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Mechanical and wear behaviours of nano and microfilled polymeric composite: Effect of filler fraction and size.

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Highlights

- Relation between the filler volume fraction/particle size & mechanical properties;
- Relation between wear resistance and mechanical properties and the contact media;
- Wear performance comparison of micro and nanofiller in: sliding and abrasive media.

Abstract

The addition of ceramic reinforced material, SiC particles, to resin matrices, results in the improvement of the overall performance of the composite, allowing the application of these materials as tribo-materials in industries such as: automotive, aeronautical and medical. Particle-reinforced polymeric composites are widely used as biomaterials, for example as dental filler materials and bone cements. These reinforced composites have improved mechanical and tribological performance and have higher values of elastic modulus and hardness, and also reduce the shrinkage during the polymerization compared with resin matrices. However, the effect of the filler level in mechanical and tribological behaviour is not quite understood.

The aim of this work is to determine the influence of the particle volume fraction and particle size in the wear loss of the composites and their antagonists. Reciprocating wear tests were conducted using a glass sphere against resin polyester silica reinforced composite in a controlled medium, with an abrasive slurry or distilled water. For 6 μm average particle dimension, seven particles contents were studied ranging from 0 % to 46 % of filler volume fraction (FVF). Afterwards, filler volume fractions of 10 % and 30 % were selected; and, for these percentages, 7 and 4 average particle dimensions were tested and were evaluated regarding their wear behaviour, respectively. The reinforcement particle dimensions used ranged from 0.1 μm to 22 μm with the 10 % filler fraction, and for 30 % of filler content the range extended from 3 μm to 22 μm. The results allow us to conclude that in an abrasive slurry medium the composite abrasion resistance decreases with the increase of the particle volume fraction, in spite of the accompanying rise in hardness and elastic modulus. With constant FVF, and abrasive slurry, the composite wear resistance increases with increasing average particle dimension. In a distilled water medium and with several FVF values, the minimum wear was registered for a median particle content of 24 %. In this medium and with constant FVF the highest wear resistance occurred for average reinforcement particles of 6 μm. The removal mechanisms involved in the wear process are discussed, taking into account the systematic SEM observations to evaluate the wear mechanisms.

Keywords: Filler content and dimension; polymeric composites; wear resistance.

1. Introduction

In the past decade, scientists have shown great interest in organic-inorganic composites since their application has dramatically improved material properties [1-7]. A composite material can provide superior and unique mechanical and physical properties because it combines the most desirable properties of its constituents while suppressing their least desirable properties. At present, composite materials play a key role in biomedical applications, the aerospace industry, automobile industry and other engineering applications, as they exhibit outstanding performance.

The attractive improvements include heat resistance, radiation resistance, mechanical and electrical properties, which usually result from the synergistic effect between organic and inorganic components. The effects of different reinforcement particles on the properties of polymers vary widely. To achieve the expected improvement by adding particles and understanding how these nano and micrometric reinforcements influence the organic matrix is fundamental.

The characteristics of filled resin composite result from a complex interplay between the properties of the individual constituent phases; the resin, the filler and the interfacial region. It is evident that the mechanical and tribological properties of composites are affected by a number of parameters such as: size, shape, aspect ratio and distribution of the particle reinforcements. This review will discuss how some of these parameters affect the experimentally observed macroscopic mechanical behaviour of particulate-filled polymers.

The full potential performance of glass and ceramic/resin composite in dental restorative materials may not yet have been achieved because the current composite materials cannot completely withstand the aggressive environment of the oral cavity.

Besides the volume and type of filler loading, the type of resin system can also influence the strength of the effect of variables such as the volume fraction of the inorganic filler, in addition to which the particle size/distribution and surface area are known to have a significant effect on the properties of composite materials. The investigation of these effects by controlled experimental studies in which the variables

are altered systematically can provide important insights into the behaviour of such systems.

Commercial composites are useful if it is necessary to compare their overall performance but never to understand how the particles and/or components influence their behaviour. This is because it is not possible to vary the reinforcement particle content or dimensions. Therefore, in order to use a parametric study and to determine the influence of the volume fraction and average particle dimension on the wear behaviour of reinforced resin composites (restorative composite material, for example), no commercial restorative materials can be used. Rueggeberg *et al*. [8] pointed out that, with the use of commercial restoratives, it was impossible to discriminate between the effect of particle size and that of filler loading. This uncertainty is mainly for compositional reasons, in the different commercial materials tested.

In the last decades the size of the filler particles in dental resin composite materials has decreased considerably, from 8-30 μm in traditional composites to 0.7-3.6 μm for modern small-particle composites [9]. This is mainly for medical or functional reasons. Larger reinforcement particles did not allow a very smooth surface, which led to increasing plaque retention, gingival irritation and negative aesthetic impacts.

Results presented by Pallav *et al*. compared a series of composites in which an increasing amount of the small-particle filler (3 μm) was replaced by microfine pyrogeneous silica (0.04 μm diameter) [10]. This showed that, of four evaluated parameters (tensile strength, hardness, in vitro wear and roughness), only 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. Other papers showed that mechanical properties such as Young's modulus and composite hardness depend mainly on the filler load [11-13].

Fillers in resin matrices are of great importance for their role in the wear resistance and mechanical properties of particulate resin composites, with several reports of theoretical and experimental evidence [14-16]. Thus, the microstructure of composites in terms of the arrangement, size, geometry, and volume fraction of particles [15-18] was the main goal of these investigators.

Only a few systematic studies regarding the effect of particle size and shape have been published [15, 16, 19], and it has been suggested that finer particles for a fixed-volume-fraction of filler result in decreased interparticle spacing and reduced wear [20].

Although manufacturers have produced composites with different filler sizes and distributions in order to enhance performance, there is no systematic study investigating the effect of these parameters on both mechanical and tribological performance.

2. Experimental work

As has been established, the influence of particles in composites cannot be studied using commercial products. Furthermore, a parametric approach has to be used. In the present work, a first study is performed in order to determine the influence of the volume fraction on the wear resistance of composites in two media: abrasive slurry and distilled water. The evaluation of the filler volume fraction on the mechanical properties of these composites has been published elsewhere [21]. With the assessment of the mechanical properties, the second stage of the work concerns the influence of the average particle dimension, for two distinct filler volume fractions: 10 % and 30 %, in abrasive slurry and distilled water media; while keeping the filler volume fraction constant, the effect of the filler's average particle size dimension was evaluated. Initially the intention was to study only one percentage of filler volume fraction (30 % of FVF), but as nano-particles are now a trend it was decided to include them, and due to their characteristic very high particle surface area, it was impossible to attain the initial volume fraction using the same mixing method. Therefore, in order to keep the same variables constant, i.e., resin, particle material and mixing procedure, the filler volume fraction corresponding to the maximum capacity of resin and silica nano-particles was 10 % in volume.

Materials

The composite material used in the present work was an unsaturated polyester resin (U-Pol Plastik, London, UK) which was reinforced with particles of high purity silica. The average particle size dimensions used in this work were: 3, 6, 16 and 22 μm for the 30 % filler fraction in volume, and 0.1, 1, 2, 3, 6, 16 and 22 μm for the 10 % filler fraction. The resin was processed according to the manufacturer's information using 2 % in volume of methyl-ethyl-ketone-peroxide (MEKPO) to initiate the polymerization. A pre-determined volume of resin was put in a container, the hardener was added and then the mixture was well stirred; finally, the volume of silica particles was progressively added and stirred continuously. To ensure the homogeneity of the desired filler volume fractions, larger volumes of the two component mixture were always used in the preparation of specimens.

The produced mixture was put in aluminium moulds. In order to attain a homogeneous cure, all the specimens were placed in an oven at 40 ºC for 8 hours. After removal from the mould, specimens were polished until the surfaces became imperfection-free and the dimensions of the specimens were homogeneous. As this type of resin tends to increase hardness as aging time increases, a previous study was done to determine the number of storing days necessary to guarantee the stabilization of the hardness value. After 20 days, it was possible to observe that no noticeable change in the hardness had occurred. Table 1 summarizes the composition of the tested resin composites, regarding the average particles dimensions and filler volume fractions.

Wear characterization

The selected wear test was of the reciprocating type, with plane-sphere contact geometry. This type of contact was selected to avoid misalignments and also because it allows an easy evaluation of the wear of both materials in contact. The composite materials were processed and polished to obtain flat-shaped specimens. The sliding behaviour of the materials in contact was investigated in two solution environments (Fig. 1): distilled water and an abrasive solution [22]. The abrasive solution, an aqueous suspension of 15 % volume of ceramic microspheres (3M Zeeospheres G-200) with an average diameter of 4 μm and a hardness of 7 Mohs was used as abrasive slurry. During tests the slurry was mechanically stirred.

Fig. 1 indicates the elements that comprise the reciprocating apparatus. The glass sphere (7) is connected to the moving stage (2) and is kept in permanent contact with 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 newtons (N). A harmonic wave, generated by an eccentric rod mechanism that was set with a stroke length of 2 mm and frequency of 1 Hz [23], imposed a reciprocating movement on the upper specimen carrier (2). The composite specimen was placed in a container, which was filled with distilled water or abrasive solution (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, allowing the assessment of the friction force along the test.

The glass sphere is connected to the moving stage and is kept in permanent contact with the horizontal surface of the stationary specimen; a soft glass sphere (hardness 4,000 MPa) with 10 mm diameter was selected because it is an inert material which does not produce adherent oxide layers. Table 2 summarizes the characteristics of the wear tests and conditions. Each test condition was replicated at least 3 times.

The duration of the distilled water tests was 10,500 cycles, while those with the abrasive slurry had 2,600 cycles. All the tests were executed with 1 Hz frequency and harmonic wave and an applied normal load of 5 N.

As concerns the number of cycles, for the abrasive tests the duration is shorter due to the fact that the associated damage is greater. The duration of 2,600 cycles allows the system to create sufficient wear volume in order to be visualized and measured on both the composites and the counterbody.

In order to measure the volume of composite material removed by wear, a laser Rodenstock RM600 (Optische Werke G. Rodenstock, München, Germany) was used. This equipment scanned across the wear scar area of all the tested specimens, obtaining 3-D profiles which allow the determination of the volume removed by wear of the composite material. For the data visualization, analysis and processing, Gwyddion software was used; this software is typically used for data originating from scanning probe microscopy techniques (like AFM), but it may also be used for the

analysis of profilometry data. The wear volume of the counterbody -glass sphere- had a spherical-caps shape and the radius, *r*, of the circular projected area 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 the sphere radius, *R*, were then used to calculate the depth, *h*, and volume, *V*, of removed material, using equations 1 and 2 respectively:

$$h = R - \sqrt{R^2 - r^2} \quad (1)$$

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

The surfaces of the wear marks were examined by SEM. All of the tested specimens were sputter-coated with gold in order to allow a better observation. The images were attained with secondary and backscattered electrons to make it possible to see the dimension and distribution of the particles and identify the wear mechanisms that occurred in the tests.

Mechanical characterization

For a complete understanding of the influence of particles in the tribological behaviour, some complementary mechanical tests were done. The mechanical evaluation included micro-hardness, elastic modulus and flexural strength. The specimen geometry used to determine the mechanical properties was a parallelepiped 50 mm long, 6 mm wide and 4 mm thick.

To determine hardness a Vickers micro-indentation test was performed using Struers Duramin testing equipment. A 1.962 newtons (N) load was applied for a period of 40 seconds; ten indentations were made on the surface of each specimen.

A bending test was carried out by four-point-flexure tests performed according to standard ASTM C1161-13. Samples were loaded with an Instron machine at a speed rate of 0.5 mm/min using a support span of 40 mm and a loading span of 20 mm. The flexural strength is calculated using equation (3). *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 (*WOF*) was calculated by numerical integration as the area below the flexural curve that can be used as a comparative value of the toughness.

$$S = \frac{3PL}{4dt^2} \quad (3)$$

The elastic modulus was measured by the impulse excitation technique as described by Braem *et al.* [24, 25] and according to the standard ASTM C1259-14. Each specimen was set in free flexural vibration by a light mechanical impulse. The fundamental frequency of the first flexural vibration mode was determined analyzing the vibration response by Fast Fourier Transform.

Elastic modulus was calculated as a function of the frequency of the first flexural vibration mode using equation (4);

$$E = 0.9465\left(\frac{mf_t^2}{d}\right)\left(\frac{l^3}{t^3}\right)T_1 \quad (4)$$

where l, d and t are: the length, width and thickness of the bar, m is the mass and f_t is the fundamental frequency of the first flexural vibration mode. According to the ASTM standard, T_1 is a correction factor to take into account the finite dimensions of the specimen. For the calculation of T_1 a constant Poisson ratio of 0.3 was assumed.

3. Results and discussion

3.1. Effect of filler volume fraction

On mechanical properties

In order to determine the influence of the reinforcement particle volume fraction of the resin composites, a 6 µm SiO_2 average particle dimension was chosen and the reinforcement particle contents ranged from 10 to 46 %. Resin specimens without particle reinforcement were included to serve as a reference.

Scanning microscope observation of fractured and polished surfaces of composites allows us to conclude that the interface bond between the matrix and the particles is very effective. The composites display a good homogeneity, as shown in Fig. 2, for 16 % and 37 % volume of particles of filler.

Concerning mechanical behaviour, Fig. 3 summarizes the obtained results. Both hardness and elastic modulus increase approximately linearly with the rise of the particle level [26, 27]. Nevertheless, the toughness, work-of-fracture, decreases significantly with increasing particle percentage.

On wear behaviour - abrasive solution tests

Concerning the wear in the abrasive solution environment, both composites and glass spheres display an increase of wear with rising particle content. The growth of the wear volume with increasing particle content is approximately linear (Fig. 4), with solid symbols for the composite and open symbols for the antagonist. The results seem to be inconsistent at first glance because, as displayed in Fig. 3, both hardness and Young's modulus rise significantly with the particle increase, and therefore an increase in the abrasion resistance should also be expected. The simplest models forecast an increase of the wear resistance with increased hardness; however, in the case of multiphase materials, both toughness and hardness must be considered, especially with abrasion produced by hard particles, as in this case. For dental composites reinforced with 2 μm particles, Li *et al.* [28] also report increasing wear with increasing particle content. In agreement with the present results, other authors report that for some testing conditions the lower filler contents display the maximum wear resistance [29].

The plot of composites' wear against toughness, considering toughness to be the energy absorbed during a 4-point bending test [30], is well correlated with an exponential relation (Fig. 5a). The relation between wear and toughness is of the type: $W = 0.1505 \cdot e^{-0.001 \cdot WOF}$, where W represents the wear volume and WOF the composite toughness. For small filler percentages and therefore high toughness values there is little variation of composites' wear. For high filler content percentages (>16 %), the small toughness values strongly influence the composites' wear, decreasing the wear resistance. Resin specimen results were not used to establish the previous relation, represented by the filled marker in Fig. 5a.

The relationship between the hardness and the elastic modulus, H/E, is a well-established parameter to forecast the wear resistance of different types of materials [31-34]. For the composites under study, the wear volume displays a negative linear

evolution with the increase of *H/E* (Fig. 5b). Even though both the elastic modulus and the hardness increase with the rise in the particle level, the relationship *H/E* varies significantly, decreasing with increasing particle content. The wear decreases with the rise of *H/E*, explaining similar small values of wear obtained for composites with 0 %, 10 % and 12 % of particles content. These composites present values of wear of less than 0.02 mm^3.

This evolution could also be clarified when observing the wear surfaces by SEM (Fig. 6), and a significant number of fractured particles can be observed in the wear scars, in Fig. 6a and 6b, where arrows mark the fractured particles. It seems that the low toughness of the silica increases the amount of material removed, which explains the rise of wear with the particle level.

On wear behaviour - distilled water tests

For tests in a distilled water medium, different amounts of wear were generated by the glass sphere on the various tested composites. Fig. 7 shows values of wear volume obtained for composites with different filler volume fractions, ranging from 0 % to 46 %. Wear volumes for composites with 37 % and 46 % particle content are enormous, respectively 0.38 mm^3 and 1.48 mm^3 (Fig. 7), compared with the rest. Wear volume for the 46 % content 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 specimens with 24 % particle content registered the least material removed by wear, but the composite with a particle content of 30 % reached a similar value.

Regarding the antagonist's glass sphere wear, tested against the various composite materials, the range on wear volume is not as wide as that registered for composite wear volumes. Again, values of antagonist wear tested against composites with 46 % and 37 % particle content are higher than the rest, even though the difference between 46 % and resin is "only" 10 times, while, for the antagonist with the least wear volume the ratio is about 30 times, identical behaviour was determined by Wetzel *et al.* [35] The glass sphere with the least wear volume was the one tested against composite with 12 % particle content; however, the difference registered between the

antagonists tested against composites of 10 %, 12 %, 16 %,24 % and 30 % is very small (Fig. 7).

Composites' wear scars from reciprocating tests in slurry, observed by SEM, revealed larger wear marks. Fig. 8 shows two abraded surfaces of composites with 0 and 12 % particle content, where some abrasive particles and micro glass spheres attached to the composite surface may be observed.

For reciprocating wear tests, scratches abrade particles and the matrix (Fig. 9). Also, in several specimens tested with distilled water a thin layer forms and agglomerates resin debris, as noticed especially in the specimens without particles (Fig. 9b).

The main difference, in terms of surface morphology, between the two types of environment is 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. 9a it is possible to see this compact and homogeneous layer with cracks.

3.2. Variation effect of particle dimension

Again a resin specimen served as reference for the composites used to evaluate the influence of average particle size in the wear behaviour of resin composite reinforced with SiO_2. Regarding the influence of the particle dimension, two filler volume fractions of 10 % and 30 % were used. These volume fractions were kept constant and the average particle size was varied. The same two test environments were considered: abrasive slurry and distilled water.

On mechanical properties

Concerning mechanical behaviour, Fig. 10a and 10b summarizes the obtained results for these composites. Both hardness and elastic modulus have higher values than resin, but with the increase in average particle dimension, while maintaining the same volume filler fraction, almost no variation occurred in the values of these two properties. The toughness of these composites is lower than for the resin and, for the same particle content, the rising particle dimension is accompanied by increasing WOF. When the WOF increases, consequently the toughness increases; for composites with higher average particle sizes the increment in fracture resistance is

due to the rise in the reinforcement particle distance, i.e. the increase in the mean free path between the brittle reinforcement particles. The toughening mechanism of particles is due to the increased debonding from the ductile polymeric matrix, and therefore an increase of energy for crack propagation and fracture. The increase in average filler size gives the filler dispersion on the polymer matrix, which is one of the most important factors determining the energy absorption mechanisms and hence the material fracture behaviour.

On wear behaviour - abrasive solution tests

10 % and 30 % filler volume fractions

Analysing the results of the reciprocating wear test with abrasive particles for 30 % filler content shows that the wear volume of resin is the smallest, whatever the particle dimensions. Composite wear resistance increases with increasing average particle size dimension. In abrasive sliding tests, composite specimens with larger particle dimensions tend to have less wear (Fig. 11).

Regarding the antagonist's body, this shows more wear when in sliding contact with composite specimens containing large particles. The glass sphere wear volumes do not show a very different volume of removed material when tested against 3 μm, 6 μm and 16 μm. Again, as for composite wear analysis, antagonist bodies in contact with polyester resin specimens tend to cause less material removal.

There is a clear tendency to a diminished wear volume of composites when the average particle size increases, while on the other hand the maximum antagonist wear was observed for the composite with the coarsest particles. Under testing conditions, the resin against the glass sphere is the material pair which shows the smallest volumes of material removed by wear.

Several authors [12, 35-38] present the "protection-hypothesis" to justify the reduction in abrasion; as the reinforcement particle distribution in terms of particle dimension has a wider range, the spaces between larger particles are occupied by smaller particles, thus decreasing the interparticle spacing and wear reduction. However, this was not observed in this study. In the present work, it was observed that friction is reduced through increased fracture toughness. Good stress-transfer at

the resin/filler interface improves the bond between the filler and matrix by increasing the filler surface area.

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

Regarding the 10 % filler volume fraction, the same trend was observed, and the best composite performance pair was the one with average filler particles of 22 μm (Fig. 12a). The best absolute values for composite and antagonist wear were from the polyester resin specimens against their antagonists. The results trend indicates, as shown for the 30 % filler volume fraction, that the increase in average filler particle dimensions tends to increase the wear resistance of the composite. The antagonist's wear volume does not vary greatly; when comparing the wear volumes of the antagonist against the composites, the differences registered range from 5 % to 19 % of the average wear volume of the glass spheres tested against the composite specimens with 22 μm filler particles (highest wear value of antagonist) [12]. The nano filled composite produces a very small amount of material removal from its antagonist but the highest value of wear of the composite material [15].

When comparing the wear results of composite material with 10 % and 30 % filler volume fraction (FVF), both percentages display the same tendency, a decrease in wear volume with increasing particle dimensions, and also an increase in composite wear volume with increasing filler content (Fig. 12b). All the wear volumes for 30 % FVF composites are higher than for 10 % FVF composites, as previously shown in Fig. 4.

This evolution could also be clarified by observing the wear surfaces under SEM (Fig. 13). No fractures are present at the abraded surface. Composite with smaller particle dimensions presents a smooth surface, and reinforcement particles are not detached from the matrix (Fig. 13a), [39]. In Fig. 13b and Fig. 13c composites with larger particles present deeper grooves, while particles still remain attached to the matrix.

On wear behaviour - distilled water tests

10 % and 30 % filler volume fractions

The results in Fig. 14 for reciprocating wear tests in a distilled water medium, for a 30 % filler volume fraction and unreinforced resin specimens, show high values of the composite wear for resin specimens and for specimens with 30 % filler and an average particle dimension of 22 μm. Specimens with particles of 6 μm and 16 μm have very similar wear volumes, 4.03 x 10^{-3} and 4.11 x 10^{-3} [mm^3], respectively. Specimens with average particles of 3 μm have volumes that are about 50 % higher. The resin specimen produced the highest wear values, 9.21 x 10^{-2} mm^3.

Regarding antagonist wear volumes, for the distilled water medium the minimum value was registered for glass sphere specimens tested against 6 μm composites specimens. As found for the composite materials, 3 μm, 6 μm and 16 μm have similar wear volumes. Antagonist materials tested against resin and 22 μm are characterized by the highest values for material removed.

Comparing the wear performance of composites with 30 % filler volume against the results obtained with 10 % filler volume for the same particle dimension in sliding wear tests with distilled water, 10 %/22 μm and 30 %/22 μm presented the same wear for composites tested, while specimens with 10 % in volume and average particle dimensions of 3 μm and 6 μm had much smaller wear volumes than specimens with 30 % filler content with the same particle dimension (Fig. 15). Regarding tests with 10 % filler content, 10 %/16 μm presents very high values of wear compared to 30 %/16 μm composite specimens. For both distinct filler contents, composites 10 %/6 μm and 30 %/6 μm are the ones with lowest wear volumes, as observed in the graph in Fig. 15.

In order to summarise the effect of filler content on the tribological behaviour of a polyester resin matrix reinforced with silica particles, Fig. 16 and Fig. 17 represent the wear volumes of composite removed in the reciprocating contact. Fig. 16 shows the amount of composite removed with an abrasive slurry solution, for a filler volume

fraction ranging from 0 to 46 % (average particle dimension of 6 μm) and for evaluating the effect of average filler size, using two volume filler fractions 10 % and 30 %.

Fig. 17 is similar to Fig. 16 but the medium in which the test was done was a distilled water solution.

When comparing, the same filler volume fraction and test conditions, all materials tested showed greater composite surface wear when exposed to the third-body medium then two-body wear [40]. Again, the columns represent the amount of material removed in reciprocating wear tests.

The surface morphology for reciprocating wear tests in an 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. 18). Due to the lower filler volume content, the resin layer observed in specimens with 10 % filler was not as clearly expressed, yet still noticeable.

For composite specimens with larger filler particles in the contact area, some places show greater degradation (Fig. 19a). Observing more closely, it is possible to see that the damage is produced in the sub-surface, causing fracture of this area (Fig. 19b). Similar situations occur in reciprocating contacts for 30 % filler volume content. Regarding 10 % filler, this phenomenon is evidenced only for specimens with average particle sizes of 16 μm and 22 μm. For specimens with nano particles, and a mixture of nano and micro particles, homogeneous wear can be seen [35].

4. Conclusions

The effect of filler volume fraction, (0–46 %) for constant filler size (6μm) and average filler size (0.1- 22 μm) for 10 % and 30 % filler volume fractions of polyester matrix composites was investigated in order to understand the effect of the particle level on wear behaviour under two sliding condition media; distilled water and abrasive slurry. The physical and mechanical properties of the composites were also evaluated in order to help explain the composites' wear behaviour.

Reciprocating tests in an abrasive solution medium were done against soft glass spheres, allowing the following conclusions:

1- The composites, with SiO_2 content ranging from 0 to 46 % vol., present a good homogeneity with a very effective bond between the matrix and the particles;

2- The composites, and also the counter-body glass spheres, display increasing wear with increasing particle volume content, and this wear growth is approximately linear for both composites and counter-bodies;

3- Hardness and elastic modulus increase linearly with the amount of reinforcement filler content. An exponential decrease is verified for WOF when the filler volume fraction increases;

4- The hardness/elastic modulus ratio, H/E, is linearly correlated with the amount of material removed by abrasive wear, decreasing the amount of material removed as H/E increases;

5- The low toughness of the silica leads to a fracture of the particles which increases the amount of material removed with the particle content. An exponential relation exists between the amount of material removed by wear and the work-of-fracture of the composites;

6- Increasing average particle dimension tends to decrease the volume removed by wear in the composite and increase it in the antagonist body. Considering the same particle dimensions but FVF of 10 % and 30 %, composites with the higher filler fraction showed more wear;

7- For the same FVF, the increase in the average particle dimension did not influence either hardness or elastic modulus;

8- Generally, the increase in particle size increased the fracture resistance of the composites, through the increase in the mean free path between the brittle reinforcement particles, inducing an increase in energy for crack propagation and fracture;

9- Nano particles did not show any noticeable advantages regarding composite wear compared with micro-particulate reinforced specimens.

Reciprocating tests in distilled water solution medium were conducted against soft glass spheres, allowing the following conclusions:

10- When the SiO_2 volume fraction is analysed from 0 to 46 % vol. (6 μm filler size), the FVFs which present the highest wear resistance are 24 % and 30 %. Filler volume fractions greater than 37 % have an exponential increase in wear;

11- Regarding average filler dimensions and considering the two filler volume percentages (10 % and 30 % FVF), smaller wear values are obtained from specimens with 6 μm particles. Resin specimens presented higher wear volumes than FVF of 10 % and 30 %.

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Figure captions

Fig. 1. Reciprocating equipment for sphere-plane contact; a) upper and lower specimen carrier, b) schematic of contact geometry and environment solution.

Fig. 2. Surface morphology of the composites with a particle volume fraction of 16 % and 37 %.

Fig. 3. The effect of volume particle content on: hardness ($HV_{0.2}$), elastic modulus (E) and work-of-fracture (WOF) [5].

Fig. 5. Composite abrasion wear volume against: a) composite toughness and resin specimen results; and b) relationship between hardness and elastic modulus, *H/E*.

Fig. 6. Wear scar morphology for composite with 30 % of SiO_2 volume content, magnification of 250X, with fractured particles indicated by arrows in the: a) centre and, b) border of the wear scar.

Fig. 7. Wear volumes of composite materials and their antagonists in a distilled water medium. Average particle content 6 μm, and filler volume fraction ranging from 0 % to 46 %.

Fig. 8. SEM observations for reciprocating tests with abrasive slurry: a) resin specimen; b) composite specimen with 12 % particle content.

Fig. 9. Reciprocating tests with distilled water: a) 46 % particle content, abrasion of the particles along with the matrix; b) 0 % particle content, with an adherent thin layer.

Fig. 10. Effect of average particle dimension on: hardness, elastic modulus and WOF, for filler volume fractions of: a) 10 %; and b) 30 %.

Fig. 11. Wear volume for reciprocating test in an abrasive slurry medium of composites with 30 % filler volume fraction and average particle dimensions of 3, 6, 16 and 22 μm.

Fig. 12. Composite materials in reciprocating wear tests in an environment with abrasive slurry: a) wear volumes of glass spheres and 10 % filler volume fraction with several average particle dimensions; and b) composite wear volumes for: 0 % (resin); 10 % and 30 % filler volume fraction (FVF).

Fig. 13. Composites morphology taken in wear scar for specimens with 30 % filler fraction and average particle dimensions of: a) 3 μm; b) 16 μm; and c) 22 μm.

Fig. 14. 30 % filler volume fraction composites with average particle dimensions of: 0 (resin), 3, 6, 16 and 22 μm and antagonist material wear volumes for reciprocating test in distilled water environment.

Fig. 15. Composite materials in reciprocating wear tests in distilled water medium against glass spheres: a) wear volumes of 10 % FVF composites with average particle dimensions of: 0 (resin), 0.1, 1, 2, 3, 6, 16 and 22 μm and antagonist glass spheres; b) composite wear volume comparison for: 0 % (resin), 10 % and 30 % filler volume fraction (FVF).

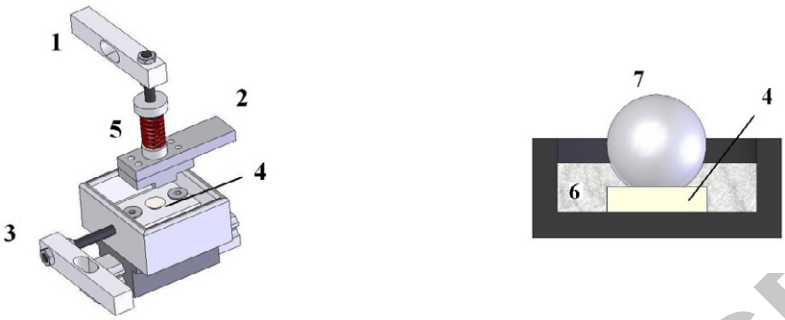
Fig. 16. Composite material wear volumes in reciprocating wear tests in abrasive

slurry medium against glass spheres for: constant filler average dimension (6 μm) and FVF of 10, 12, 16, 24, 30, 37 and 46 %; constant FVF (10 %) and average filler dimension 0.1, 1, 2, 3, 6, 16 and 22 μm and constant FVF (30 %) and average filler dimension 3, 6, 16 and 22 μm. Resin specimens served as reference and correspond to 0 % FVF and 0 μm average particle dimension.

Fig. 17. Composite material wear volumes in reciprocating wear tests in distilled water medium against glass spheres for: constant filler average dimension (6 μm) and FVF of 10, 12, 16, 24, 30, 37 and 46 %; constant FVF (10 %) and average filler dimension 0.1, 1, 2, 3, 6, 16 and 22 μm and constant FVF (30 %) and average filler dimension 3, 6, 16 and 22 μm. Resin specimens served as reference and correspond to 0 % FVF and 0 μm average particle dimension.

Fig. 18. Composites morphology of wear contact area for specimens in reciprocating distilled water medium: a) 10 %/16 μm; and b) 30 %/6 μm.

Fig. 19. Composites morphology taken in wear contact area for specimens with 10 % filler content in reciprocating distilled water environment, for specimens 10 %/16 μm: a) 100x and b) 1000x, magnification.



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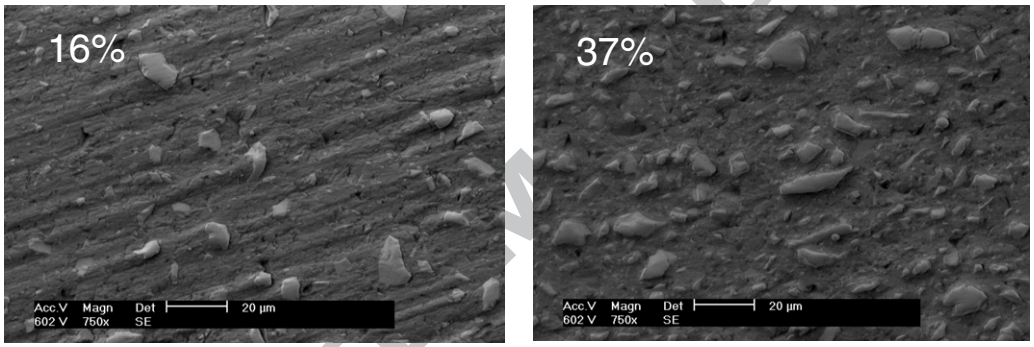

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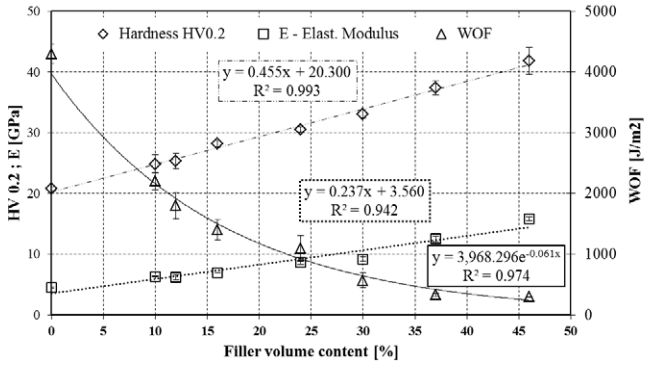

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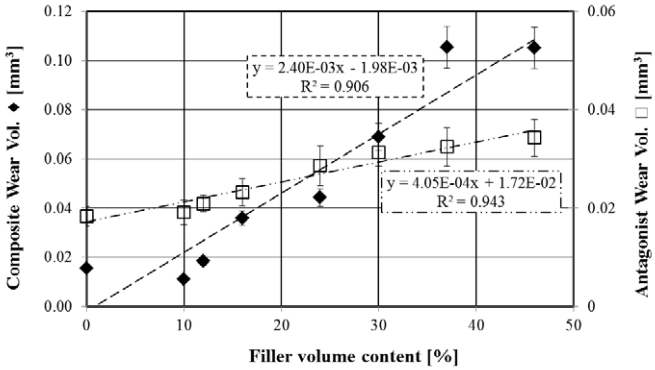
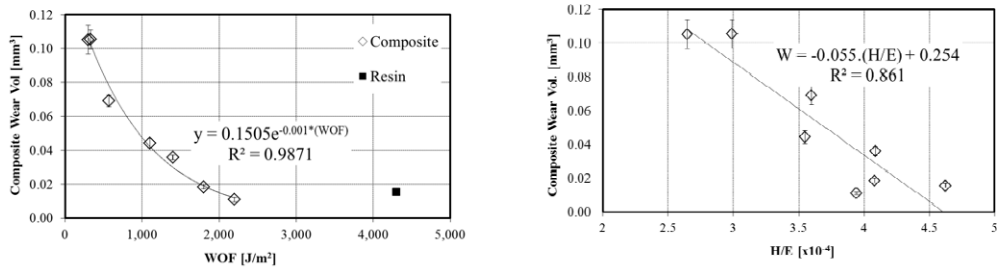


Fig. 4. Plot of wear volumes of composites and glass antagonists, as a function of composite filler content, tested in an abrasive solution medium.



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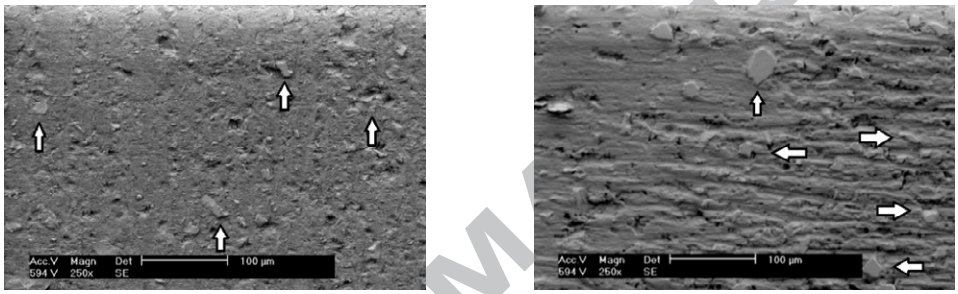

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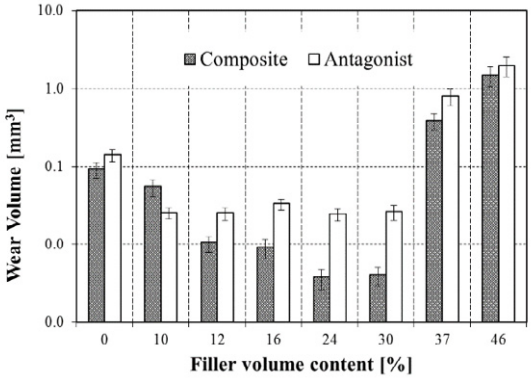

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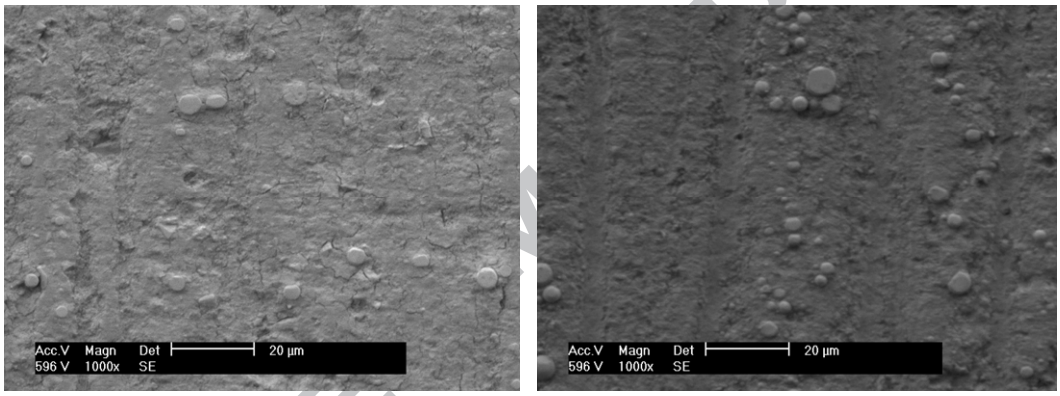

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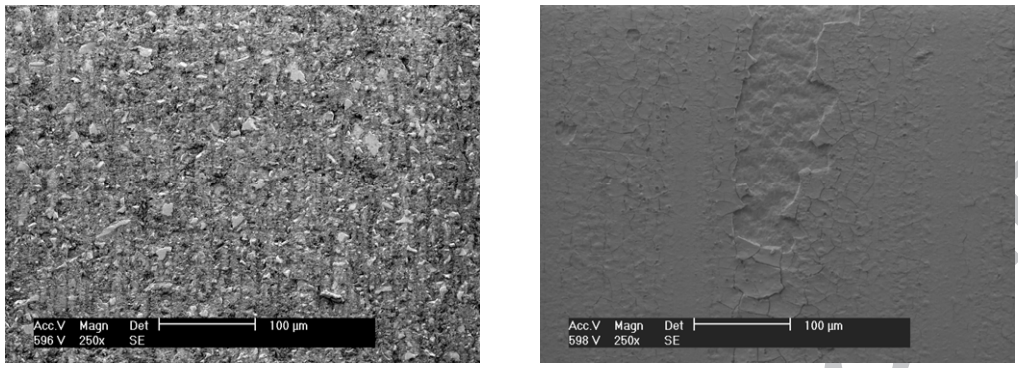

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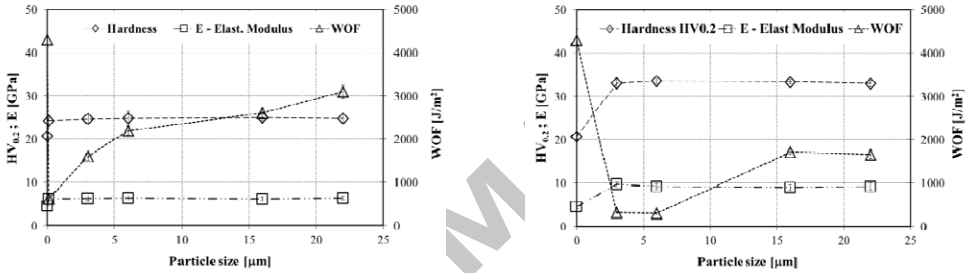

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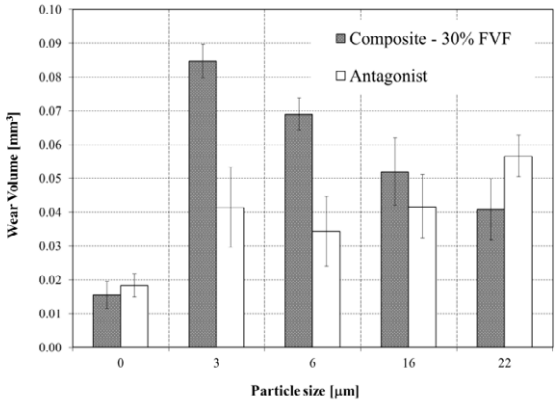

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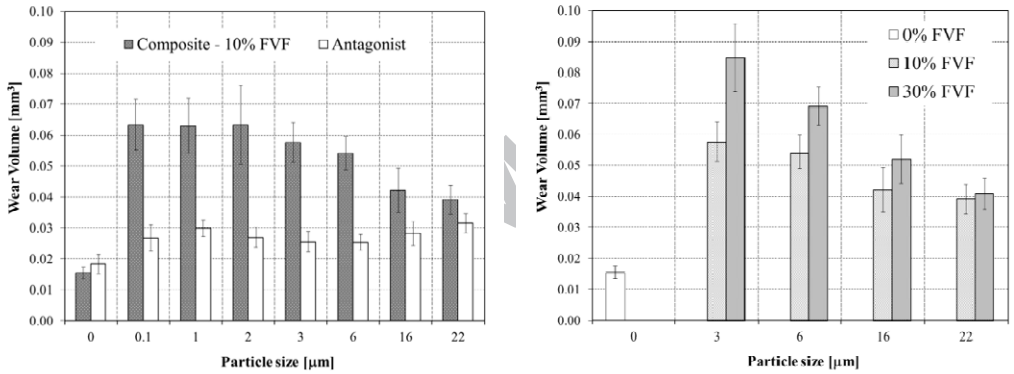

a) b)

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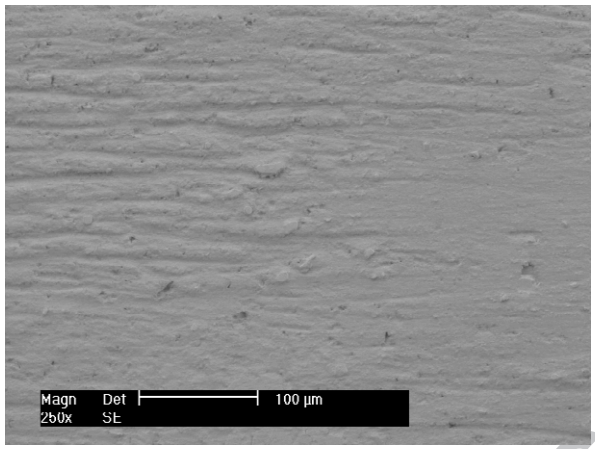

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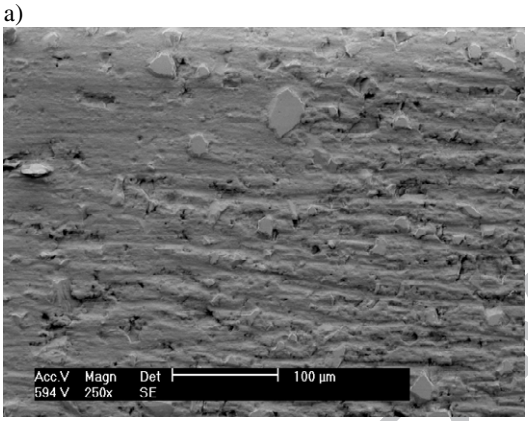

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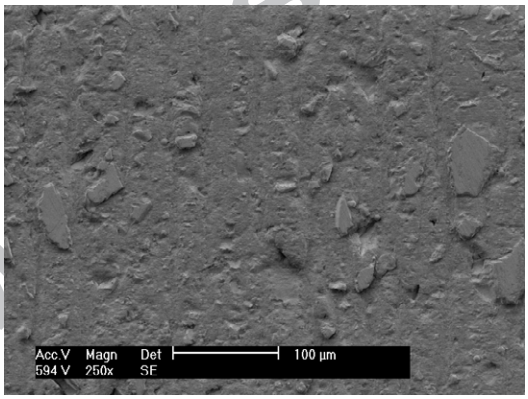

c)

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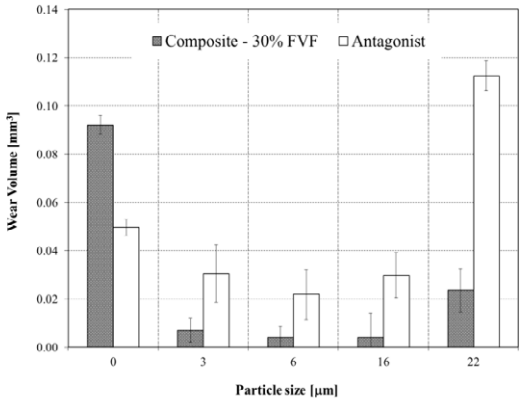

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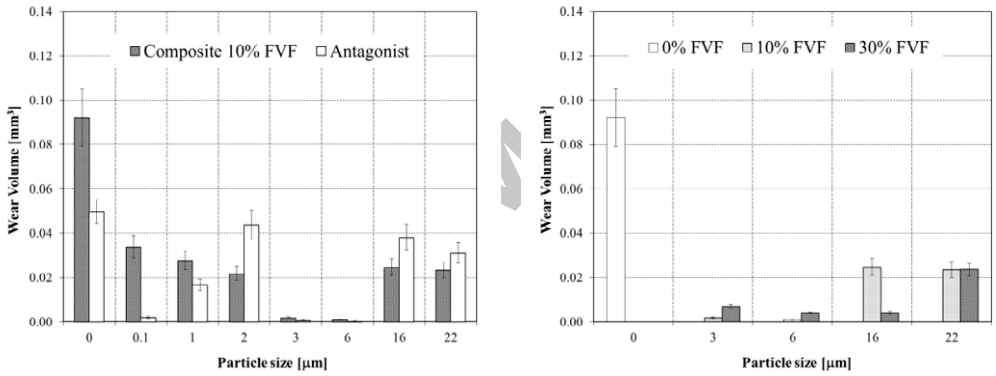

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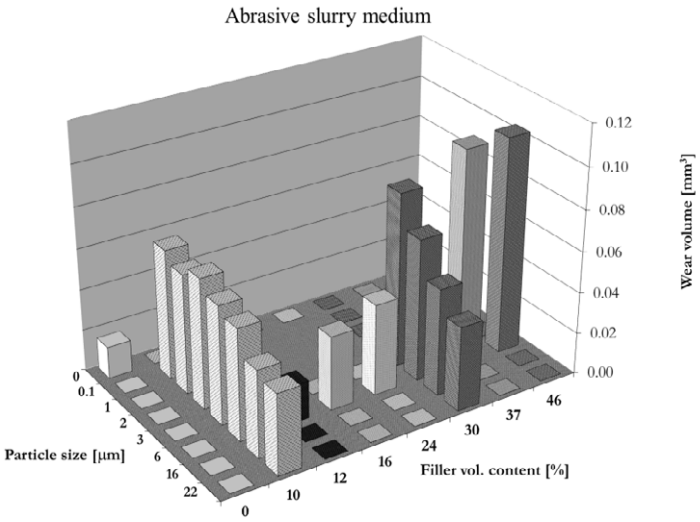
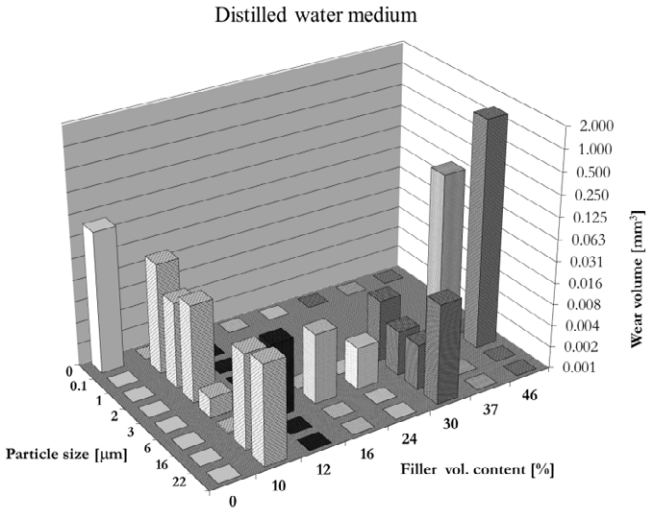


Fig. 16. Composite material wear volumes in reciprocating wear tests in abrasive slurry medium against glass spheres for: constant filler average dimension (6 μm) and FVF of 10, 12, 16, 24, 30, 37 and 46 %; constant FVF (10 %) and average filler dimension 0.1, 1, 2, 3, 6, 16 and 22 μm and constant FVF (30 %) and average filler dimension 3, 6, 16 and 22 μm. Resin specimens served as reference and correspond to 0 % FVF and 0 μm average particle dimension.



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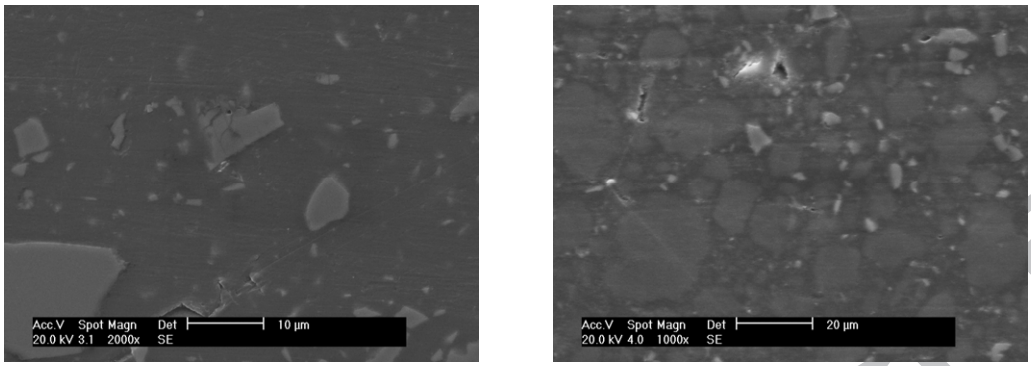

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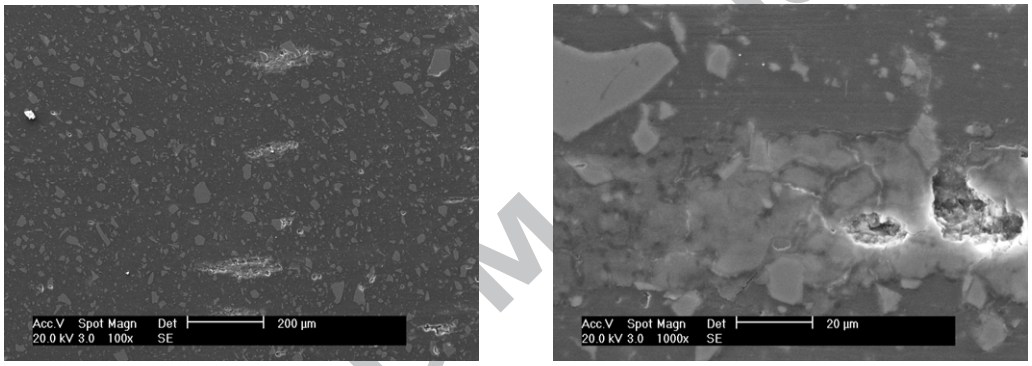

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Fig. 19. Composites morphology taken in wear contact area for specimens with 10 % filler content in reciprocating distilled water environment, for specimens 10 %/16 µm: a) 100x and b) 1000x, magnification.

List of tables

Table 1: Average particle dimensions and volume filler fraction of all composite materials produced and evaluated.

	Average particle dimension [µm]							
Filler volume fraction [%]	**0**	**0.1**	**1**	**2**	**3**	**6**	**16**	**22**
0	X							
10		X	X	X	X	X	X	X
12						X		
16						X		
24						X		
30					X	X	X	X
37						X		
46						X		

Table 2: Wear test conditions; stroke, frequency, duration, load, antagonist and media.

Conditions	Test type	
	Abrasive slurry	Distilled water
Stroke length [mm]	2	
Frequency [Hz]	1	
Duration [Cycles]	2,600	10,500
Normal load [N]	5	
Antagonist body	ϕ10 mm, glass sphere (Hardness 4,000 MPa)	
Media	Aqueous suspension of 0.35 g of glass micro-spheres (~ϕ4 µm) per ml of distilled water	Distilled water