MPa]	**Dynamic elastic modulus** [GPa]	**Flexural strength** [MPa]	**WOF** [J/m^2]	**Static elastic modulus** [GPa]
Against Glass						
1.4×10^{-2} (Saliva)	5.25×10^{-1} (Slurry)	554.0 (50.7)	15.5 (1.10)	58.78 (7.95)	2.24×10^{3} (150.32)	8.94 (0.89)
Against tooth						
4.22×10^{-3} (Saliva)	— (Slurry)					

Commercial composites In order to evaluate the influence of all studied parameters, result analyses were separated in: tribological and mechanical results. The charts presented in fig. 6.2 show the variation range, in terms of percentage, of commercial composites relatively to Synergy regarding mechanical properties. As for hardness the variation range is of about 40%, with a decrease of 3% (Pyramid Dentin) to plus 40% (Filtek P60), representing an overall variation of about 43%. Dynamic elastic modulus values for commercial composites tested present a variation of about 44%, very similar to what occurs to hardness, from −3% (Pyramid Dentin) to +41% (Quixfil). Concerning four point bending tests and the properties assessed, the composites properties variation is wider than the previous properties analyzed. Work-to-fracture ranged from −171% (Quixfil) to +49% (Pyramid Enamel) relatively to the reference composite Synergy. Flexural strength registered a variation from −31% (CeramX) to +35% (Pyramid Enamel). Finally, static elastic modulus had the same qualitative results as dynamic tests (impulse excitation of vibration) with composites of higher and lower value being the same with an increase and decrease of respectively −35% and +46% relatively to Synergy results.



Dynamic elastic modulus

Hardness



WOF

Flexural strength

Static elastic modulus

Fig. 6.2: Mechanical Characteristics — Commercial Composites.

The following two figs. represent the summarizing of results for external parameters which influence the tribological (fig. 6.3) and mechanical (fig. 6.4) behaviors of commercial composites, namely; pH, aging period, environment conditions, test severity and antagonist material.

Tribological behavior is then classified regarding severity influence (test duration times normal load) for both types of antagonists tested. When Synergy is tested against tooth the influence of severity increases wear until a maximum of 66%. When the antagonist is glass the severity increase on composite wear volume reaches up to 90%. Results of the study as to aging and pH effect, revealed a very high variation for all composites; the results of Synergy are representative of all studied commercial composites. To determine the effect of pH values on the wear volume of composite first a pH value of 9 was selected, and then wear results were compared. There is an increase of composite wear volume for increasing aging period, were the 22 month period registered a maximum value of 576% regarding the reference value for Synergy.

Regarding pH effect on wear performance, aging period was selected and the wear volumes of the different pH values were compared. Thus, pH 9 registered the highest wear volume with an increase of 576% while pH 3 registered a value of 102% and pH 7 presented a minimum of the composite wear when synergy was tested after 22 month aging period.

When environment conditions were analyzed, for slurry and/or saliva the influence was very different. When the abrasive slurries were present the overall variation on composite wear ranged in ±10%, except for Prodigy which had a decrease in removed material of 72%. Regarding saliva environment medium all composites performed worse than Synergy. Wear volumes were higher for Prodigy specimens with the highest value of 86%.

The effects of pH and aging time on mechanical properties of composites are mirrored in fig. 6.4. Regarding Synergy hardness values and concerning the effect of pH, the aging period analyzed was 22 months. All pH values analyzed registered a decrease in hardness, and the smallest reduction was for pH 7 buffer solutions, with −7% in removed composite volume. When analyzing the effect of aging time and for pH 3 conditions (which showed the highest variation) the wear volumes decrease with the passage of time.

The dynamic elastic modulus demonstrates a decrease of values for increasing aging period and increasing pH values. The worse condition is pH 7 at 22 month aging period, a 66% decrease.

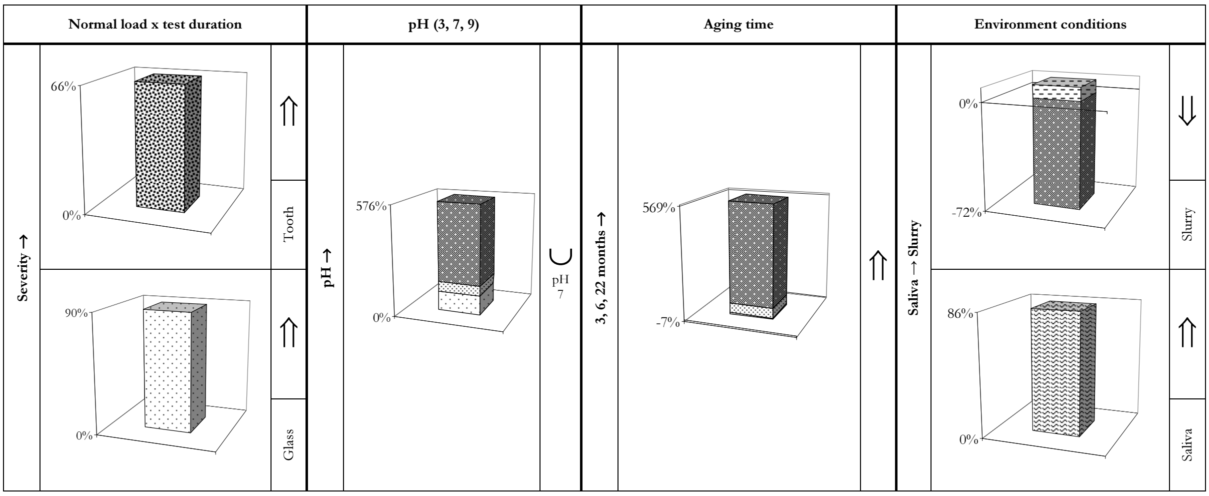


Fig. 6.3: Wear volume of commercial composites — tribological characterization.

Produced composites Concerning produced composites, fig. 6.5 to fig. 6.10 present the overall summarization of the results regarding tribological and mechanical properties. Table 6.2 presents the values of polypropylene resin properties, which serve as reference for the other produced specimens with reinforcement filler.

With respect to the result analysis and in order to understand the evolution of the parameters in study a standard had to be established and therefore the resin served as reference. Again, as previously explained for commercial composites 100% stacked column charts are presented relatively to resin specimens (reference material for produced composites) with the highest value and lowest value of the property and/factor in study of the best and worst resin composite relative to it.

The great advantage of studying these composites is the possibility to produce changes at a structural level; the tribological and mechanical behavior was determined through the variation of filler volume fraction, filler size and matrix variation (namely altering the UDMA mol %).

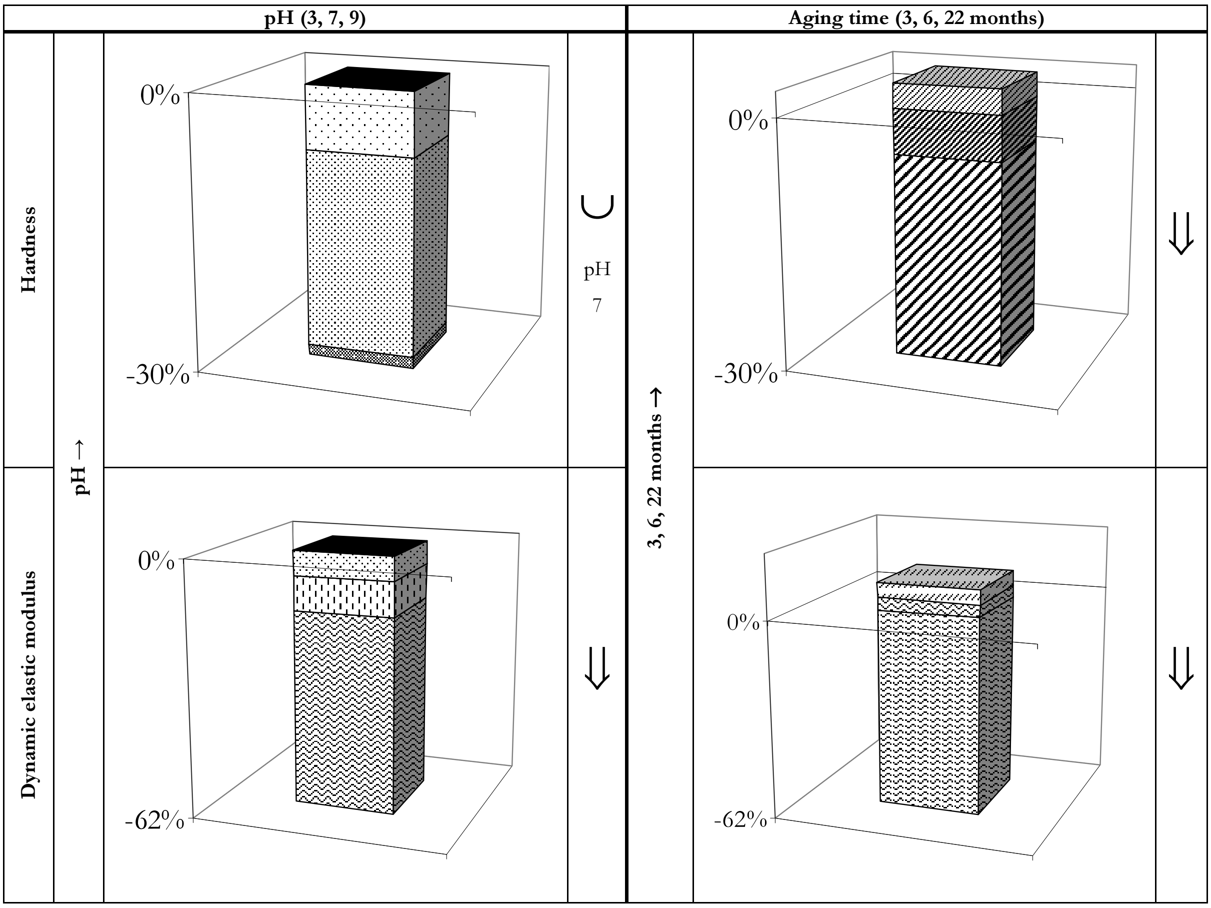


Fig. 6.4: Effect of pH values and aging time on the mechanical characteristics of commercial composites.

Increasing the percentage of filler in the composite in reciprocating sliding test within abrasive slurry environment increases the amount of composite removed by wear (fig 6.5) of up to a maximum of 85% in relation to the reference resin material. When the environment is artificial saliva, instead of increasing wear removal of composite, a minimum value is obtained for a 24% of filler volume fraction (−2400%). Regarding filler size influence, for slurry environment a decrease in composite wear is recorded for increasing filler size up to a minimum of minus 107% in respect to resin specimens. With respect to filler size influence in artificial saliva environment smaller values are registered for composites with average filler size of 6 μm (−73%) and the highest value for specimens with filler size reinforcements of 22 μm (+70%).

In terms of the UDMA mol % (matrix influence) in wear: for resins a maximum value is obtained for 10% mol UDMA (+95%). When the composite wear is assessed the increase of UDMA percentages produces a rise of composite wear, of up to a maximum of 99%.

Fig. 6.6 to fig. 6.10 show the compilation results for produced composites and their mechanical properties relatively to the evaluated parameters; filler volume content, particle size and matrix composition.

Fig. 6.6 shows hardness values relatively to:

- Filler volume percentage: an increase is registered for increasing filler volume fraction up to a maximum of 49% (corresponding to 46% filler volume fraction);

Table 6.2: Values of resin propylene specimen assessed properties for mechanical and tribological tests, (STD).

Composite wear volume [mm^3]		**Hardness** [MPa]	**Dynamic elastic modulus** [GPa]	**Flexural strength** [MPa]	**WOF** [J/m^2]	**Static elastic modulus** [GPa]
Against Glass						
9.21×10^{-2} (Saliva)	1.55×10^{-2} (Slurry)	208.4 (0.87)	4.51 (0.341)	54.2	4.3×10^3	2.93

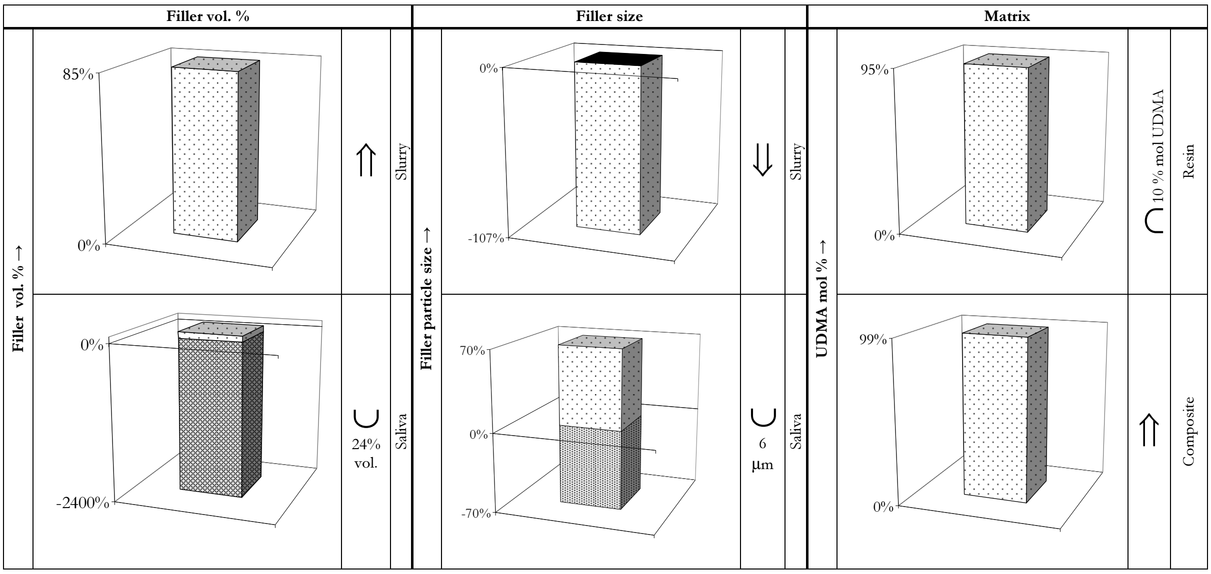


Fig. 6.5: Effects of, filler volume content, particle size and matrix variation on the wear volume of produced composites — Tribological characterization.

- Filler particle size: was determined for a constant filler volume fraction, reference is the resin specimens, therefore an increase of 36% in hardness is relatively to this material. Hardness values for the composite, all with the same filler volume fraction is approximately the same, thus two arrows indicate an increase (⇑), from resin reference value, and similar values for all composites (⇔);
- Matrix composition: influence is analogous both in the resin and composite; a maximum is obtained for the higher value of UDMA (20 mol %). The composite is not as sensible to the UDMA quantity as the resin specimens, with resin ranging 15% while composite's hardness range 7% relatively to the reference.

Fig. 6.7 shows dynamic elastic modulus values relatively to:

- Filler volume percentage: an increase is registered for increasing filler volume fraction up to a maximum of 71% (corresponding to the maximum value of filler volume fraction);
- Filler particle size: again the influence of the parameter is similar to what occurred relatively to hardness. An increase of 50% in elastic modulus relatively to the resin and similar

values for all composites;

- Matrix composition: regarding the resin, the maximum is obtained for the highest value of UDMA mol percentage, with an increase of 7% of elastic modulus relatively to the reference. The elastic modulus variation for composite is higher, with the smaller value of −19% for the composite with 20% mol of UDMA.

As for the evaluation of bending tests results, the analysis is done for work-of-fracture (WOF), flexural strength and static elastic modulus and their variation in function of filler fraction, filler size and matrix content.

Fig. 6.8 shows work-of-fracture values relatively to:

- Filler volume percentage: the increase of filler content produces a significant decrease in WOF values, up to a minimum of −1333% (corresponding to the maximum value of filler volume fraction);

- Filler particle size: the introduction of reinforcement particles results in a decrease of WOF values, this reduction is higher for reinforcement particles of 6 μm, where the decrease in the property is of 1315%;

- Matrix composition: resin specimens decrease their WOF with increasing molecular percentage of UDMA, this reduction being highest for 20%. Values of WOF for composites increase relatively to composite with 0% mol UDMA and 10% and 20% have an increase of 578% and 57% in WOF, respectively.

Fig. 6.9 shows flexural strength values relatively to:

- Filler volume percentage: The behavior is similar to WOF, although variation values aren't as high. There is a general decrease of flexural strength with increasing filler content, maximum value of flexural strength is obtained for 37% of filler volume;

- Filler particle size: flexural strength values tend to increase with increasing average filler dimension. The highest value compared with resin specimens was obtained for composites with 22 μm filler size (−25%) and the lowest value, for 3 μm filler size (−128%);

- Matrix composition: resin and composites specimens have comparable behaviors. Percentages of UDMA other than 0% present comparable values of flexural strength; for resin 10% and 20% mol UDMA corresponds to an increase of 11% and 13% respectively. For composite specimens: 10% and 20% mol UDMA correspond to 34% and 26% increase in flexural strength.

Fig. 6.10 shows static elastic modulus values relatively to:

- Filler volume percentage: The behavior is similar to dynamic elastic modulus. The percentage of increase relatively to the resin is almost the same (69% for static and 71% for dynamic elastic modulus), again the highest value was obtained for 46% of filler volume content;

- Filler particle size: again the similarity is high. Composites have static elastic modulus higher then resin and very similar between them ($\approx$ 49% for static while dynamic elastic modulus was 50%);

- Matrix composition: resin and composite have antagonist behavior relatively to the variation of mol % of UDMA. Resin increases elastic modulus with increasing UDMA mol % (+24% for 20% UDMA mol) and composite registers the greatest decreases for the same mol % of UDMA (–27% static elastic modulus).

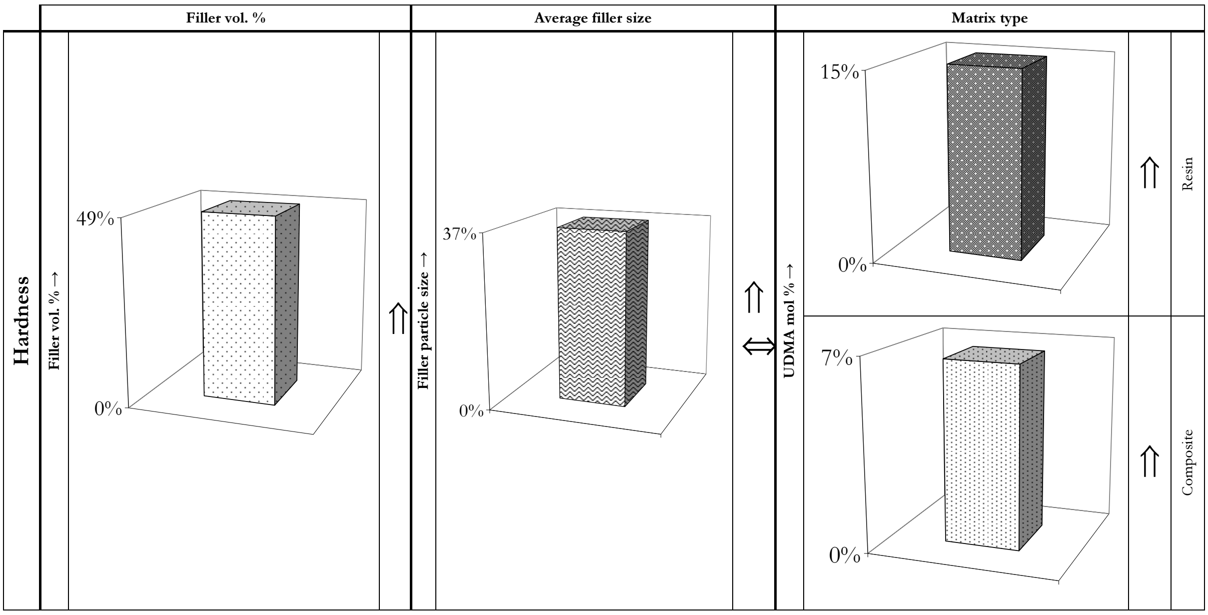


Fig. 6.6: Effects of, filler volume content, particle size and matrix variation on hardness — Produced composites.

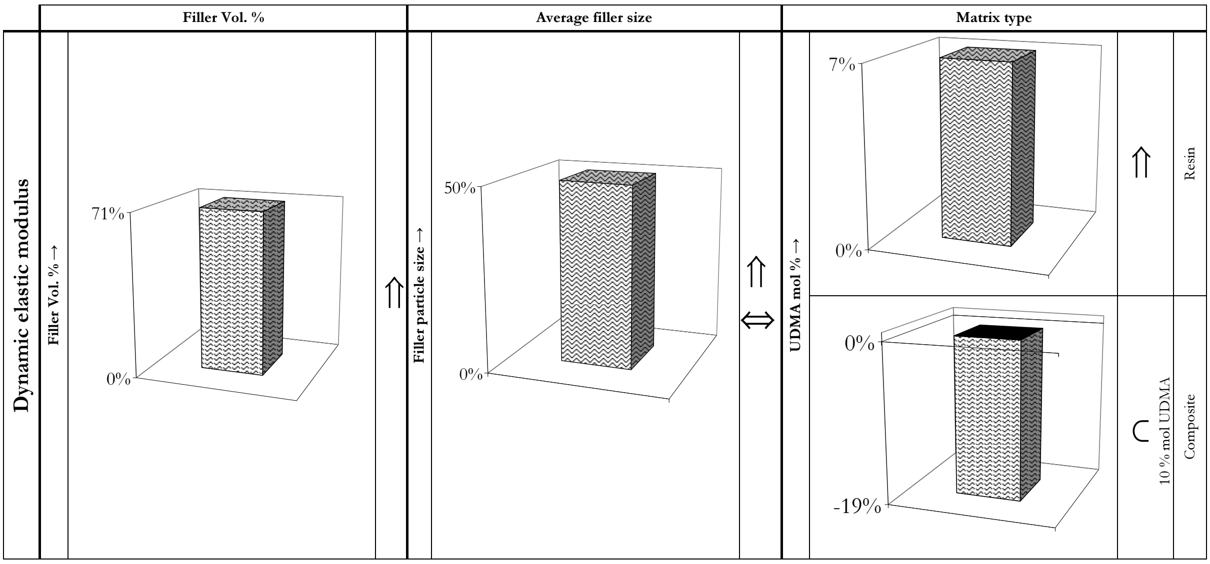


Fig. 6.7: Effects of, filler volume content, particle size and matrix variation on dynamic elastic modulus — Produced composites.

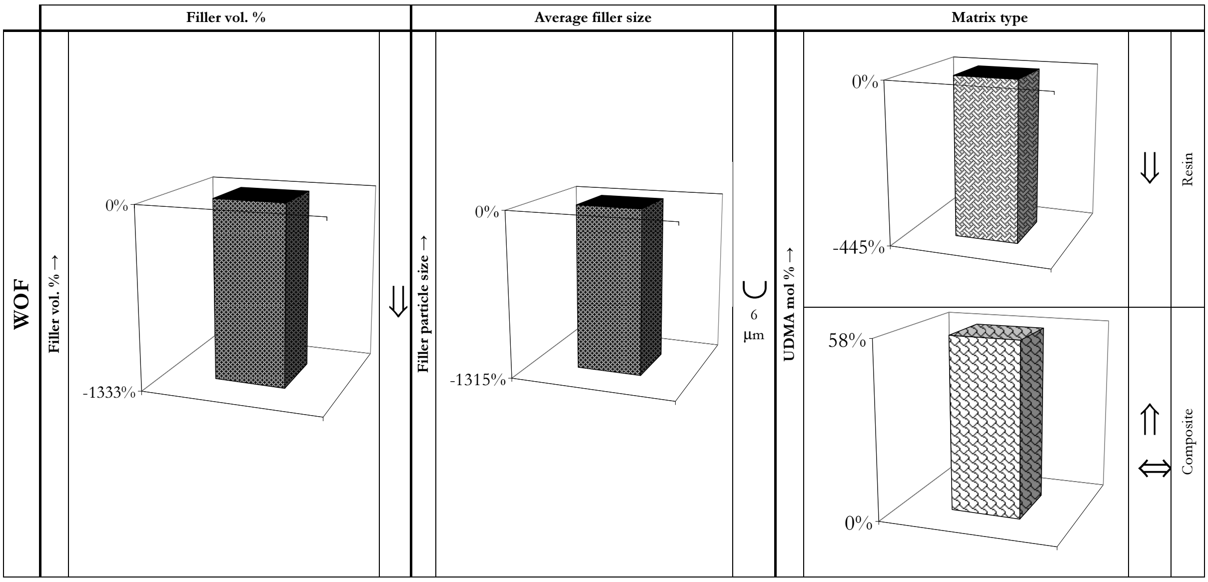


Fig. 6.8: Effects of, filler volume content, particle size and matrix variation on work-of-fracture (WOF) — Produced composites.

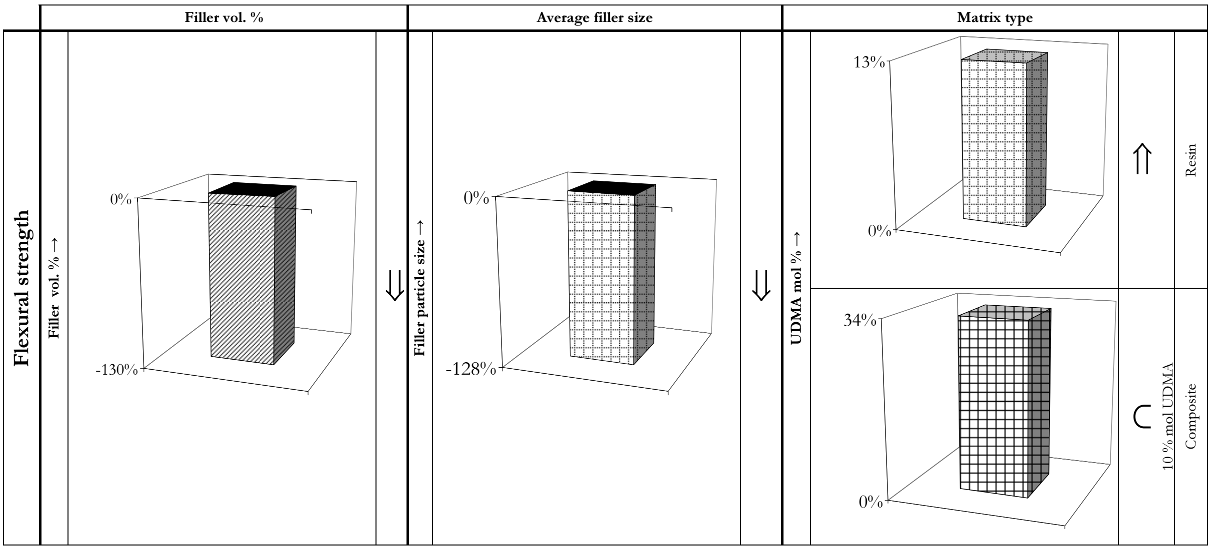


Fig. 6.9: Effects of, filler volume content, particle size and matrix variation on flexural strength — Produced composites.

6.2 Conclusions

Due to differences in the composition of commercial composites it was very difficult to compare their performance or make conclusion as to the influence of external factors on the property variation. There are too many variables which have distinct importance on the overall behavior. Due to the complexity of the composites components, it is very difficult to establish a direct relation, cause and effect, because what in one composite may increase a property, in another, may decrease, not due solely to the characteristic itself but due to several factors that concur for the overall performance of the composite. Thus, from the general information of the study

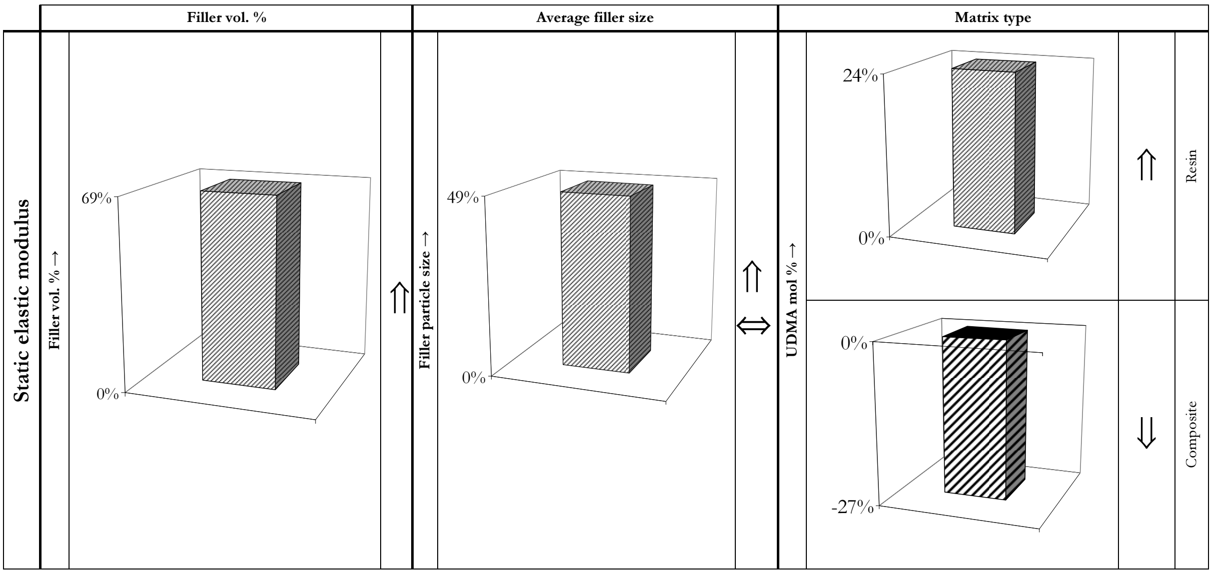


Fig. 6.10: Effects of, filler volume content, particle size and matrix variation on static elastic modulus — Produced composites.

it was possible to conclude:

Mechanical behavior

- The absolute hardness value is not a safe criterion for correctly choosing a composite for dental application when abrasive resistance is the more important factor. Although, for each of the materials tested, an increase in the hardness value usually led to improved abrasion resistance;
- Commercial composites with higher values of filler weight fraction present higher hardness values. Produced composites clearly showed this effect of filler content on hardness;
- Matrix composition affects composites hardness values. Resins produced for the study showed variation in hardness depending on the different percentage of UDMA (0%, 10% and 20% mol). This demonstrates the dependence of hardness in respect to the matrix constitution, when varying only one component;
- Average filler particle dimension did not affect composite's hardness values. Considering the five average filler particle dimensions and an even mixture of nano- and micro- filler, for the same filler fraction, no variation in hardness was registered;
- As observed with hardness, there is a general tendency to increase elastic modulus with filler fraction, for commercial composites and confirmed in the produced composites evaluation;
- Particle dimension variation, with constant filler volume fraction, did not have any influence in specimen's average dynamic elastic modulus nor hardness;
- Although dynamic elastic modulus and quasi-static elastic modulus presented different values, their tendency was the same; elastic modulus obtained from static bending tests have the same tendency that is registered for dynamic test ones;

- Matrix composition, for the filler volume fraction considered, had no noticeable influence in elastic modulus values;
- For commercial composites and observing the bending test results there is no unmistakable relation between filler weight fraction and any one of the three properties analyzed in this flexural test. It is possible to conclude that flexural strength and work-of-fracture have the same tendency for all composites in study;
- Increasing filler content produced an exponential decrease of composite's flexural strength and work-of-fracture and the opposite effect was determined for elastic modulus (exponential increase);
- The introduction of inorganic filler in resin specimens formulations matrices lead to a decrease in flexural strength and work-of-fracture and, conversely, an increase in elastic modulus values for composites;
- When average particle dimension increases, maintaining constant particle filler volume fraction, a linear increase in flexural strength and work-of-fracture is produced. Although static elastic modulus was not affected by average particle dimension;
- Regarding the effect of matrix it is possible to conclude that while matrices with higher values of mol % UDMA increase flexural strength and elastic modulus they also decrease work-of-fracture;
- Concerning elastic modulus mol % UDMA has an opposing effect on resin and composites; for elastic modulus and work-of-fracture increasing percentage of UDMA made resin have higher values of these properties while for composites these values decreased. Regarding flexural strength the increase in mol % of UDMA had the same effect in resins and composites;
- pH effect combined with long aging periods affected composites tribological and mechanical performance. Smaller aging periods, 3 and 6 month aging time, did not have an important influence on composites behavior;
- Morphologically, aging, independent of the pH value tends to degrade the interface between matrix and reinforcement particles;
- Specimens aged in alkaline solution pH 9, combined with long aging time, were more affected than other solutions demonstrating higher variations in wear volumes. pH 3 and pH 7 also affected commercial composites, therefore it cannot be concluded that some pH solution are more aggressive than others.

Tribological behavior

- A linear relation between wear volume and the applied load times sliding distance is in accordance with the Archard's wear equation; $V \propto N \cdot x$. The ratio between wear volume and normal load times sliding distance represents the wear coefficient for the materials in study, considering a classical approach;
- An energetic approach establishes a linear relationship between the wear volume and the energy dissipated by friction; $V \propto$ Energy. This energy is obtained by multiplying friction force by the sliding distance;

- In reciprocating wear tests for dental restorative composite materials tested against soft glass spheres a linear relation can be obtained between removed material by wear and sliding distance considering testing under constant normal load;

- In reciprocating wear tests for dental restorative composite materials tested against soft glass spheres an increasing linear relation can be obtained between removed materials by wear and increasing normal load applied, considering testing under constant sliding distance;

- It is admissible and reliable to predict and extrapolate results of composite materials against teeth if composites are previously tested against glass;

- With both restorative materials (commercial or produced composites) antagonist wear volumes are greater for tests with abrasive slurry environment than the ones with saliva;

- In tests with abrasive slurry amalgam performs better than any of the tested composites. However, in the tests with artificial saliva one composite showed better wear resistance then amalgam;

- Most composite materials reveal a linear relation between wear volume of restorative material and their hardness, for abrasive slurry or saliva environments. However, hardness effect on improvement of wear resistance is more marked in tests with saliva;

- For tests with produced composites in abrasive slurry environment, hard abrasive particles trapped between the contacting surfaces lead to large and deep scratches. In the wear tests with saliva the surfaces present less scratches and the particles are worn along with matrix;

- Reciprocating wear tests of produced composites in artificial saliva environment show lower composite wear values for 24% and 30% filler content. Therefore, there is an optimum composite volume filler percentage to produce less wear;

- For abrasive slurry environment and wear volumes of composite specimens there is a gradual increase in wear volumes for increasing particle content of composites. Composite materials with less filler content perform better;

- Transition in wear behavior is associated with a marked change of coefficient of friction, due to local failure induced by friction. In cases of low friction values, tangential force between spherical surface and composite surface is very low when compared to the normal load. Thus in the contact stress distribution, the hertzian component is predominant, inducing occurrence of maximum tangential stress underneath the surface. This stress distribution induces failure beneath the surface by a fatigue process that starts with the initiation of small cracks at the sub-surface followed by their propagation up to the surface;

- Increase in wear relatively to reference followed, in general, a COF increase;

- Morphologically, aging independent of pH values tends to degrade the interface between matrix and reinforcement particles;

- All composites presented the widest variations, increase or decrease, in wear volume for the longest aging period: 22 months.

6.3 Future work

More and more tooth-colored direct dental filling materials have long been generally accepted as the first choice for restoration of teeth, even though they do not tolerate the same masticatory force as amalgam. Duration of resin composite restorative materials is the primordial reason for choosing amalgam as treatment of caries. This clear trend to replace amalgam with resin dental filling materials in general implies great development of these materials.

Amalgam fillings still show higher longevity than composite fillings, even though the latter have improved, through improved material properties.

In order to improve direct filling materials it is necessary to investigate the following aspects:

- Assess the influence of external factors on direct filling materials, which are present in the mouth, mainly influence of temperature;
- Parametric study of direct restorative materials with commercial formulation but with the possibility to alter their constituents;
- Complement an *in vitro* study with an *in vivo* study associated with regular control of restoration dimensions;
- The weakest link in the physical integrity of composite materials is probably the bonding between the organic resin and the surfaces of the inorganic filler particles. Development of a contact zone, resin, to bond to tooth structure without etching or bonding systems;
- Thermal properties to attain similar tooth characteristics; areas for further studies concern, amongst other things, mechanical properties such as elastic modulus, fracture toughness, flexural strength and wear. Also, handling characteristics need to be evaluated and improved to assure a rapid user learning curve of this type of material. The aesthetics is also an area of further improvement. Long-term evaluation of material properties and long-term statistically relevant clinical evaluations are areas of great need.

Bibliography

[Abe *et al.*, 2001] Abe Y., Lambrechts P., Inoue S., Braem M.J.A., Takeuchu M. and Vanherle G., Dynamic elastic modulus of “packable” composites, Dent Mater, 17, (2001): 520-525.

[ADA, 2010] American Dental Association (ADA) professional product review. Restor Mater, 5 (2), (2010): 1-16.

[Adabo *et al.*, 2003] Adabo G.L., Cruz C.A.S., Fonseca R.G. and Vaz L.G., The volumetric fraction of inorganic particles and the flexural strength of composites for posterior teeth, J Dent, 31, (2003): 353-359.

[Ahmed and Jones, 1990] Ahmed S. and Jones F.R., A review of particulate reinforcement theories for polymer composites, Journal of Materials Science, 25(12), (1990): 4933-4942.

[Akihiro and Ferracane, 1996] Fujishima A. and Ferracane J.L., Comparison of four modes of fracture toughness testing for dental composites, Dent Mater, 12, (1996): 38-43.

[Alster *et al.*, 1997] Alster D., Feilzer A.J., de Gee A.J. and Davidson C.L., Polymerization contraction stress in thin resin composite layers as a function of layer thickness, Dent Mater, 13, (1997): 146-150.

[Antunes *et al.*, 2007] Antunes P.V., Pinho-da-Cruz J., Oliveira J.A., Teixeira-Dias F., Ramalho A.; Determinação Experimental e Análise Numérica da Influência da Fracção Volúmica de Partículas de Reforço nas Propriedades Mecânicas de um Material Compósito de Matriz Polimérica; Actas do Congresso de Métodos Numéricos em Engenharia 2007 — CMNE 2007 — e do XXVIII Congresso Ibero-Latino-Americanos obre Métodos Computacionais — CILAMCE 2007 —, J.C. Sá, R. Delgado, A.D. Santos, A. Rodríguez-Ferran, J. Oliver, P.R.M. Lyra, J.L.D. Alves (Eds.), p. 388 CD- ROM (Art.° n.° 796); 13 a 15 de Junho, Faculdade de Engenharia da Universidade do Porto — FEUP —, Porto, Portugal — 2007.

[Antunes and Ramalho, 2003] Antunes P.V. and Ramalho A., Study of abrasive resistance of composites for dental restoration by ball-cratering, Wear 255 (2003) 990-998.

[Anusavice and de Rijk, 1990] Anusavice K.J., de Rijk W.G., Performance of dental biomaterials: conference report. Dent Mater, 6, (1990): 69-72.

[Anusavice, 2005] Anusavice K.J., Present and future approaches for the control of caries, J Dent Educ, 69(5), (2005): 538-554.

[Anusavice, 2003] Anusavice K.J., Phillips' Science of Dental Materials, Restorative resin, Rawls H.R. and Esquivel-Upshaw J., 8th ed. Toronto: W.B. Saunders Co. (2003): 74-98, 417-432.

[Archard, 1953] Archard J.F., ”Contact and Rubbing of Flat Surface, J. Appl Phis: 24 (8), (1953): 981-988.

[Ashby and Jones, 1980] Ashby M.F. and Jones D.R.H., Engineering Materials I: An introduction to their properties and applications, New York: Pergamon Press, Inc; (1980).

[Asmussen and Peutzfeldt, 1998] Asmussen E. and Peutzfeldt A., Influence of UEDMA, BisGMA and TEGDMA on selected mechanical properties of experimental resin composites, Dent Mater, 14(1), (1998): 51-56.

[Asmussen, 1984] Asmussen E., Softening of BISGMA-based polymers by ethanol and by organic acids of plaque, Scand J Dent Res, 92, (1984): 257-261.

[Asmussen, 1982] Asmussen, E., Restorative Resins: Hardness and Strength *vs.* Quantity of remaining double bonds, Scand J Dent Res, 90, (1982): 490-496.

[ASTM WK27978, 2010] ASTM WK27978 - Revision of E384 - 10 Standard Test Method for Microindentation Hardness of Materials, (2010).

[ASTM C1327-08, 2008] ASTM C1327 - 08 Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics, (2008).

[ASTM E 111-04, 2004] ASTM E 111-04, Standard test method for Young's modulus, tangent modulus, and chord modulus. In: Annual book of ASTM standards, ASTM International, vol. 03.01; (2004).

[ASTM E 1304-97, 2002] ASTM E 1304-97, Standard Test Method for Plane-Strain (ChevronNotch) Fracture Toughness of Metallic Materials, ASM Standards, (2002).

[ASTM C1161-96, 1996] ASTM: Standard test method for Flexural strength of advanced ceramics at ambient temperature, C1161 (1996): 304-310.

[ASTM C1259-96, 1996] ASTM C1259-96, Parameters for Advanced Ceramics C1259 - 08e1 Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio for Advanced Ceramics by Impulse Excitation of Vibration, (1996).

[ASTM E399, 1983] ASTM E399-83, Standard test method for plane-strain fractures toughness of metallic materials, (1983).

[Atai *et al.*, 2004] Atai M., Nekoomanesh M., Hashemi S.A. and Amani S., Physical and mechanical properties of an experimental dental composite based on a new monomer, Dent Mater, 20, (2004): 663-668.

[Atsuta and Turner, 1982] Atsuta, M. and Turner, D.T., Optimum strength of composite of ceramic particle in poly (methyl methacrylate), Polymer Composites 3, (1982): 83-87.

[Attin *et al.*, 2009] Attin T., Schmidlin P.R., Wegehaupt F. and Wiegand A., Influence of study design on the impact off bleaching agents on dental enamel microhardness: A review, Dent Mater, 25(2), (2009): 143-157.

[Bader and Shugars, 2006] Bader J.D. and Shugars D.A., The evidence supporting alternative management strategies for early occlusal caries and suspected occlusal dentinal caries, J Evid Based Dent Pract, 6 (1), (2006): 91-100.

[Barber and Ciavarell, 2000] Barber J.R. and Ciavarella M., Contact mechanics, Int J Solids Struct, 37(1-2), (2000): 29-43.

[Bates, 2006] Bates M.N., Mercury amalgam dental fillings: an epidemiologic assessment, Int J Hyg Environ Health, 209 (2006): 309-316.

[Bayne et al., 1994] Bayne S.C., Heymann H.O. and Swift E.l., Update on dental composite restorations, I Am Dent Assoc, 125, (1994): 687-701.

[Bayne *et al.*, 1992] Bayne S.C., Taylor D.F. and Heymann H.O., Protection hypothesis for composite wear, Dent Mater, 8, (1992): 305-309.

[Bayer, 1990] Bayer R.G., Wear testing. Mechanical testing. ASM Handbook, Vol. 18, ASM International, (1992): 602-604.

[Bayne, 1992] Bayne S.C., Dental composites/glass ionomers. Clinical reports. Adv Dent Res, 6, (1992): 65-77.

[Beatty *et al.*, 1998] Beatty M.W., Swartz M.L., Moore B.K., Phillips R.W. and Roberts T.A., Effect of microfiller fraction and silane treatment on resin composite properties, J Biomed Mater Res, 40, (1998): 12-23.

[Beauchamp *et al.*, 2008] Beauchamp J., Caufield P.W. and Crall J.J., Evidence-based clinical recommendations for the use of pit-and-fissure sealants: a report of the American Dental Association Council on Scientific Affairs, JADA, (2008), 139(3):257-268.

[Bec *et al.*, 1996] Bec S., Tonck A., Georges J.M., Georges E. and Loubet J.L., Improvements in the indentation method with a surface force apparatus, Phil Mag A, 74(5), (1996): 1061-1072.

[Bellinger *et al.*, 2008] Bellinger D.C., Trachtenberg F., Zhang A., Tavares M., Daniel D. and McKinlay S., Dental amalgam and psychosocial status: the New England children's amalgam trial, J Dent Res, 87, (2008): 470-474.

[Bellinger *et al.*, 2007] Bellinger D.C., Daniel D., Trachtenberg F., Tavares M. and McKinlay S., Dental amalgam restorations and children's neuropsychological function: the New England children's amalgam trial, Environ Health Perspect, 115 (2007): 440-446.

[Bellinger *et al.*, 2006] Bellinger D.C., Trachtenberg F., Barregard L., Tavares M., Cernichiari E., Daniel D. and McKinlay S., Neuropsychological and renal effects of dental amalgam in children: a randomized clinical trial, J Am Med Assoc, 295 (2006): 1775-1783.

[Bergman, 1990] Bergman M., Side-effects of amalgam and its alternatives: local, systemic and environment, Int Dent J, 40 (1990): 4-10.

[Beun *et al.*, 2007] Beun S., Glorieux T., Devaux J., Vreven J. and Leloup G., Characterization of nanofilled compared to universal and microfilled composites, Dent Mater, 23, (2007): 51-59.

[Black, 1896] Black G.V., The physical properties of the silver-tin amalgams, Dent Cosmos, 38, (1896): 965-992.

[Blackham *et al.*, 2009] Blackham J.T., Vandewalle K.S. and Lien W., Properties of hybrid resin composite systems containing prepolymerized filler particles, Oper Dent, 34, (2009): 697-702.

[Blanpain *et al.*, 1993] Blanpain B., Celis J.-P., Roos J.R., Ebberink J. and Smeets J., A comparative study of the fretting wear of hard carbon coatings, Thin Solid Films, 223, (1993): 65-67.

[Bobji and Biswas, 1999] Bobji M.S. and Biswas S.K., Deconvolution of hardness from data obtained from nano-indentation of rough surfaces, J Mater Res, 14(6), (1999): 2259-2268.

[Bonilla *et al.*, 2001] Bonilla E.D., Mardirossian G. and Caputo A.A., Fracture toughness of posterior resin composites, Dent Mater, 32(3), (2001): 206-210.

[Bowen and Reed, 1976] Bowen R.L. and Reed L.E., Semiporous Reinforcing Fillers for Composite Resins: I. Preparation of Provisional Glass Formulations, J Dent Res, 55(5), (1976): 738-747.

[Bowen, 1964] Bowen, R.L., Effects of Particle Shape and Size Distribution in a Reinforced Polymer, J Am Dent Assoc, 69, (1964): 482-497.

[Bowen, 1963] Bowen, R.L., Properties of a silica-reinforced polymer for dental restorations, J Am Dent Assoc, 66, (1963): 57-62.

[Bowen, 1956] Bowen, R.L., Use of epoxy resins in restorative materials, J Dent Res, 35, (1956): 360-364.

[Boyer *et al.*, 1982] Boyer D.B., Chalkley Y. and Chan K.C., Correlation between strength of bonding to enamel and mechanical-properties of dental composites, J Biomed Mater Res, 16, (1982): 775-783.

[Braem *et al.*, 1987] Braem M., Vandoren V.E., Lambrechts P. and Vanherle G., Determination of Young modulus of dental composites - a phenomenological model, J Mater Sci, 22, (1987): 2037-2042.

[Braem *et al.*, 1986] Braem M., Lambrechts P., Van Doren V. and Vanherle G., The impact of composite structure on its elastic response, J Dent Res, 65, (1986): 648-653.

[Braem, 1985] Braem M., An in-vitro investigation into the physical durability of dental composites, PhD thesis, Leuven, Belgium, (1985): 7, 42-55, 63-70, 139.

[Braem *et al.*, 1989] Braem M., Finger W., Van Doren V.E., Lambrechts P. and Vanherle G., Mechanical properties and filler fraction of dental composites, Dent Mater, 5, (1989): 346-348.

[Braem *et al.*, 1987] Braem M., Lambrechts P., Vanherle G. and Davidson C.L., Stiffness increase during the setting of dental composite resins, J Dent Res, 66, (1987): 1713-1716.

[Braga *et al.*, 2007] Braga S.R., Vasconcelos B.T., Macedo M.R., Martins V.R. and Sobral M.A., Reasons for placement and replacement of direct restorative materials in Brazil, Quintessence Int 2007, 38(4): 89-94.

[Brantley *et al.*, 1995] Brantley C.F., Bader J.D., Shugars D.A., Nesbit S.P., Does the cycle of rerestoration lead to larger restorations? JADA, (1995), 126 (10): 1407-1413.

[Brizmer *et al.*, 2006] Brizmer V., Kligerman Y. and Etsion I., The effect of contact conditions and material properties on the elasticity terminus of a spherical contact, International Journal of Solids and Structures, 43, (2006): 5736-5749.

[Broek, 1986] Broek D., Elementary Engineering Fracture Mechanics (4th ed.), Martinus-Nijhoff, Boston (1986): 130-140.

[Brown *et al.*, 1972] Brown W.S., Jacobs H.R., Thompson R.E., Thermal fatigue in teeth, J Dent Res, 51, (1972): 461-467.

[Burke, 2004] Burke F.J., Amalgam to tooth-coloured materials: implications for clinical practice and dental education, Governmental restrictions and amalgam-usage survey results, J Dent, 32 (5), (2004): 343-50.

[Calais and Söderholm, 1988] Calais J.G. and Söderholm K.-J.M., Influence of filler type and water exposure on flexural strength of experimental composite resins, J Dent Res 67, (1988): 836-840.

[Caldwell *et al.*, 1957] Caldwell R.C., Muntz M.L., Gilmore R.W. and Pigman W., Microhardness studies of intact surface enamel, J Dent Res, 36, (1957): 732-738.

[Caughman *et al.*, 1991] Caughman W.F., Caughman G.B., Shiflett R.A., Rueggeberg F. and Schuster G.S., Correlation of cytotoxicity, filler loading and curing time of dental composites, Biomaterials, 12, (1991): 737-740.

[Chabrier *et al.*, 1999] Chabrier F., Lloyd C.H. and Scrimgeour S.N., Measurement at low strain rates of the elastic properties of dental polymeric materials, Dent Mater, 15, (1999): 33-38.

[Chadwick *et al.*, 1990] Chadwick R.G., McCabe J.F., Walls A.W.G. and Storer R., The effect of storage media upon the surface microhardness and abrasion resistance in three composites, Dent Mater, 6, (1990): 123-128.

[Chantler *et al.*, 1999] Chantler P.M., Hu X. and Boyd N.M., An extension of a phenomenological model for dental composites, Dent Mater, 15, (1999): 144-149.

[Chen, 2010] Chen M.-H., Update on Dental Nanocomposites, J Dent Res, 89(6), (2010): 549-560.

[Chung and Greener, 1990] Chung K.-H. and Greener E.H., Correlation between degree of conversion, filler concentration and mechanical properties of posterior composite resins, Journal of Oral Rehabilitation, 17(5), (1990): 487-494.

[Chung *et al.*, 2004] Chung S.M., Yap A.U., Koh W.K., Tsai K.T. and Lim C.T., Measurement of Poisson's ratio of dental composite restorative materials, Biomaterials, 25, (2004): 2455-2460.

[Chung, 1990] Chung K.H., The relationship between composition and properties of posterior resin composites, J Dent Res, 69, (1990): 852.

[Clarkson, 2002] Clarkson T.W., The three modern faces of mercury, Environ Health Perspect, 110 (Suppl. 1), (2002): 11-23.

[Condon and Ferracane, 1997] Condon J.R. and Ferracane J.L., In vitro wear of composite with varied cure filler level, and filler treatment, J Dent Res, 76 (7), (1997): 1405-1411.

[Condon and Ferracane, 1997a] Condon J.R. and Ferracane J.L., Factors effecting dental composite wear in vitro, J Dent Res, 38, (1997a): 303-313.

[Condon and Ferracane, 1998] Condon J.R. and Ferracane J.L., Reduction of composite contraction stress through non-bonded microfiller particles, Dent Mater, 14, (1998): 256-260.

[Condon and Ferracane, 1996] Condon J.R. and Ferracane J.L., Evaluation of composite wear with a new multi-mode oral wear simulator, Dent Mater, 12, (1996): 218-226.

[Constantinescu *et al.*, 2007] Constantinescu I.R., Ursache M. and Mardarez D., Effect of pH on the surface roughness of heat cured denture base acrylic resins, Rev Med Chir Soc Med Nat Iasi, 111(2), (2007): 477-481

[Cook and Johannson, 1987] Cook W.D. and Johannson M., The influence ofpostcuring on the fracture properties of photo-cured dimethacrylate based dental composite resin, J Biomed Mater Res, 21, (1987): 979-989.

[Cook and Standish, 1983] Cook W.D., and Standish P.M., Polymerization kinetics of resin-based restorative materials, Journal of Biomedical Materials Research, 17(2), (1983): 275-282.

[Craig, 2002] Craig R.G. and Powers J.M., Restorative dental materials, 11th ed. Mosby: St Louis; (2002).

[Craig, 1989] Craig R.G., Mechanical properties, In: Restorative dental materials, St Louis, C.V. Mosby Company, (1989): 65-112.

[Crawford, 1982] Crawford R.J., Microhardness testing of plastics, Polymer Testing, 3(1), (1982): 37-54.

[Cross *et al.*, 1983] Cross M., Douglas W.H. and Fields R.F., The relationship between filler loading and particle size distribution in composite resin technology, Dent Res, 62, (1983): 850-852.

[Cui *et al.*, 1992] Cui W.C., Wisnom M.R. and Jones M., Failure mechanisms in three and four point short beam bending tests of unidirectional glass/epoxy, The Journal of Strain Analysis for Engineering Design, 27, (1992): 235.

[Cung *et al.*, 2004] Chung S.M., Yap A.U.J., Chandra S.P. and Lim C.T., Flexural strength of dental composite restoratives: Comparison of biaxial and three-point bending test, Journal of Biomedical Materials Research, 71B (2), (2004): 278-283.

[Curtis *et al.*, 2009] Curtis A.R., Palin W.M., Fleming G.J., Shortall A.C. and Marquis P.M., The mechanical properties of nanofilled resin-based composites: the impact of dry and wet cyclic pre-loading on bi-axial flexure strength, Dent Mater, 25, (2009): 188-197.

[Curtis *et al.*, 2008] Curtis A.R., Shortall A.C., Marquis P.M. and Palin W.M., Water uptake and strength characteristics of a nanofilled resin-based composite, Journal of Dentistry, 36(3), (2008): 186-193.

[Czichos, 1978] Czichos H., Tribology: a system approach to the science and technology of friction, lubrication and wear, Elsevier, Amsterdam, 1978, Wear, 54(1), (1979): 193.

[Darvell, 2002] Darvell B., Materials science for dentistry, Hong Kong: B.W. Darvell; (2002).

[Dauvillier *et al.*, 2000] Dauvillier B.S., Feilzer A.J., de Gee A.J. and Davidson C.L., Viscoelastic parameters of dental restorative materials during setting, J Dent Res, 79, (2000): 818-823.

[Davidson and Feilzer, 1997] Davidson C.L. and Feilzer A.J., Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives, J Dent, 25, (1997): 435-440.

[Davidson-Kaban *et al.*, 1997] Davidson-Kaban S.S., Davidson C.L., Feilzer A.J., DeGee A.J. and Erdilek N., Effect of curing light variations on bulk curing and wall-to-wall quality of two types and various shades of resin composites, Dent Mater, 13(6), (1997): 344-352.

[Davis and Water, 1987] Davis D.M. and Water N.E., An investigation into the fracture behavior of a particulate-filled BisGMA resin, J Dent Res, 66, (1987): 1128-1133.

[Debnath *et al.*, 2004] Debnath S., Ranade R., Wunder S.L., McCool J., Boberick K. and Baran G., Interface effects on mechanical properties of particle-reinforced composites, Dent Mater, 20(7), (2004): 677-686.

[DeLong *et al.*, 1989] DeLong R., Sasik C., Pintado M.R. and Douglas W.H., The wear of enamel when opposed by ceramic systems, Dent Mater, 5, (1989): 266-271.

[Denisova *et al.*, 2004] Denisova L.A., Maev R.G., Poyurovskaya I.Y., Grineva T.V., Denisov A.F. and Maeva E.Y., The use of acoustic microscopy to study the mechanical properties of glass-ionomer cement, Dent Mater, 20, (2004): 358-363.

[Dennison and Hamilton, 2005] Dennison J.B., Hamilton J.C., Treatment decisions and conservation of tooth structure, Dent Clin North Am, 49 (4), (2005): 825-845.

[Department of Health and Human Services, 1993] Department of Health and Human Services: Public Health Service, 1993. Dental amalgam: a scientific review and recommended Public Health Service strategy for research, education, regulation. Final Report of the Subcommittee on Risk Management of the Committee to Coordinate Environmental Health and Related Programs, Washington, (1983).

[DeRouen *et al.*, 2006] DeRouen T.A., Martin M.D., Leroux B.G., Townes B.D., Woods J.S., Leitao J., Castro-Caldas A., Luis H., Bernardo M., Rosenbaum G. and Martins I.P., Neurobehavioral effects of dental amalgam in children: a randomized clinical trial, J Am Med Asso, 295, (2006): 1784-1792.

[Deyhle *et al.*, 2011] Deyhle H., Bunk O. and Müller B., Nanostructure of healthy and caries-affected human teeth, Nanomedicine: Nanotechnology, Biology and Medicine (2011), In Press, Accepted Manuscript.

[Dong, 2002] Dong X. and Jahanmir S., Wear transition diagram for silicon nitride, Wear, 165(2), (1993): 169-180.

[Dowson, 1998] Dowson D., History of Tribology, Professional Engineering Publishing Limited, London, UK, (1998): 577.

[Draughn and Harrison, 1978] Draughn R.A., and Harrison A., Relationship between abrasive wear and microstructure of composite resins, J Prosthet Dent, 40, (1978): 220-224.

[Draughn, 1981] Draughn R.A., Effects of temperature on mechanical-properties of composite dental restorative materials, J Biomed Mater Res, 15, (1981): 489-495.

[Duarte Jr. *et al.*, 2009] Duarte Jr. S., Phark J.H., Varjão F.M. and Sadan A., Nanoleakage, ultramorphological characteristics, and microtensile bond strengths of a new low-shrinkage composite to dentin after artificial aging, Dent Mater, 25(5), (2009): 589-600.

[Duymus *et al.*, 2008] Yesil Z.D, Alapati S., Johnston W. and Seghi R.R., Evaluation of the wear resistance of new nanocomposite resin restorative materials, The Journal of Prosthetic Dentistry, 99(6), (2008): 435-443.

[Dwyer-Joyce *et al.*, 1994] Dwyer-Joyce R.S., Sayles R.S. and Ioannides E., An investigation into the mechanisms of closed three-body abrasive wear, Wear, 175, (1994): 133-142.

[Ekstrand *et al.*, 1998] Ekstrand K.R., Ricketts D.N.J. and Kidd E.A.M., Do occlusal carious lesions spread laterally at the enamel — dentin junction, Clin Oral Invest, (2), (1998): 15-20.

[Eneström and Hultman, 1995] Eneström S., and Hultman P., Does amalgam affect the immune system? A controversial issue, Int Arch Allergy Immunol, 106, (1995): 180-203.

[Evans, 1973] Evans A.G., A simple method for evaluating slow crack growth in brittle materials, International Journal of Fracture, 9(3), (1973): 267-275.

[FDA Part 58 52 FR 33780, 2004] FDA, Good Laboratory Practice (GLP), Part 58 52 FR 33780, 1978, last revision (2004).

[Feilzer *et al.*, 1990] Feilzer A.J., de Gee A.J. and Davidson C.L., Relaxation of polymerization contraction shear stress by hygroscopic expansion, J Dent Res, 69, (1990): 36-39.

[Feilzer *et al.*, 1990a] Feilzer A.J., de Gee A.J. and Davidson C.L., Quantitave determination of stress reduction by flow in composite restorations, Dent Mater, 6, (1990a): 167-171.

[Feilzer *et al.*, 1987] Feilzer A.J., de Gee A.J. and Davidson C.L., Setting stress in composite resin in relation to configuration of the restoration, J Dent Res, 66, (1987): 1636-1639.

[Ferracane and Berge, 1995] Ferracane J.L. and Berge H.X., Fracture toughness of experimental dental composites aged in ethanol, J Dent Res, 74, (1995): 1418-1423.

[Ferracane and Marker, 1992] Ferracane J.L. and Marker V.A., Solvent degradation and reduced fracture toughness in aged composites, J Dent Res, 71, (1992): 13-19.

[Ferracane *et al.*, 1998] Ferracane J.L., Berge H.X. and Condon J.R., In vitro aging of dental composites in water-effect of degree of conversion, filler volume, and filler/matrix coupling, I Biomed Mater Res, 42 (1998): 465-472.

[Ferracane *et al.*, 1987] Ferracane J.L., Antonio R.C. and Matsumoto H., Variables affecting the fracture toughness of dental composites, J Dent Res, 66, (1987): 1140-1145.

[Ferracane, 2011] Ferracane J.L, Resin composite-State of the art, Dent Mater, 27, (2011): 29-38.

[Ferracane, 2006] Ferracane J.L., Hygroscopic and hydrolytic effects in dental polymer networks, Dent Mater, 22 (3), (2006): 211-222.

[Ferracane, 1994] Ferracane J.L., Elution of leachable components from composites, J Oral Rehabil, 21, (1994): 441-452.

[Ferracane, 1989] Ferracane J.L., Indentation fracture toughness testing of and crack propagation mode in dental composites, Mater Res Symp Proc, 110, (1989): 619-624.

[Flanders *et al.*, 2003] Flanders L.A., Quinn J.B., Wilson O.C. and Lloyd I.K., Scratch hardness and chipping of dental ceramics under different environments, Dent Mater, 19, (2003): 716-724.

[Floyd and Dickens, 2006] Floyd C.J.E. and Dickens S.H., Network structure of bis-GMA- and UDMA-based resin systems, Dent Mater 22, (2006): 1143-1149.

[Freund and Munksgaard, 1990] Freund M. and Munksgaard E.C., Enzymatic degradation of BISGMA/TEGDMA-polymers causing decreased microhardness and greater wear in vitro, Scand I Dent Res, 98, (1990): 351-355.

[Fu *et al.*, 2008] Fu S.-Y., Feng X.-Q., Lauke B. and Mai Y.-W., Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites, Composites Part B: Engineering, 39(6), (2008): 933-961.

[Fu *et al.*, 1998] Fu S.-Y. and Lauke B., The elastic modulus of misaligned short-fiber-reinforced polymers, Composites Science and Technology, 58(3-4), (1998): 389-400.

[Fujishima and Ferracane, 1996] Fujishima A. and Ferracane J.L., Comparison of four modes of fracture toughness testing for dental composites, Dent Mater, 12(1), (1996): 38-43.

[Fujishima *et al.*, 1991a] Fujishima A., Miyazaki T., Aoyama M., Suzuki E. and Miyaji T., Fracture toughness of composite resin inlay, J Jpn Dent Mater, 10, (1991): 137-145.

[Fujishima *et al.*, 1991b] Fujishima A., Miyazaki T., Aoyama M,. Suzuki E. and Miyaji T., Fracture toughness and fracture behavior of composite resins for posterior restorative materials, J Jpn Conserv Dent, 34, (1991):45-53.

[Gahr, 1987] Gahr K.-H.Z., Classification of wear processes, In: Microstructure and Wear of Materials. Amsterdam: Elsevier, (1987): 80-131.

[Ganss *et al.*, 1999] Ganss C., Schlechtriemen M. and Klimek J., Dental erosions in subjects living on a raw food diet, Caries Res, 33, (1999): 74-80.

[Gee *et al.*, 1996a] Gee A.J., Duinen R.N.B., Wener A. and Davidson C.L., Early and long-term wear of convencional and resin-modified glass ionomers, J Dent Res, 75 (8), (1996a): 1613-1619.

[Gee *et al.*, 1996b] Gee A.J., Wendt S.L., Werner A. and Davidson C.L., Influence of enzymes and plaque acids on in vitro wear of dental composites, Biomaterials, 17, (1996b): 1327-1332.

[Gere and Timoshenko, 1984] Gere J.M. and Timoshenko S.P., Mechanics of Materials, Wadsworth Publishing Co Inc; 2nd edition (1984).

[Geurtzen, 1998] Geurtzen W., Substances released from dental resin composites and glass ionomer cements, Eur J Oral Sci, 106, (1998): 687-695.

[Giannini *et al.*, 2004] Giannini M., Soares C.J. and Carvalho R.M., Ultimate tensile strength of tooth structures, Dent Mater, 20, (2004): 322-329.

[Glenn, 1982] Glenn J.F., Biocompatibility of Dental Materials, vol. 3, (1982): Smith, D.C., Williams, D.F. (Eds.) Boca Raton, Florida: CRC Press: 97-130.

[Goldman, 1985] Goldman M., Fracture properties of composite and glass ionomer dental restorative materials, J Biomed Mater Res, 19, (1985): 777-783.

[Goldmann and Himmlova, 2008] Goldmann T. and Himmlova L., Experimental detection of chewing force, Journal of Biomechanics, 41, Supplement 1, (2008): S341.

[Grieve *et al.*, 1991] Grieve A.R., Alani A. and Saunders W.P., The effects on the dental pulp of a composite resin and two dentine bonding agents and associated bacterial microleakage, Int Endod 1, 24, (1991): 108-118.

[Gwinnett *et al.*, 1992] Gwinnett A.J., Structure and composition of enamel, Oper Dent, Suppl 5, (1992): 10-17.

[Hahnel *et al.*, 2010] Hahnel S., Henrich A., Bürgers R., Handel G. and Rosentritt M., Investigation of mechanical properties of modern dental composites after artificial aging for one year, Oper Dent, 35, (2010): 412-419.

[Hamilton, 1983] Hamilton G.M., Explicit equations for the stresses beneath a sliding spherical contact, Proceedings of the Institution of Mechanical Engineers C: Journal of Mechanical Engineering Science, 197, (1983): 53-59.

[Hansel *et al.*, 1998] Hansel C., Leyhausen G., Mai U. and Geurtsen W., Effects of various resin composite (co)monomers and extracts on two-caries associated micro-organisms in vitro, I Dent Res, 77, (1998): 60-67.

[Hara and Nemoto, 1986] Hara R. and Nemoto K., Studies on dental restorative composite resin-influence of shape and ratio of filler on the physical properties, Jpn J Dent Mater, 5, (1986): 1-16.

[Harrison and Draughn, 1976] Harrison A. and Draughn R.A., Abrasive wear, tensile strength, and hardness of dental composite resins. Is there a relashionship? J Prosthet Dent, 36, (1976): 395-398.

[Harsha *et al.*, 2003] Harsha A.P., Tewari U.S. and Venkatraman B., Three-body abrasive wear behaviour of polyaryletherketone composites, Wear, 254, (7-8), (2003): 680-692.

[Hassan *et al.*, 1981] Hassan R., Caputo A.A. and Bunshah R.F., Fracture toughness of human enamel, J Dent Res, 60, (1981): 820-827.

[Hauert *et al.*, 2009] Hauert A., Rossoll A. and Mortensen A., Young's modulus of ceramic particle reinforced aluminium: Measurement by the Impulse Excitation Technique and confrontation with analytical models, Composites Part A: Applied Science and Manufacturing, 40(4), (2009): 524-529.

[Heintze *et al.*, 2011] Heintze S.D., Barkmeier W.W., Latta M.A. and Rousson V., Round robin test: Wear of nine dental restorative materials in six different wear simulators - Supplement to the round robin test of 2005, Dent Mater, 27, (2011): e1-e9.

[Heintze *et al.*, 2008] Heintze S.D., Cavalleri A., Forjanic M., Zellweger G. and Rousson V., Wear of ceramic and antagonist - A systematic evaluation of influencing factors in vitro, Dent Mater, 24, (2008): 433-449.

[Heintze *et al.*, 2007] Heintze S.D., Zellweger G. and Zappini G., The relationship between physical parameters and wear rates of dental composites, Wear, 263 (7-12), (2007): 1138-1146.

[Heintze, 2006] Heintze S.D., How to qualify and validate wear simulation devices and methods, Dent Mater, 22, (2006): 712-734.

[Helvatjoglu-Antoniades *et al.*, 2006] Helvatjoglu-Antoniadesa M., Papadogiannis Y., Lakes R.S., Dionysopoulos P. and Papadogiannis D., Dynamic and static elastic moduli of packable and flowable composite resins and their development after initial photo curing, Dent Mater, 22, (2006): 450-459.

[Higo *et al.*, 1991] Higo Y., Damri D., Nunomura S., Kumada K., Sawa N., Hanaoka K., Teranaka T. and Iwamoto T., The fracture toughness characteristics of three dental composite resins, Biomed Mater Eng, 1, (1991): 223-231.

[Hilton *et al.*, 1997] Hilton T.J., Ferracane J.L. and Lamerand S., The effect of colloidal silica surface treatment on composite properties, J Dent Res, 76, (1997): 220, Abstract n. 2449.

[Holm, 1946] Holm R., Electrical Contacts, Stockholm (1946): H. Gerber.

[Hörsted-Bindslev, 2004] Hörsted-Bindslev P., Amalgam toxicity-environmental and occupational hazards, Journal of Dentistry, 32 (5), (2004): 359-365.

[Hu *et al.*, 1999] Hu X., Marquis P.M. and Shortall A.C., Two-body in vitro wear study of some current dental composites and amalgams, The Journal of Prosthetic Dentistry, 82 (2), (1999): 214-220.

[Huq and Celis, 2002] Huq M.Z. and Celis J.-P., Expressing wear rate in sliding contacts based on dissipated energy, Wear, 252, (2002): 375-383.

[Ikejima *et al.*, 2003] Ikejima I., Nomoto R. and McCabe J.F., Shear punch strength and flexural strength of model composites with varying filler volume fraction, particle size and silanation, Dent Mater, 19(3), (2003): 206-211.

[Ilie and Hickel, 2009a] Ilie N. and Hickel R., Investigations on mechanical behavior of dental composites, Clin Oral Invest, 13, (2009a): 427-438.

[Ilie and Hickel, 2009b] Ilie N. and Hickel R., Macro-, micro- and nano-mechanical investigations on silorane and methacrylate-based composites, Dent Mater, 25, (2009b): 810-819.

[Indrani *et al.*, 1995] Indrani D.J., Cook W.D., Televantos F., Tyas M.J. and Harcourt J.K., Fracture toughness of water-aged resin composite restorative materials, Dent Mater, 11 (3), (1995): 201-207.

[Irie *et al.*, 2006] Irie M., Hatanaka K., Suzuki K. and Watts D.C., Immediate versus water-storage performance of Class V flowable composite restoratives, Dent Mater, 22, (2006): 875 -883.

[ISO 14569-2, 2001] International Organization of Standardization, Dental materials-Guidance on testing of wear. Part 2: Wear by two-and/or three body contact, Techn Specific (2001), No. 14569-2.

[Jaarda *et al.*, 1993] Jaarda M.J., Lang B.R., Wang R.F. and Edwards C.A., Measurement of composite resin filler particles by using scanning electron microscopy and digital imaging, J Prosthet Dent, 69, (1993): 416-424.

[Jaarda *et al.*, 1996] Jaarda M.J., Wang R.F. and Lang B.R., A regression analysis of filler particle content to predict composite wear, J Prosthet Dent, 69, (1996): 57-67.

[Jacobs *et al.*, 1973] Jacobs H.R., Thompson R.E. and Brown W.S., Heat transfer in teeth, J Dent Res, 52, (1973): 248-252.

[Jager *et al.*, 2004] De Jager N., Pallav P. and Feilzer A.J., The apparent increase of the Young's modulus in thin cement layers, Dent Mater, 20, (2004): 457-462.

[Jøgersen and Asmussen, 1978] Jøgersen K.D. and Asmussen E., Occlusal abrasion of a composite restorative resin with ultra-fine filler — An initial study, Quint Int, 9, (1978): 73-78.

[Johnson *et al.*, 1993] Johnson W.W., Dhuru V.B. and Brantley W.A., Composite microfiller content and its effect on fracture toughness and diametral tensile strength, Dent Mater, 9, (1993): 95-98.

[Jøgersen *et al.*, 1979] Jøgersen K.D., Hørst P., Janum O., Krogh J. and Schultz J., Abrasion of class I restorative resins, Scand J Dent Res, 87, (1979): 140-145.

[Johnson, 1985] Johnson K.L., Contact Mechanics, 1st ed., Cambridge University Press, Cambridge, (1985): 202-210.

[Jokstad *et al.*, 1994] Jokstad A., Mjùr I.A. and Qvist V., The age of restorations in situ, Acta Odontol. Scand, 52 (4), (1994): 234-242.

[Jontell *et al.*, 1995] Jontell M., Hanks C.T., Bratel J. and Bergenholtz G., Effects of unpolymerized resin components on the function of accessory cells derived from the rat incisor pulp, J Dent Res, 74, (1995): 1162-1167.

[Jørgensen *et al.*, 1979] Jørgensi N.K.D., Hørstl D.P., Janum O., Krogh J. and Shultz J., Abrasion of Class I Restorative Resins, Scand 1 Dent Res, 87, (1979): 140-145.

[Kawaguchi *et al.*, 1989] Kawaguchi M., Fukushima T. and Horibe T., Effect of monomer structure on the mechanical properties of light-cured composite resins, Dent Mater, 8, (1989): 40-45.

[Kawai and Leinfelder, 1995] Kawai K. and Leinfelder K.F., In vitro evaluation of OCA wear resistance of posterior composites, Dent Mater, 11, (1995): 246-251.

[Kelly, 1999] Kelly J.R., Clinically revelant approach to failure testing of all-ceramic restorations, J Prosthet Dent, 82, (6), (1999): 652-61.

[Kelly, 1995] Kelly J.R., Prespective on strength, Dent Mater, 11, (1995): 103-110.

[Kim *et al.*, 1994] Kim K.H., Park J.H., Imai Y. and Kishi T., Microfracture mechanisms of dental resin composites containing spherically shaped filler particles, J Dent Res, 73, (1994): 499-504.

[Kim J.W.*et al.*, 2002] Kim J.W., Jang K.T., Lee S.H., Kim C.C., Hahn S.H. and Godoy F.G., Effect of curing method and curing time on the microhardness and wear of pit and fissure sealents, Dent Mater, 18, (2002): 120-127.

[Kim K.H.*et al.*, 2002] Kim K.H., Ong J.L. and Okuno O., The effect of filler loading and morphology on the mechanical properties of contemporary composites, J Prosthet Dent, 87, (2002): 642-649.

[Kinney *et al.*, 1996] Kinney J.H., Balooch M., Marshall S.J., Marshall Jr G.W. and Weihs T.P., Hardness and Young's modulus of human peritubular and intertubular dentine, Archives of Oral Biology, 41 (1), (1996): 9-13.

[Kishen and Asundi, 2001] Kishen A. and Asundi A., Investigations of thermal property gradients in the human dentine, J Biomed Mater Res, 55, (2001): 121-130.

[Kishen *et al.*, 2000] Kishen A., Ramamurty U. and Asundi A., Experimental studies on the nature of property gradients in the human dentine, J Biomed Mater Res, Part A, 51, (2000): 650-659.

[Klapdohr and Moszner, 2005] Klapdohr S. and Moszner N., New inorganic components for dental filling composites, Monatsh Chem, 136, (2005): 21-45.

[Kovarik and Fairhurst, 1993] Kovarik R.E. and Fairhurst C.W., Effect of Griffith precracks on measurement of composite fracture toughness, Dent Mater, 9, (1993): 222-228.

[Kovarik *et al.*, 1991] Kovarik R.E., Ergle J.W. and Fairhurst C.W., Effect of specimen geometry on the measurement of fracture toughness, Dent Mater, 7, (1991): 166-169.

[Kraft, 2002] Kraft L., Calcium Aluminate Cement as Dental restorative Materials, ACTA Universitstis Upsalaiensis, UPPSALA, (2002).

[Kunzelmann *et al.*, 1998] Kunzelmann K.-H., Verschleissanalyse und -quantifizierung von Fu llungsmaterialien in vivo und in vitro, Aachen: Shaker Verlag, (1998).

[Labella *et al.*, 1999] Labella R., Lambrechts P., Van Meerbeek B. and Vanherle G., Polymerization shrinkage and elasticity of flowable composites and filled adhesives, Dent Mater, 15, (1999): 128-137.

[Lakes *et al.*, 2002] Lakes R.S., Kose S. and Bahia H., Analysis of high volume fraction irregular particulate damping composites, J Eng Mater Tech, 124, (2002): 174-178.

[Lambrechts *et al.*, 2006a] Lambrechts P., Goovaerts K., Bharadwaj D., De Munck J., Bergmans L., Peumans M. and Van Meerbeek B., Degradation of tooth structure and restorative materials: A review, Wear, 261(9), (2006): 980-986.

[Lambrechts *et al.*, 2006b] Lambrechts P., Debels E., Landuyt K.V., Peumans M. and Meerbeek B.V., How to simulate wear? Overview of existing methods, Dent Mater, 22 (8), (2006): 693-701.

[Lambrechts *et al.*, 1985] Lambrechts P., Vuylsteke M., Vanherle G. and Davidson C.L., Quantitative in vivo wear of posterior dental restorations. Four year results, J Dent, 64, (1985): 370, Abst N 1759.

[Lambrechts *et al.*, 1984] Lambrechts P., Vanherle G., Vuylsteke M. and Davidson C.L., Quantitative evaluation of the wear resistance of posterior dental restorations: a new three dimension measuring technique, J Dent, 12, (1984): 252-267.

[Langeland, 1987] Langeland K., Tissue response to dental caries, Dental Traumatology, 3 (4), (1987): 149-171.

[Larsen and Munksgaard, 1991] Larsen I.B. and Munksgaard E.C., Effect of human saliva on surface degradation of composite resins, Scand J Dent Res, 99, (1991): 254-261.

[Larsen *et al.*, 1992] Larsen I.B., Freund M. and Munksgaard E,C., Change in surface hardness of Bis-GMA/TEGDMA polymer due to enzymatic action, J Dent Res, 71, (1992): 1851-1853.

[Lawn *et al.*, 1993] Lawn B.R., Dabbs T.P. and Fairbanks C.J., Kinetics of shear-activated indentation cracks initiation in soda-line-glass, J Mater Sci, 19 (9), (1993): 2785-2797.

[Leinfelder and Suzuki, 1999] Leinfelder K.F. and Suzuki S., In vitro wear device for determining posterior composite wear, JADA, 130, (1999): 1347-1353.

[Lewis and Dwyer-Joyce, 2005] Lewis R. and Dwyer-Joyce R.S., Wear of human teeth: a tribological perspective, Proc Inst Mech Eng J J Eng Tribol, 219 (1), (2005): 2.

[Li and Zhou, 2002] Li H., Zhou Z.R., Wear behavior of human teeth in dry and artificial saliva conditions, Wear, 249, (2002): 980-984.

[Li *et al.*, 1985] Li Y., Swartz M.L., Phillips R.W., Moore B.K. and Roberts T.A., Effect of filler content and size on properties of composites, J Dent Res, 64, (1985): 1396-1401.

[Lim *et al.*, 2002] Lim B.S., Ferracane J.L., Condon J.R. and Adey J.D., Effect of filler fraction and filler surface treatment on wear of microfilled composites, Dent Mater, 18, (2002): 1-11.

[Lingstrom *et al.*, 1993] Lingstrom P., Imfeld T. and Birkhed D., Comparison of three different methods for measurements of plaque-pH in humans after consumption of soft bread and potato chips, J Dent Res, 72(5), (1993): 865-870.

[Liu *et al.*, 2009] Liu Y., Tan Y., Lei T., Xiang Q., Huang B. and Han Y., Effect of porous glass-ceramic fillers on mechanical properties of light-cured dental resin composites, Dent Mater, 25 (6), (2009): 709-715.

[Liu *et al.*, 1999] Liu C., Ren L., Arnell R.D. and Tong J., Abrasive wear behavior of particle reinforced ultrahigh molecular weight polyethylene composites, Wear, 225-229(1), (1999): 199-204.

[Lloyd and Adamson, 1987] Lloyd C.H. and Adamson H., The development of fracture toughness and fracture strength in posterior restorative materials, Dent Mater, 3, (1987): 225-231.

[Lloyd and Ianetta, 1982] Lloyd C.H. and Ianetta R.V., The Fracture Toughness of Dental Composites, Part I: The Development of Strength and Fracture Toughness, J Oral Rehabil, 9, (1982): 55-56.

[Lutz and Phillips, 1983] Lutz F. and Phillips R.W., A classification and evaluation of composite resin systems, J Prosthet Dent, 50 (4), (1983): 480-488.

[Lysaght and DeBellis, 1969] Lysaght V.E. and DeBellis A., Microhardness testing. In: Hardness testing handbook, First edition, USA: American Chain and Cable Company, (1969): 76-105.

[Ma *et al.*, 2003] Ma R., Krewski D. and Burnett R.T., Random effects Cox models: A Poisson modelling approach, Biometrika, 90 (1), (2003): 157-169.

[Mackert and Wahl, 2004] Mackert Jr. J.R. and Wahl M.J., Are There Acceptable Alternatives to Amalgam? CDA Journal, 32 (7), (2004): 601-610.

[Magne *et al.*, 1999] Magne P., Oh W.S., Pintado M.R. and DeLong R., Wear of enamel and veneering ceramics after laboratory and chairside finishing procedures, J Prosthet Dent, 82, (1999): 669-679.

[Mair and Vowles, 1987] Mair L.H. and Vowles R., The effect of thermal cycling on the fracture toughness of seven composite restorative materials, Dent Mater, 5 (1987): 23-26.

[Mair *et al.*, 1996] Mair L.H., Stolarskij T.A., Vowles R.W. and Lloyd C.H., Conference report Wear: mechanisms, manifestations and measurement, Report of a workshop, Journal of Dentistry, 24 (1-2), (1996): 141-148.

[Mäkinen, 2010] Mäkinen K.K., Sugar alcohols, caries incidence, and remineralization of caries lesions: a literature review, Int J Dent, 2010: 981072.

[Mandel, 1991] Mandel I.D., Living with amalgam: an environment perspective, Quint Int, 22, (1991): 337-339.

[Mandikos *et al.*, 2001] Mandikos M.N., McGivney G.P., Davis E., Bush P.J. and Carter J.M., A comparison of the wear resistance and hardness of indirect composite resins, The Journal Of Prosthetic Dentistry, 85 (4), (2001): 386-395.

[Manhart *et al.*, 2000a] Manhart J., Kunzelmann K.-H., Chen H.Y. and Hickel R., Mechanical Properties of New Composite Restorative Materials Journal of Biomedical Materials Research Special Issue: Dental Biomaterials, 53 (4), (2000): 353-361.

[Manhart *et al.*, 2000b] Manhart J., Kunzelmann K.-H., Chen H.Y. and Hickel R., Mechanical properties and wear behavior of light-cured packable composite resins, Dent Mater, 16, (2000): 33-40.

[Marghalani and Al-jabab, 2004] Marghalani H.Y., and Al-Jabab A.S., Compressive creep and recovery of light-cured packable composite resins, Dent Mater, 20, (6), (2004): 600-610.

[Marshall Jr. *et al.*, 1997] Marshall Jr. G.W, Inai N., Magidi I.C.W., Balooch M., Kinney J.H, Tagami J. and Marshall S.J., Dentin demineralization: Effects of dentin depth, pH and different acids, Dent Mater, 13 (5-6), (1997): 338-343.

[Masouras *et al.*, 2008] Masouras K., Silikas N. and Watts D.C., Correlation of filler content and elastic properties of resin-composites, Dent Mater, 24 (7), (2008): 932-939.

[Matos *et al.*, 2003] Matos A.B., Tate W.H. and Powers J.M., Influence of enamel surface preparation on composite bond strength, Am J Dent, 16, (2003): 37A-40A.

[Matos *et al.*, 2011] Matos I.C., Borge M.A.P., Mendes L.C., Gomes A.S. and Miranda M.S., Degradation of polymeric restorative materials subjected to a high caries challenge, Dent Mater, 27 (3), (2011): 244-252.

[Mayworm *et al.*, 2008] Mayworm C.D., Camargo Jr. S.S. and Bastian F.L., Influence of artificial saliva on abrasive wear and microhardness of dental composites filled with nanoparticles, Journal of Dentistry, 36 (9), (2008): 703-710.

[Mazer *et al.*, 1992] Mazer R.B., Leinfelder K.F. and Russell C.M., Degradation of microfilled posterior composite, Dent Mater, 8 (3), (1992): 185-189.

[McCabe and Walls, 2008] McCabe J.F. and Walls A., Requirements of Direct Filling Materials and Historical Perspectives. In: John F. McCabe and Angus W.G. Walls. Editors. Applied Dental Materials, 9th Edition: (2008): Oxford: Blackwell Publishing.

[McCabe and Wassell, 1999] McCabe J.F. and Wassel R.W., Hardenss of model dental composites-the effect of filler volume fraction and silanation, J Mater Sci: Mater Med, 10, (1999): 291-294.

[McHugh, 1992] McHugh W.D., Effects and side-effects of dental restorative materials, Adv Dent Res, 6, (1992): 139-144.

[Meckel *et al.*, 1965] Meckel A.H., Griebstein W.J. and Neal R.J., Structure of mature human dental enamel as observed by electron microscopy, Arch Oral Biol, 10, (1965): 775-783.

[Min *et al.*, 2010] Min S.-H., Ferracane J.L. and Lee I.-B., Effect of shrinkage strain, modulus, and instrument compliance on polymerization shrinkage stress of light-cured composites during the initial curing stage, Dent Mater, 26 (10), (2010): 1024-1033.

[Mitchell *et al.*, 2007] Mitchell R.J., Koike M. and Okabe T., Posterior Amalgam Restorations - Usage, Regulation, and Longevity, The Dental Clinics of North America, 51, (2007): 573-589.

[Mitra *et al.*, 2003] Mitra S.B., Wu D. and Holmes B.N., An application of nanotechnology in advanced dental materials, J Am Dent Assoc, 134, (2003): 1382-1390.

[Mjör, 1972] Mjör I.A., Human coronal dentine: structure and reactions, Oral Surg Oral Med Oral Pathol, 33, (1972): 810-823.

[Mjör, 1966] Mjör I.A., Microradiography of human coronal dentine, Arch Oral Biol, 11, (1966): 225-234.

[Mohsen an Craig, 1995] Mohsen N.M. and Craig R.G., Effect of silanisation of fillers on their dispersability by monomer systems, J Oral Rehabil, 22, (1995): 183-189.

[Mohsen *et al.*, 1998] Mohsen N.M., Craig R.G. and Hanks C.T., Cytotoxicity of urethane dimethacrylate composites before and after aging and leaching, J Biomed Mater Res, 39, (1998): 252-260.

[Montes-G and Draughn, 1987] Montes-G G.M. and Draughn R.A., Slow crack propagation in composite restorative materials, J Biomed Mater Res, 21, (1987): 629-642.

[Moshaverinia *et al.*, 2010] Moshaverinia A., Brantley W.A., Chee W.W.L., Rohpour N., Ansari S., Zheng F.Y., Heshmati R.H., Darr J.A., Schricker S.R. and Rehman I.U., Measure of microhardness, fracture toughness and flexural strength of N-vinylcaprolactam (NVC)-containing glass-ionomer dental cements, Dent Mater, 26 (12), (2010): 1137-1143.

[Moszner and Klapdohr, 2004] Moszner N. and Klapdohr S., Nanotechnology for dental composites, Int J Nanotechnol, 1, (2004): 130-156.

[Mota *et al.*, 2006] Mota E.G., Oshima H.M.S., Burnett Jr. L.H., Pires L.A.G. and Rosa L.S., Evaluation of diametral tensile strength and knoop microhardness of five nanofilled composites in dentin and enamel shades, Stomatologija, Baltic Dental and Maxilofacial Journal , 8, (2006): 67-79.

[Mucci *et al.*, 2009] Mucci V., Arenas G., Duchowicz R., Cook W.D. and Vallo C., Influence of thermal expansion on shrinkage during photopolymerization of dental resins based on bis-GMA/TEGDMA, Dent Mater, 25(1), (2009): 103-114.

[Munksgaard and Freund, 1990] Munksgaard E.C. and Freund M., Enzyme hydrolysis of (di)methacrylates and their polymers, Scand J Dent Res, 98, (1990): 261-267.

[Musanje and Davell, 2003] Musanje L. and Davell B.W., Aspects of water sorption from the air, water and artificial saliva in resin composite restorative materials, Dent Mater, 19 (5), (2003): 414-422.

[Musanje and Ferracane, 2004] Musanje L. and Ferracane J.L., Effects of resin formulation and nanofiller surface treatment on the properties of experimental hybrid resin composite, Biomaterials, 25 (18), (2004): 4065-4071.

[Nagarajan *et al.*, 2004] Nagarajan V.S., Jahanmir S. and Thompson V.P., In vitro contact wear of dental composites, Dent Mater, 20, (2004): 63-71.

[Nagarajan *et al.*, 2000] Nagarajan V.S., Hockey B.J., Jahanmir S. and Thompson V.P., Contact wear mechanisms of a dental composite with high filler content, J Mater Sci, 35, (2000): 487-496.

[Nakayama *et al.*, 1974] Nakayama W.T., Hall D.R., Grenoble D.E. and Katz J.L., Elastic properties of dental resin restorative materials, J Dent Res, 53, (1974): 1121-1126.

[Nielsen, 1967] Nielsen L.E., Mechanical Properties of Particulate-Filled Systems, Journal of Composite Materials, 1, (1967): 100-119.

[Nomoto *et al.*, 2001] Nomoto R., Carrick T.E. and McCabe J.F., Suitability of a shear punch test for dental restorative materials, Dent Mater, 17 (5), (2001); 415-421.

[O'Neil, 1967] O'Neill H., Hardness relations with other physical properties. In: Hardness measurement of metals and alloys. 2nd edition. London: Chapman and Hall Ltd, (1967): 191-207.

[O'Brien, 2002] O'Brien W.J., Dental Materials and Their Selection - 3rd Ed, Quintessence Publishing Co. Inc., (2002).

[O'Brien, 1997] O'Brien W.J., Dental materials and their selection, 2nd ed. Chicago, USA, Quintessence, (1997): 13-19, 100-105.

[Øilo, 1992] Øilo G., Biodegradation of dental composites/glass-ionomer cements, Adv Dent Res, 6, (1992): 50-54.

[Ørstavik and Hensten-Pettersen, 1978] Ørstavik D. and Hensten-Pettersen A., Antibacterial activity of tooth-colored dental restorative materials, J Dent Res, 57, (1978): 171-174.

[Örtengren *et al.*, 2001] Örtengren U., Andersson F., Elgh U., Terselius B. and Karlsson S., Influence of pH and storage time on the sorption and solubility behaviour of three composite resin materials, Journal of Dentistry, 29 (1), (2001): 35-41.

[Örtengren *et al.*, 2000] Ortengren U., Elgh U. and Spasenoska V., Water sorption and flexural properties of a composite resin cement after water storage, Int J Prosthodontics, 13 (2), (2000): 141-147.

[Osorio *et al.*, 2005] Osorio R., Erhardt M.C.G., Pimenta L.A.F., Osorio E. and Toledano M., EDTA Treatment Improves Resin-Dentin Bonds' Resistance to Degradation, J Dent Res, 84 (8), (2005): 736-740.

[Øysæd and Ruyter, 1986a] Øysæd H. and Ruyter I.E., Composites for use in posterior teeth. Mechanical properties tested under dry and wet conditions, J Biomed Mater Res, 20, (1986a): 261-271.

[Øysæd and Ruyter, 1986b] Øysæd H. and Ruyter I.E., Water sorption and filler characteristics of composites for use in posterior teeth, J Dent Res, 65, (1986b): 1315-1318.

[Øysaed *et al.*, 1988] Øysaed H., Ruyter I.E. and Kleven U.S., Release of formaldehyde from dental composites, J Dent Res, 67, (1988): 1289-1294.

[Pallav *et al.*, 1989] Pallav P., de Gee A.J., Davidson C.L., Erickson R.L. and Glasspoole E.A., The influence of admixing microfiller to small-particle composite resin on wear, tensile strength, hardness and surface roughness, J Dent Res, 68, (1989); 489-490.

[Papadogianis *et al.*, 2003] Papadogianis Y., Boyer D.B., Helvatjoglu-Antoniades M., Lakes R.S. and Kapetanios C., Dynamic viscoelastic behavior of resin cements measured by torsional resonance, Dent Mater, 19 (6), (2003): 510-516.

[Papadogianis *et al.*, 1984] Papadogianis Y., Boyer D.B. and Lakes R.S., Creep of conventional and microfilled dental composites, J Biomed Mater Res, 18, (1984): 15-24.

[Peutzfeld, 1997] Peutzfeld A., Resin composites in dentistry: the monomer systems, Eur J Oral Sci, 105, (1997): 97-116.

[Phillips, 1982] Phillips R.W., Science of Dental Materials, 8th ed. Toronto, W.B. Saunders Co. (1982).

[Pilliar *et al.*, 1987] Pilliar R.M., Vowles R. and Williams D.T., The effect of environmental aging on the K_{1C} of dental composites, J Dent Res, 66, (1987): 722-726.

[Pilliar *et al.*, 1986] Pilliar R.M., Smith D.C. and Maric B., K_{1C} of dental composites using the short-rod K_{1C} test, J Dent Res, 65, (1986): 1308-1314.

[Powers and Bayne, 1992] Powers J.M. and Bayne S.C., Friction and wear of dental Materials, ASM Handbook, Vol. 18, ASM International, (1992): 665-681.

[Prakki *et al.*, 2009] Prakki A., Pereira P.N.R. and Kalachandra S., Effect of propionaldehyde or 2,3-butanedione additives on the mechanical properties of Bis-GMA analog-based composites, Dent Mater, 25 (1), (2009): 26-32.

[Pukanszky and Voros, 1993] Pukanszky B. and Voros G., Mechanism of Interfacial Interactions in Particulate Filled Composites, Composite Interfaces, 1 (5), (1993): 411-427.

[Ramalho and Antunes, 2007] Ramalho A. and Antunes P.V., Reciprocating wear test of dental composites against human teeth and glass, Wear, 263 (7-12), (2007): 1095-1104.

[Ramalho and Miranda, 2006] Ramalho A. and Miranda J.C., The relationship between wear and dissipated energy in sliding systems, Wear, 260, (2006): 361-367.

[Ramalho and Antunes, 2005] Ramalho A. and Antunes P.V., Reciprocating wear test of dental composites: effect on the antagonist, Wear, 259 (7-12), (2005): 1005-1011.

[Ramalho *et al.*, 2006] Ramalho A., Antunes P.V., Carvalho M.D.B., Gil H. and Rocha J., Mechanical Properties of Particle Reinforced Resin Composites, Materials Science Forum, Vol. 514-516, (2006): 619-623.

[Ramalho, 2004] Ramalho A., Study of the relationships friction-contact stresses using load scanner tests, Proc of 11th Nordic Symposium on Tribology, Tromso, Noruega, June, (2004): 699-707.

[Raptis *et al.*, 1979] Raptis C.N., Fan P.L. and Powers J.H., Properties of Microfilled and Visible Light Cured Composite Resins, J Am Dent Assoc, 99, (1979): 631-633.

[Rasmussen *et al.*, 1976] Rasmussen S.T., Patchin R.E., Scott D.B. and Heuer A.H., Fracture properties of human enamel and dentin, J Dent Res, 55, (1976): 154-164.

[Rizkalla and Jones, 2004] Rizkalla A.S. and Jones D.W., Indentation fracture toughness and dynamic elastic moduli for commercial feldspathic dental porcelain materials, Dent Mater, 20, (2004): 198-206.

[Roberts and Shaw, 1984] Roberts T.A. and Shaw D.J., Cure Profiles of Photoinitiated Microfilled Composites by Laser Raman Spectroscopy, J Dent Res, 63, (1984): 265, Abst. No. 1098.

[Rodrigues *et al.*, 2008] Rodrigues Jr. S.A., Ferracane J.L. and Della Bona A., Flexural strength and Weibull analysis of a microhybrid and a nanofill composite evaluated by 3- and 4-point bending tests, Dent Mater, 24 (3), (2008): 426-431.

[Rodrigues *et al.*, 2007] Rodrigues Jr. S.A., Zanchi C.H., de Carvalho R.V. and Demarco F.F., Flexural strength and modulus of elasticity of different types of resin-based composites, Brazilian Oral Research, 21 (1), (2007): 16-21.

[Roulet, 1987] Roulet J.F., Degradation of dental polymers, Basel-New York: Karger PressCo, (1987): 60-90.

[Ruddell *et al.*, 2002] Ruddell D.E., Maloney M.M. and Thompson J.Y., Effect of novel filler particles on the mechanical and wear properties of dental composites, Dent Mater, 18, (2002): 72-80.

[Ruyter and Øysæd, 1987] Ruyter I.E. and Øysæd H., Composites for use in posterior teeth: Composition and conversion, Journal of Biomedical Materials Research, 21 (1), (1987): 11-23.

[Ruyter and Svendsen, 1978] Ruyter I.E. and Svendsen S.A., Remaining Methacrylate Groups in Composite Restorative Materials, Acta Odontol Scand, 36, (1978): 75-82.

[Ryge *et al.*, 1961] Ryge G., Foley D.E. and Fairhurst C.W., Micro-indentation Hardness, J Dent Res, 40, (1961): 1116-1126.

[Sabbagh *et al.*, 2004] Sabbagh J., Ryelandt L., Bacherius L., Biebuyck J.J., Vreven J. and Lambrechts P., Characterization of the inorganic fraction of resin composites, J Oral Rehabil, 31, (2004): 1090-1101.

[Sabbagh, 2002] Sabbagh J., Vreven J. and Leloup G., Dynamic and static moduli of elasticity of resin-based materials, Dent Mater, 18 (1),(2002): 64-71.

[Said, 2000] Said J., Wear behavior of dental Ceramics, 7th Portuguese Conference on Tribology, Porto, June, (2000).

[Sakaguchi *et al.*, 2004] Sakaguchi R.L., Wiltbank B.D. and Murchison C.F., Prediction of composite elastic modulus and polymerization shrinkage by computational micromechanics, Dent Mater, 20, (2004): 397-401.

[Sakaguchi *et al.*, 2002] Sakaguchi R.L., Shah N.C., Lim B.S., Ferracane J.L. and Borgersen S.E., Dynamic mechanical analysis of storage modulus development in light-activated polymer matrix composites, Dent Mater, 18, (2002): 197-202.

[Santerre *et al.*, 2001] Santerre J.P., Shalii L. and Leung B.W., Relation of dental composite formulations to their degradation and the release of hydrolyzed polymeric-resin derived products, Crit Rev Oral Biol Med, 12 (2), (2001):136-151.

[Sarrett *et al.*, 2000] Sarrett D.C., Coletti D.P. and Peluso A.R., The effects of alcoholic beverages on composite wear, Dent Mater, 16, (2000): 62-67.

[Sawa, 1993] Sawa N., The effect of filler shape and size of resin composite on fracture toughness, J Jpn Conserv Dent, 36, (1993): 507-518.

[Seghi *et al.*, 1991] Seghi R.R., Rosenstiel S.F. and Bauer P., Abrasion of human enamel by different dental ceramics in vitro, J Dent Res, 70, (1991): 221-225.

[Shah, 2008] Shah M.B., Mechanistic Aspects of Fracture and Fatigue in Resin Based Dental Restorative Composites, Dissertation Submitted to Oregon State University, (2008).

[Shahdad *et al.*, 2007] Shahdad S.A., McCabe J.F, Bull S., Rusby S. and Wassell R.W., Hardness measured with traditional Vickers and Martens hardness methods, Dent Mater, 23, (2007): 1079-1085.

[Shortall *et al.*, 2002] Shortall A.C., Hu X.Q. and Marquis P.M., Potential countersample materials for in vitro simulation wear testing, Dent Mater, 18, (2002): 246-254.

[Sideridou *et al.*, 2007] Sideridou I.D., Karabela M.M. and Bikiaris D.N., Aging studies of light cured dimethacrylate-based dental resins and a resin composite in water or ethanol/water, Dent Mater, 23 (9), (2007): 1142-1149.

[Smith and Knight, 1984] Smith B.G.N. and Knight J.K., A comparison of patterns of tooth wear with aetiological factors, Br Dent J, 157, (1984): 16-19.

[Smith, 1989] Smith B.G.N., Toothwear: aetiology and diagnosis, Dent Update, 16, (1989): 204-212.

[Smith, 1985] Smith D.C., Posterior composites Resin Dental Restorative Materials, Vanherle G., Smith D.C. (Eds.). Amsterdam: Peter Szulc, (1985): 47-60.

[Söderholm and Richard, 1998] Söderholm K.-J.M. and Richard N.D., Wear resistance of composites: a solved problem? General Dentistry, 46, (1998): 256-263.

[Söderholm and Roberts, 1990] Söderholm K.-J.M. and Roberts M.J., Influence of water exposure on the tensile strength of composites, J Dent Res, 69, (1990): 1812-1816.

[Söderholm *et al.*, 1996] Söderholm K.-J.M., Mukherjee R. and Longmate J., Filler leachability of composites stored in distilled water or artificial saliva, Journal of Dental Research, 75 (9), (1996): 1692-1699.

[Söderholm *et al.*, 1984] Söderholm K.-J.M. and Zigan M., , Hydrolytic degradation of dental composites, J Dent Res, 63 (19), (1984): 1248-1254.

[Söderholm, 2010] Söderholm K.-J.M., Review of the fracture toughness approach, Dent Mater, 26, (2010): e63-e77.

[Söderholm, 1985] Söderholm K.-J.M., Filler systems and resin interface in posterior composite resin dental restorative materials, Vanherle G., Smith DC, (Eds.). Utrecht: Peter Szulc, (1985): 139-160.

[Srivicharnkul *et al.*, 2005] Srivicharnkul P., Kharbanda O.P., Swain M.V., Petocz P. and Ali Darendeliler M., Physical properties of root cementum: Part 3. Hardness and elastic modulus after application of light and heavy forces, American Journal of Orthodontics and Dentofacial Orthopedics, 127 (2), (2005): 168-176.

[Stookey, 2008] Stookey G.K., The effect of saliva on dental caries, J Am Dent Assoc, 139, (2008): 11S-17S.

[Strassler *et al.*, 2005] Strassler H.E., Porter J., Serio C.L., Contemporary treatment of incipient caries and the rationale for conservative operative techniques, Dent Clin North Am, 49 (4), (2005): 867-887.

[Suansuwan and Swain, 2001] Suansuwan N. and Swain M.V., Determination of elastic properties of metal alloys and dental porcelains, J Oral Rehabil, 28, (2001): 133-139.

[Sunnegardh-Gröberg *et al.*, 2009] Sunnegardh-Gröberg K., VanDijken J.W.V. and Funegard U., Selection of dental materials and longevity of replaced restorations in Public Dental Health clinics in northern Sweden, J Dent, 37, (2009): 673-678.

[Suzuki *et al.*, 1996] Suzuki S., Suzuki S.H. and Cox C.F., Evaluating the antagonist wear of restorative materials when placed against human enamel, JADA, 127, (1996): 74-80.

[Tabor, 2000] Tabor D., The hardness of metals, New York: Oxford University Press, (2000).

[Takeshige, 1994] Takeshige F., Fatigue crack propagation in composite resins, J Jpn Conserv Dent, 37, (1994): 31-49.

[Tanaka *et al.*, 1991] Tanaka K., Taira M., Shintani H. and Wakasa K., Residual monomers (TEGDMA and Bis-GMA) of a set visible-light-cured dental composite resin when immersed in water, J Oral Rehabil, 18, (1991): 353-362.

[Traebert *et al.*, 2005] Traebert J., Marcenes W., Kreutz J.V., Oliveira R., Piazza C.H. and Peres M.A., Brazilian dentists' restorative treatment decisions, Oral Health Prev Dent, 2005, 3 (1): 53-60.

[Tronstad, 1973] Tronstad L., Quantitative microradiography of intact and worn human coronal dentine, Archives of Oral Biology, 18 (4), (1973): 533-542.

[Truong and Tyas, 1988] Truong V.T. and Tyas M.J. Prediction of in vivo wear in posterior composite resins: A fracture mechanics approach, Dent Mater, 4, (1988): 318-327.

[Turssi *et al.*, 2005] Turssi C.P., Ferracane J.L., and Vogel K., Filler features and their effects on wear and degree of conversion of particulate dental resin composites, Biomaterials, 26, (2005): 4932-4937.

[Tyas *et al.*, 2000] Tyas M.J., Anusavice K.J., Frencken J.E. and Mount G.J., Minimal intervention dentistry: a review-FDI Commission Project 1-97, Int Dent J, (2000), 50 (1): 1-12.

[Tyas, 2005] Tyas M.J., Placement and replacement of restorations by selected practitioners, Aust Dent J, 50 (2), (2005): 81-89.

[Tyas, 1990] Tyas M.J., Correlation between fracture properties and clinical-performance of composite resins in class-IV cavities, Australian Dental Journal, 35 (1), (1990): 46-49.

[Tyldesley, 1950] Tyldesley W.R., The mechanical properties of human enamel and dentine, Br Dent J, 106, (1950): 269-278.

[Uctasli *et al.*, 1993] Uctasli S., Wilson H.G. and Zaimoglu L., Variables affecting the fracture toughness of resin-based inlay/onlay systems, J Oral Rehabi, 120, (1993): 423-431.

[United Nations Environment Programme, 2002] United Nations Environment Programme (UNEP) Chemicals, Global mercury assessment, Geneva, Switzerland, United Nations Environment Programme, (2002): 266.

[Uno and Asmussen, 1991] Uno S., and Asmussen E., Marginal adaptation of a restorative resin polymerized at a reduced rate, Scand J Dent Res, 99, (1991): 440-444.

[Urabe *et al.*, 2000] Urabe I., Nakajima M., Sano H. and Tagami J., Physical properties of the dentin-enamel junction region, Am J Dent, 13, (2000): 129-135.

[Van Meerbeek *et al.*, 1993] Van Meerbeek B., Willems G., Celis J.P., Roos J.R., Braem M. and Lambrechts P., Assessment by nano-indentation of the hardness and elasticity of the resin-dentin bonding area, J Dent Res, 72, (1993): 1434-1442.

[Van Noort, 1994] Van Noort R., Introduction to dental materials, Times Mirror International Publishers Limited, (1994): 5, 75, 89-90, 95.

[Vankerckhoven *et al.*, 1981] Vankerckhoven H., Lambrechts P., van Beylen M. and Vanherle G., Characterization of composite resins by NMR and TEM, J Dent Res, 60, (1981): 1957-1965.

[Van Nieuwenhuysen *et al.*, 2003] Van Nieuwenhuysen J.-P., D'Hoore W., Carvalho J. and Qvist V., Long-term evaluation of extensive restorations in permanent teeth, J Dent, 31, (2003): 395-405.

[Venhoven *et al.*, 1996] Venhoven B.M.A., de Gee A.J., Werner A. and Davidson C.L., Influence of filler parameters on the mechanical coherence of dental restorative resin composites, Biomaterials, 17, (1996): 735-740.

[Wahl, 2001] Wahl M.J., Amalgam: resurrection and redemption. Part 1: the clinical and legal mythology of anti-amalgam, Quintessence Int, 32 (7), (2001): 525-35.

[Wang *et al.*, 2002] Wang Y.L., Lin Z., Lin J.P., Peng J.H. and Chen G.L., Influence of sample surface condition on nano indentation experiment, Rare Metals, 21 (2), (2002): 131-142.

[Warfield *et al.*, 1968] Warfield R.W., Cuevas J.E. and Barnet F.R., Single specimen determination of Young's and bulk moduli, J Appl Polym Sci, 12, (1968): 1147-1149.

[Wassel *et al.*, 1994] Wassel R.W., McCabe J.F. and Walls A.W.G., Wear characteristics in a two-body wear test, Dent Mater, 10, (1994): 269-274.

[Watanabe *et al.*, 2008] Watanabe H., Khera S.C., Vargas M.A. and Qian F., Fracture toughness comparison of six resin composites, Dent Mater, 24 (3), (2008): 418-425.

[Watts, 1994] Watts D.C., Elastic moduli and visco-elastic relaxation, J Dent, 22, (1994): 154-158.

[Watts, 1992] Watts D.C., Materials Science and Technology, Vol. 14, Medical and Dental Materials. Editors Cahn R.W., Haasen P., Kramer E.J., VCH Publishers Inc., New York. Basel Cambridge, (1992): 214-217, 251-254.

[Wei *et al.*, 2011] Wei Y., Silikas, Zhang Z. and Watts D.C., Hygroscopic dimensional changes of self-adhering and new resin-matrix composites during water sorption/desorption cycles, Dent Mater, 27 (3), (2011): 259-266.

[Weiner *et al.*, 1990] Weiner J.A., Nylander M. and Berglund F., Does mercury from amalgam restorations constitute a health hazard? Sci. Total Environ, 99, (1990): 1-2.

[Wetton, 1984] Wetton R.E., Dynamic mechanical method in the characterization of solid polymers, Polym Test, 4, (1984): 117-129.

[Willems *et al.*, 1992] Willems G., Lambrechts P., Braem M., Celis G.P. and Vanherle G., A classification of dental composites according to their morphological and mechanical characteristics, Dent Mater, 8, (1992): 310-319.

[Willems *et al.*, 1991] Willems G., Lambrechts P., Braem M., Vuylsteke-Wauters M. and Vanherle G., The surface roughness of enamel-to-enamel contact areas compared with the intrinsic roughness of dental resin composites, J Dent Res, 70, (1991): 1299-1305.

[Willems, 1992] Williems G., Multi Standard Criteria for the Selection of Potential Posterior Composites, Ph.D. Thesis, Katholieke Universiteit, (1992): 2, 30-33, 44.

[Willytec, 2001] Willytec, Multifunctional chewing simulator — Instructions of use, (2001): 1-39.

[Wolff *et al.*, 2007] Wolff M.S., Allen K. and Kaim J., A 100-year journey from GV Black to minimal surgical intervention, Compend Contin Educ Dent, 28 (3), (2007): 130-134.

[Wolter *et al.*, 1994] Wolter H., Storch W. and Ott H., New inorganic/organic copolymers (ORMOCERs) for dental applications, Mat Res Soc Symp Proc, 346, (1994): 143-149.

[Wu and McKinney, 1982a] Wu W. and McKinney J.E., Influence of chemicals on wear of dental composites, J Dent Res, 61 (10), (1982): 1180-1183.

[Xu *et al.*, 2004] Hockin H., Xu K., Quinn J.B., Giuseppetti A.A, Eichmiller F.C., Parry E.E. and Schumacher G.E., Three-body wear of dental resin composites reinforced with silica-fused whiskers, Dent Mater, 20 (3), (2004): 220-227.

[Xu *et al.*, 2003a] Xu H.H.K., Schumacher G.E., Eichmiller F.C., Peterson R.C., Antonucci J.M. and Mueller H.J., Continuous-fiber preform reinforcement of dental resin composite restorations, Dent Mater, 19 (6), (2003): 523-530.

[Xu *et al.*, 2003b] Xu H.H.K, Quinn J.B, Smith D.T., Giuseppetti A.A. and Eichmiller F.C., Effects of different whiskers on the reinforcement of dental resin composites, Dent Mater, 19 (5), (2003): 359-367.

[Xu *et al.*, 2000] Xu H.H.K., Smith D.T., Schumacher G.E., Eichmiller F.C. and Antonucci J.M., Indentation modulus and hardness of whisker-reinforced heat-cured dental resin composites, Dent Mater, 16 (4),(2000): 248-254.

[Xu *et al.*, 1998] Xu H.H.K., Smith D.T., Jahanmir S., Romber E., Kelly J.R., Thompson V.P. and Relow E.D., Indentation damage and mechanical properties of human enamel and dentin, J Dent Res, 77, (1998): 472-480.

[Yap and Teoh, 2003] Yap A.U.J. and Teoh S.H., Comparison of flexural properties of composite restoratives using the ISO and mini-flexural tests, J Oral Rehabil, 30 (2), (2003): 171-177.

[Ye et al, 2009] Ye X., Qian H., Xu P., Zhu L., Longnecker M.P. and Fu H., Nephrotoxicity, neurotoxicity, and mercury exposure among children with and without dental amalgam fillings, International Journal of Hygiene and Environmental Health, 212 (4), (2009): 378-386.

[Yap *et al.*, 2004a] Yap A.U., Wang X., Wu X. and Chung S.M., Comparative hardness and modulus of tooth-colored restoratives: A depth-sensing microindentation study, Biomaterials, 25(11), (2004): 2179-2185.

[Yap *et al.*, 2004b] Yap A.U., Chung S.M., Rong Y. and Tsai K.T., Effects of aging on mechanical properties of composite restoratives: A depth-sensing micro-indentation approach, Oper Dent, 29 (5), (2004): 547-553.

[Yesil *et al.*, 2008] Yesil Z.D., Alapati S., Johnston W. and Seghi R.R., Evaluation of the wear resistance of new nanocomposite resin restorative materials, J Prosthet Dent, 99, (2008): 435-443.

[Yoshida *et al.*, 2002] Yoshida Y., Shirai K., Nakayama Y., Itoh M., Okazaki M., Shintani H., Inoue S., Lambrechts P., Vanherle G. and Van Meerbeek B., Improved Filler-Matrix Coupling in Resin Composites, J Dent Res, 81, (2002): 270.

[Zantner *et al.*, 2004] Zantner C., Kielbassa A.M., Martus P. and Kunzelmann K.H., Sliding wear of 19 commercially available composites and compomers, Dent Mater, 20, (2004): 277-285.

[Zheng *et al.*, 2003] Zheng J., Zhou Z.R., Zhang J., Li H. and Yu H.Y., On the friction and wear behaviour of human tooth enamel and dentin, Wear, 225, (2003): 967-974.