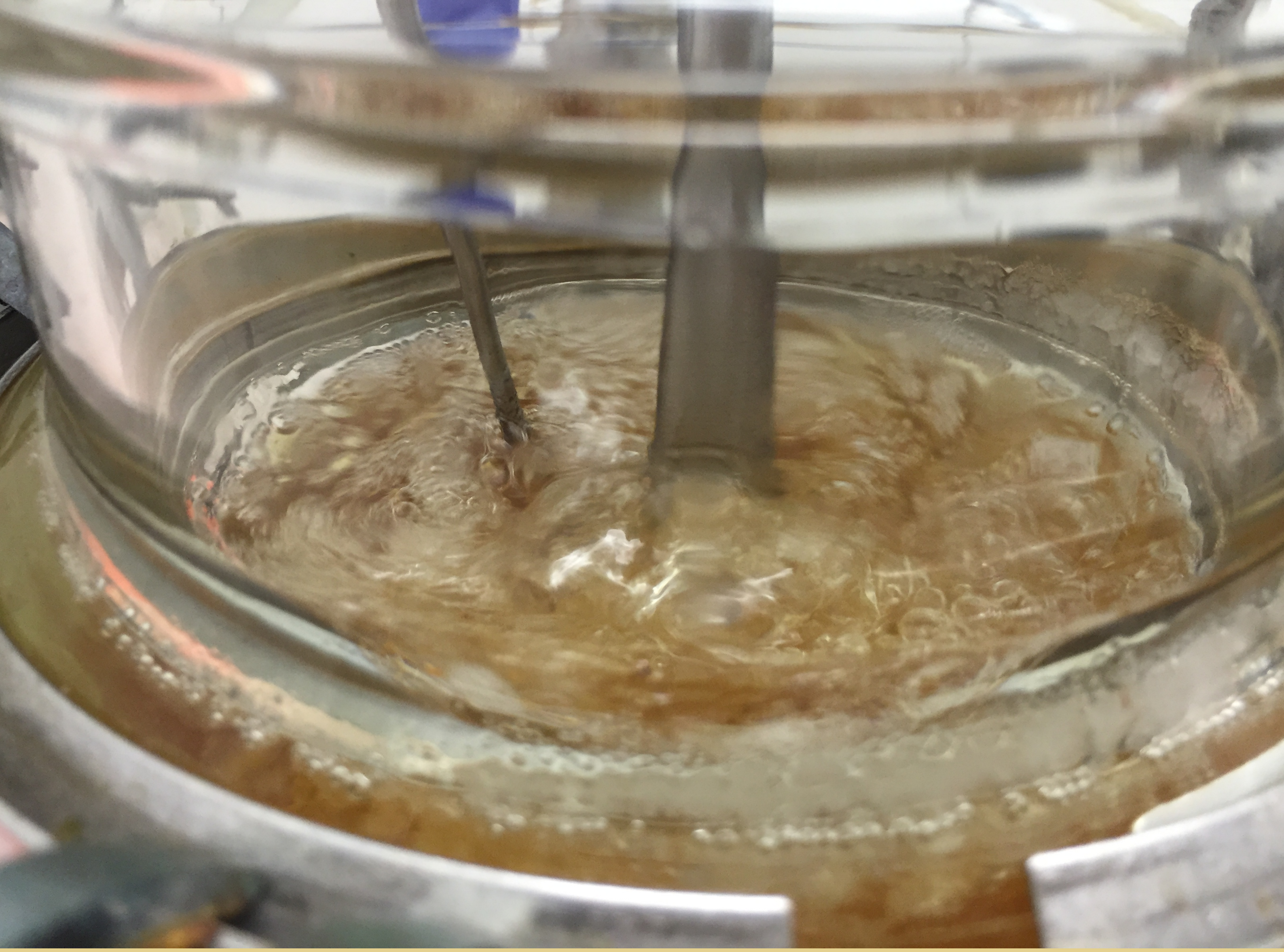

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Doctoral Thesis in Chemical Engineering, supervised by Professor Doctor Arménio Serra, Doctor Ana Fonseca and Professor Doctor Jorge Coelho, submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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Ao João e a ti…

“Não sou nada. Nunca serei nada. Não posso querer ser nada.

À parte disso, tenho em mim todos os sonhos do mundo…”

Fernando Pessoa

ACKNOWLEDGMENTS

Ao Professor Doutor Arménio Serra, meu orientador científico, por meter acompanhado nesta aventura e por puxar sempre por mim, quando achava que já não tinha mais para dar. Por me colocar questões mais que pertinentes (apesar de, na altura, nem sempre pensar assim) que me permitiram melhorar e crescer a nível profissional. Por me mostrar; à sua maneira, que podemos sempre ir mais além e que nunca nos devemos conformar com resultado nenhum, por melhor que ele seja.

À Doutora Ana Fonseca que, mais que minha co- orientadora, é também só colega e amiga. Por ser a minha "mãe científica", por nunca me deixar baixar os braços, por acreditar em mim quando eu já colocava tudo em questão, por me mostrar que posso ser sempre melhor e por me ajudar a acreditar nas minhas capacidades. Porque um simples obrigada não chega para agradecer tudo aquilo em que me ajustaste (sabes do que falo)... Se hoje cheguei aqui muito te devo...

Ao professor Doutor Jorge Coelho, também meu co- orientador, por ter sido a primeira pessoa que acreditou em mim e no meu valor, quando eu ainda era estudante. Por ter valorizado as minhas capacidades e por me ter estendido a mão, assim que lhe foi possível. Por todas as oportunidades que me deu, por acreditar em mim, por ter permitido que esta aventura acontecesse e por me ajudar a chegar tão longe.

À equipa da Resiquímica, principalmente ao Doutor Jorge Moniz e à Maria, por me abrirem as portas da empresa e por me ensinarem com tão grande sorriso aquilo que sabem, mostrando que há muito mais investigação para além do que costumava praticar. Por acreditarem em mim e por todos os desafios que lançaram e que nos fizeram alcançar metas que nunca pensei alguma vez atingir.

Aos meus colegas que, de uma forma direta ou indireta, participaram neste trabalho e colaboraram em alguns dos desafios que encontrei nestes anos porque, sem eles, teria sido mais difícil ultrapassar todos os obstáculos com as quais me deparei.

A todos os meus colegas do grupo de polímeros (*PolySyc*), por me apoiarem sempre e incondicionalmente e por me darem sempre mais um pouquinho de força e alento quando eu achava que já não conseguia mais.

A todos os meus amigos, fora e dentro do DEQ, por acreditarem sempre no meu valor e nas minhas capacidades e por nunca me deixarem desistir dos meus sonhos e dos meus objetivos

Por me mostrarem um grande sorriso quando as lágrimas já corriam pela cara e por me levantarem sempre quando já não o conseguia fazer sozinha. Não me atrevo a escrever qualquer nome com medo de falhar alguém, sabem quem são e do fundo do coração obrigado por estarem sempre ao meu lado.

Aos meus pais e aos meus sogros, por todo o apoio e confiança, por acreditarem sempre no meu valor e por o demonstrarem diariamente.

À minha irmã, que mesmo apesar de estar agora longe, desde sempre que me mostrou o seu grande orgulho em mim e sempre me fez acreditar que poderia um dia chegar onde chego hoje e por nunca me deixar desistir de nenhum dos meus sonhos.

Aos meus padrinhos, porque são muito mais que isso, e porque desde sempre me fizeram sentir que era especial e que, independentemente de tudo, era um grande orgulho para eles. Sempre falaram de mim com um brilho nos olhos, mesmo quando achava que não tinha qualquer valor, e porque se sempre sacrificaram para eu ter o que tenho hoje. Sei que, chegue onde chegar, vos vou encher sempre de orgulho e espero nunca vos desiludir e ser aquilo que me ensinaram a ser, com os valores que me transmitiram e com a vontade de chegar sempre mais longe.

Ao João... Porque palavras não chegam para gradecer tudo o que és para mim e o que me permitiste ser. Porque desde sempre acreditaste no meu valor e sempre soubeste que ia chegar longe e atingir os meus objetivos. Obrigada por me ouvires sempre, mesmo quando não dizia coisa com coisa, e por me limpares as lágrimas quando achava que estava tudo perdido. Sempre me mostraste que era capaz e que não podia desistir, que era forte e determinada e que ainda podia fazer mais e melhor. Porque mais que um companheiro sempre foste um amigo e nunca me deixaste baixar os braços. Porque nunca me deixaste sentir sozinha, estando (ou não) presente fisicamente, e me mostraste sempre que tinha mais força que aquela que eu pensava...Obrigada porque, graças a ti, me tornei a pessoa que sou hoje...

Abstract

Unsaturated polyester resins (UPRs) are currently one of the most important class of thermosets that, due to their properties, are suitable for a wide range of applications. UPRs are obtained from the free radical crosslinking reaction of an unsaturated polyester (UP) with an unsaturated monomer (UM), usually styrene (Sty). Currently, the petroleum-based maleic anhydride (MA), phthalic anhydride (PhA) and propylene glycol (PG) are the most commonly employed monomers in the industry of UPRs due to their reactivity, and also due to the fact that such combination of monomers give UPRs with excellent thermomechanical properties. However, the increasing environmental concerns, as well as the need to develop sustainable alternatives to fossil-based monomers, have led to a remarkable interest in the development of partially or totally biobased UPRs. In this sense, this PhD work aimed at developing novel biobased UPs that, upon crosslinking with Sty, would lead to UPRs with properties similar or even better than those fossil-based counterparts. The biobased monomers were judiciously selected in order to not compromise the properties of the final UPR. Another very important aspect that was covered in this PhD work was the replacement of Sty by biobased UMs in the UPRs' formulations. Sty replacement is eagerly needed in the field of UPRs since the use of this UM carries important environmental (it is considered a hazardous air pollutant) and health (it is considered a potential carcinogenic) concerns.

The initial work was focused on increasing the biobased content of a commercial UPR. For that purpose, different partially biobased UPs were synthesized, making use of the non-catalyzed azeotropic polycondensation. The UPs were then crosslinked with Sty and the ensuing UPRs were fully characterized. It should be pointed out that both the synthesis of the UPs and the preparation of the UPRs were carried out according to industrial procedures. Overall, the results showed that the partially biobased UPRs presented gel contents, water contact angles, thermal stability and shrinkage values similar to the commercial fossil-based resin. It is noteworthy that one of the developed partially biobased UPR showed thermal and thermomechanical properties very similar to the commercial UPR. This biobased UPR is already produced at an industrial scale.

The work continued with the development of fully biobased UPs, which upon crosslinking with Sty, would lead to UPRs able to replace the fossil-based ones. In this case, the UPRs were prepared by bulk polycondensation, a more environmental-friendly process when compared to azeotropic polycondensation. Upon crosslinking with Sty, different UPRs with gel contents and thermal stabilities close to the commercial UPR were obtained. One of the developed UPRs, using an UP based on succinic acid (SuAc), itaconic acid (ItaAc) and PG, exhibited thermomechanical properties very similar to those presented by a commercial resin. It was the first time that a fully biobased UP was able to led to an UPR with characteristics able to compete with fossil-based UPRs.

The next step of this work dealt with the development of UPRs based on vegetable oils. Due to their abundance, low cost and distinct chemical structure, soybean oil (SO) and coconut oil (CO) were used to prepare UPs, by bulk polycondensation. The UPs were crosslinked with Sty and vegetable oils based UPRs were obtained. The results showed that the thermal and thermomechanical properties of the novel UPRs could be easily tailored by changing the monomers and the type of oil in the UPs' formulation.

The design and synthesis of the new biobased UMs with the ability to partially or totally replace Sty in UPR formulations was the next goal of this project. Two biobased materials, vanillin (Van) and sobrerol (Sob), were modified with the methacrylate functionality and were used as UM in a commercial UP and in a biobased UP, developed also within the scope of this PhD. The novel UMs presented a significant lower volatility when compared to Sty, which is a highly desirable characteristic in a possible Sty substitute. The formulations containing only the biobased UMs presented a viscosity substantially higher than that presented by the formulations containing Sty, especially those in which methacrylated vanillin (MetVan) was used as the UM. In this case, Sty (50 wt.% relatively to the total amount of UM) was added to the formulations and a significant reduction in their viscosity was observed. The UPRs obtained from the biobased UMs presented lower gel content and lower thermal stabilities when compared to those obtained from Sty or a mixture of Sty/MetVan. The thermomechanical properties of the UPRs were also studied and showed that when the biobased UMs were used, a decrease in the thermomechanical performance was observed. Nevertheless, when the biobased UM was used along with Sty, better thermomechanical properties were obtained.

The last part of the work undertaken aimed at the development of a new class of UPRs from citric acid (CiAc) or tartaric acid (TaAc) and the study of their structure/properties relationship. The UPs were prepared by bulk polycondensation and were afterwards crosslinked with 2-hydroxyethyl methacrylate (HEMA). These novel UPRs presented a hydrophilic nature and similar thermomechanical properties. The swelling capacity and the *in vitro* hydrolytic degradation tests could be adjusted by changing the formulation's compositions. The overall results suggest that the materials proved to be promising candidates to be used in the biomedical fields.

To sum up, this PhD work had an important contribute regarding the development of UPRs derived from renewable resources. The obtained materials presented a set of interesting characteristics, in which the final properties were fine-tuned by changing the building blocks. Moreover, some of the developed materials exhibited the capacity to compete directly with fossil-based products that are commercially available.

Resumo

As resinas de poliéster insaturado (UPRs) constituem uma das mais importantes classes de materiais termoendurecíveis, sendo obtidas a partir de uma reação de copolimerização radicalar entre um poliéster insaturado (UP) e um monómero insaturado (UM), geralmente o estireno (Sty). Devido à excelência de propriedades apresentadas, estes materiais podem ser encontrados nas mais diversas aplicações como, por exemplo, nas indústrias automóvel e da construção.

Atualmente, na sua produção, os UPs são comummente preparados a partir de monómeros de origem petroquímica, sendo os mais comuns o anidrido maleico (MA), anidrido ftálico (PhA) e propilenoglicol (PG). A utilização destes monómeros prende-se com a sua boa reatividade e também com as excelentes propriedades termomecânicas que conferem às UPRs. Contudo, dadas as crescentes preocupações ambientais e a constante procura por modelos de desenvolvimento mais sustentáveis, torna-se premente a preparação de novas UPRs que incorporem matérias-primas de fontes renováveis. Assim, o objetivo do presente trabalho prende-se com o desenvolvimento de uma nova classe de UPR parcial ou totalmente constituídas por matérias-primas renováveis e que, simultaneamente, apresentem propriedades análogas ou até superiores às exibidas pelos materiais atualmente comercializados, de origem fóssil. Para tal, aquando da síntese dos respetivos UPs, foram criteriosamente selecionados diferentes monómeros que permitissem a substituição dos comummente utilizados sem, com isso, comprometer as propriedades finais das UPRs obtidas. Um outro aspeto de elevada relevância abordado neste trabalho diz respeito à substituição do Sty nas formulações de UPRs por um UM também de origem renovável. Na verdade, a substituição do Sty surge como um dos desafios de maior relevância uma vez que a utilização deste UM apresenta importantes preocupações tanto para o ambiente, uma vez que é considerado um poluente atmosférico perigoso, como para a saúde devido ao seu elevado potencial cancerígeno.

A primeira fase do trabalho focou-se no aumento do teor “verde” de uma UPR comercial. Para tal, diferentes UPs foram sintetizados por policondensação com destilação azeotrópica, , com a incorporação parcial de monómeros de fonte renovável na sua estrutura. Os UPs desenvolvidos foram posteriormente reticulados com Sty, seguindo-se a avaliação das propriedades das UPRs obtidas. De acordo com os resultados, as novas UPRs apresentaram valores de teor em gel, ângulos de contacto, estabilidade térmica e retração muito próximos da resina comercial. Adicionalmente, estas UPRs foram caracterizadas pela análise das propriedades térmica e termomecânicas verificando-se no final uma semelhança às UPRs comerciais. Uma das novas formulações desenvolvidas é já produzida à escala industrial.

Numa outra parte do trabalho, diferentes UPs foram sintetizados recorrendo exclusivamente a matérias-primas renováveis. Em alternativa à destilação azeotrópica, os UPs foram preparados por policondensação na massa, sendo este um processo mais “amigo do ambiente”. Após reticuladas com Sty, todas as UPRs revelaram teores em gel e estabilidades térmicas próximas de uma resina comercial. É ainda de salientar que a UPR preparada a partir de ácido succínico (SuAc), ácido itacónico (ItaAc) e PG apresentou propriedades termomecânicas muito próximas de uma resina comercial sendo, por isso, uma formulação muito promissora para utilização futura.

O trabalho prosseguiu com o desenvolvimento de UPRs a partir de óleos vegetais. Devido à elevada abundância, baixo custo e composição, os óleos de soja e coco foram selecionados para o desenvolvimento destes novos UPs, também preparados por policondensação na massa. Diferentes formulações foram testadas, sendo os novos UPRs obtidos posteriormente por reticulação com Sty. De acordo com os resultados obtidos, as propriedades térmicas e termomecânicas das UPRs mostraram ser dependentes dos monómeros e do tipo de óleo utilizados nas respetivas formulações.

De seguida, com o intuito de substituir o Sty como agente de reticulação em formulações de UPRs, novos UMs foram desenvolvidos. Para tal, vanilina (Van) e o sobrerol (Sob) foram modificados com a funcionalidade metacrilato e posteriormente estudados como UMs. Para este estudo, foi utilizado um UP comercial (100% fóssil) e um UP totalmente obtido a partir de fontes renováveis, este último também desenvolvido no âmbito deste doutoramento. Os novos UM apresentaram baixa volatilidade, em comparação com o Sty, sendo esta uma característica de extrema importância no desenvolvimento de substitutos para este monómero. Contudo, as formulações constituídas apenas pelos novos UMs apresentaram uma viscosidade substancialmente maior da apresentada pelas formulações contendo Sty, especialmente aquando da utilização do metacrilato da vanilina (MetVan). Neste caso, foi necessário utilizar uma mistura de MetVan com Sty (50% em massa relativamente à quantidade total de UM), tendo-se observado uma redução significativa na viscosidade final das formulações. Os UPRs obtidos a partir dos UM de origem renovável apresentaram valores de teor em gel e estabilidade térmica inferiores às resinas preparadas com Sty ou com a mistura Sty/MetVan. As propriedades termomecânicas foram também avaliadas e mostraram que, para a substituição total do Sty, UPRs com desempenhos inferiores são obtidos. É, no entanto, de salientar que, aquando da utilização da mistura Sty/MetVan, melhores propriedades termomecânicas foram observadas, sendo estes resultados apresentados como um grande avanço no estudo aqui referenciado.

A última parte do trabalho incidiu no desenvolvimento de uma nova classe de UPRs obtidas a partir de ácido cítrico (CiAc) e ácido tartárico (TaAc), sendo também avaliada a influência da estrutura nas propriedades finais dos materiais. Os UPs foram preparados por policondensação na massa e reticulados com o metacrilato de 2-hidroxietilo (HEMA). Após cura, os materiais obtidos apresentaram uma natureza hidrofílica e boas propriedades termomecânicas. A capacidade de inchamento dos UPRs e o seu perfil de degradação foram também avaliados e mostraram que podem ser facilmente modificados e ajustados de acordo com a formulação utilizada. Tendo em consideração os resultados obtidos os materiais desenvolvidos poderão ser interessantes candidatos para futuras aplicações, nomeadamente na área biomédica.

Assim, todos os materiais preparados ao longo deste trabalho constituem um importante contributo para desenvolvimento de UPRs obtidas a partir de matérias-primas de origem renovável, apresentando um conjunto de características relevantes. Adicionalmente, provou-se também que as suas propriedades podem ser facilmente modificadas e melhoradas através de uma criteriosa seleção dos materiais utilizados. É ainda de realçar que os materiais desenvolvidos demonstraram elevada potencialidade para competirem diretamente com os produtos de base fóssil atualmente disponíveis no mercado.

Thesis Outline

The main goal of this PhD work is to develop a new class of biobased unsaturated polyesters (UPs) with properties similar to those obtained from the fossil-based UPs and also to replace styrene (Sty) by biobased and less volatile monomer. Using this approach, it will be possible the development of unsaturated polyester resins (UPRs) with the 'green stamp', having a lower CO_2 footprint. The PhD thesis is organized in seven chapters:

In Chapter 1, it is presented an overview about the importance of UPs and UPRs. In this chapter, special focus is given to the biobased monomers that can be applied in the UPs and UPRs formulations.

In Chapter 2, it is studied the influence of the partial replacement of fossil-based monomers by biobased monomers in an UPR formulation widely used in industry. The UPRs were prepared using an industrial protocol. The final thermal and mechanical properties were compared with those of a commercial and petroleum-based UPR.

In Chapter 3, it is discussed the preparation of UPs using only monomers from renewable origin. The obtained UPs were crosslinked with Sty and their thermomechanical properties were compared with those of a commercial UPR of fossil-based origin.

In Chapter 4, it is presented the development of UPs based on vegetable oils, namely soybean oil (SO) and coconut oil (CO). The UPs were crosslinked with Sty and the influence of the inclusion of these two different oils in the structure of the UPRs is discussed in terms of thermomechanical performance.

In Chapter 5, it is reported the preparation of new biobased unsaturated monomers (UMs) to replace Sty in UPR formulations. The first part of this chapter is devoted to the synthesis and characterization of the new UMs. The second part deals with the partial or total replacement of Sty in both commercial formulations and the most promising formulation obtained in Chapter 3. The impact of the Sty replacement in the final properties of the UPRs was studied and discussed.

Chapter 6 reports the synthesis and characterization of UPs based on citric acid (CiAc) and tartaric acid (TaAc), which are monomers currently used to afford polyesters for biomedical applications. The crosslinking reaction was made with 2-hydroxymethyl methacrylate

(HEMA). The new UPRs were characterized in terms of their gel content, swelling capacity and *in vitro* hydrolytic degradation behavior.

Chapter 7 reports the most relevant conclusions from this PhD research as well as further recommendation on future work.

List of Acronyms

AdAc	Adipic Acid
AcAc	Acrylic Acid
AESO	Acrylated Epoxidized Soybean Oil
AV	Acid Value
BDDMA	Butanediol Dimethacrylate
BDO	1,4-Butanediol
BPE	Poly(Propylene Sebacate)
BPO	Benzoyl Peroxide
CAC	4,4-(Adipoyldioxy)dicinnamic Acid
CALB	Lipase B from *Candida Antarctica*
$CDCl_3$	Deuterated Chloroform
$CHCl_3$	Chloroform
CHDM	1,4-Cyclohexanedimethanol
CiAc	Citric Acid
CO	Coconut Oil
CoO	Cobalt Octoate
COPERMA	Castor Oil Pentaerythritol Glyceride Maleate
DACC	3,4-Diacetoxycinnamoyl Chloride
DAH	1,4:3,6-Dianhydrohexitol
DB	Double Bonds
DBTL	Ditin Butyl Dilaurate
DEAP	2,2-Diethoxyacetophenone
DEG	Diethylene Glycol
DHCA	3,4-Dihydroxycinnamic Acid
DLLA	D,L-Lactic Acid

DMAP	4-Dimethylaminopyridine
DMI	Dimethyl Itaconate
DMTA	Dynamic Mechanical Thermal Analysis
DSA	Dimethyl Succinate
DSC	Differential Scanning Calorimetry
***D*-MA**	*D*-Mannitol
EG	Ethylene Glycol
EML	Epoxidized Methyl Linseedate
EMS	Epoxidized Methyl Soyate
EPO	Epoxidized Palm Oil
ESO	Epoxidized Soybean Oil
FA-GM	Furoic Acid Glycidyl Methacrylate
FDCA	2,5-Furandicarboxylic Acid
FuAc	Fumaric Acid
FeAc	Ferulic Acid
FM	Furfuryl Methacrylate
FTIR	Fourier-Transform Infrared
FU	Diethyl Fumarate
GL	Diethyl *trans*-Glutaconate
GM	Guaiacol Methacrylate
HAP	Hazardous Air Pollutant
HDA	10-Hydroxycapric Acid
HDO	1,6-Hexanediol
HEMA	2-Hydroxyethyl Methacrylate
HQ	Hydroquinone
HM	Diethyl *trans*-*β*-Hydromuconate
HMF	5-Hydroxymethylfurfural

ItaAc	Itaconic Acid
IBOMA	Isobornyl Methacrylate
ICA	5-Cinnamoyloxyisophthalic Acid
Iso	Isosorbide
IM	Isomannide
IsAc	Isophthalic Acid
IT	Diethyl Itaconate
LA	Lactic Acid
LCA	Lithocholic Acid
LMA	Lauryl Methacrylate
MA	Maleic Anhydride
ME	Methacrylated Eugenol
MeAn	Methacrylic Anhydride
MEKP	Methyl Ethyl Ketone Peroxide
MetVan	Methacrylated Vanillin
MFA	Methacrylated Fatty Acid
MG	Methacrylated Guaiacol
MLA	Methacrylated Lauric Acid
MMA	Methyl Methacrylate
MPD	3-Methyl-1,5-Pentanediol
NMR	Nuclear Magnetic Resonance
NVP	*N*-Vinyl-2-Pyrrolinone
PBI	Poly(Butylene Itaconate)
PBIBS	Poly(Butylene Itaconate-*co*-Butylene Succinate)
PBuS	Poly(Butylene Succinate)
PBSI	Poly(Butylene Succinate-*co*-Itaconate)

PBS	Phosphate Buffered Saline Solution
PCDMI	Poly(1,4-Cyclohexane Dimethanol-Itaconate)
PDDI	Poly(Dodecyl Itaconate)
PDO	1,3-Propanediol
PEG	Poly(Ethylene Glycol)
PEOI	Poly(Oligoethyleneoxy Itaconate)
PET	Poly(Ethylene Terephthalate)
PFu	Poly(Butylene Fumarate)
PG	Propylene Glycol
PGI	Poly(Glycerol Itaconate)
PhA	Phthalic Anhydride
PIBG	Poly(Itaconic Acid-1,4-Butanediol-Glycerol)
PII	Poly(Icosyl Itaconate)
PLLA	Poly(L- Lactide)
POMG	Palm Oil Monoglyceride
PPI	Poly(Propylene Itaconate)
PPISI	Poly(Propylene Itaconate-*co*-Sorbitol Itaconate)
PTFE	Polytetrafluoroethylene
PTT	Poly(Trimethylene Terephthalate)
PTSA	*p*-Toluenesulfonic Acid
PVC	Poly(Vinyl Chloride)
RAc	Rinoleic Acid
RI	Refractive Index
SuAc	Succinic Acid
SeAc	Sebacic Acid
SEC	Multi Size Exclusion Chromatography
SEM	Scanning Electron Microscopy

SO	Soybean Oil
Sob	Sobrerol
SOMG	Soybean Oil Monoglyceride
Sty	Styrene
St	Stokes
TaAc	Tartaric Acid
TBPT	*tert*-Butyl Peroxybenzoate
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
THF-d_8	Deuterated Tetrahydrofuran
TMP	Trimethylolpropane
TMS	Tetramethylsilane
UM	Unsaturated Monomer
UP	Unsaturated Polyester
UPR	Unsaturated Polyester Resin
VaAc	Vanillic Acid
Van	Vanillin
VE	Vinyl Ester
VL	Vinyl Levulinate
VOC	Volatile Organic Compounds
WCA	Water Contact Angle
XRD	X-Ray Diffraction
4HBA	4-Hydroxybenzoic Acid
4HCA	4-Hydroxycinnamic Acid
μSTL	Microstereo-Thermal-Lithography

Nomenclature

$Đ$	Polydispersity
E'	Elastic Modulus
E''	Loss Modulus
M_c	Molecular Weight Between Crosslinking
M_n	Molecular Weight
n	Crosslink Density
T_g	Glass Transition Temperature (°C)
T_p	Peak Temperature (DTG curve) (°C)
$T_{5\%}$	Temperature for 5% of Mass Loss (°C)
$T_{10\%}$	Temperature for 10% of Mass Loss (°C)
α	Thermal Transition
β	Thermal Transition
γ	Thermal Transition
σ_{max}	Tensile Strength
σ_f	Flexural Strength

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Motivation and Objectives

Nowadays, unsaturated polyesters (UPs) represent one of the most relevant groups of polymers and the development of these materials is growing continuously at robust rates. Generally, for industrial purposes, UPs are crosslinked with an unsaturated monomer (UM) to generate, after cure, the so-called unsaturated polyester resins (UPRs). Due to the excellent balance between their properties, UPRs are widely used as coatings and reinforcement materials in construction, marine and automotive industries. Traditionally, the monomers used to prepare these materials are mostly derived from petroleum-based resources. However, in the past few years, the growing concern about the declining of fossil fuel reserves has stimulated the interest in exploring renewable resources for the polymer industry. Renewable raw materials supply a wide variety of monomers and polymers capable of replacing their fossil-based counterparts, providing additional properties such as environmental compatibility and the capacity of chemical modifications to fit custom-made applications.

Currently, one of the major challenges in the development of UPRs is definitely the use of renewable resources. For the past few years, important efforts have been done in the development of new biobased UPs for different applications and important studies have reported alternatives to petrochemical based counterparts. However, the properties presented by these new biobased polymers are far from those presented by the common petroleum-based UPRs, and reliable alternatives are still eagerly needed. In addition, the major challenge remains in the development of a new biobased monomer able to replace styrene (Sty), the most common UM to prepare the UPRs, with a huge impact on the final performance of the materials.

This project had different objectives that complement each other. Firstly, the purpose was to develop new UPs, making use of building blocks from renewable resources. Thermal and mechanical properties were manipulated by changing the composition of the polyester to find out a perfect balance between the structure and the thermomechanical properties of the materials. The UPs were crosslinked, in the presence of the Sty, and UPRs with high biobased content were obtained, having final properties comparable to those of commercial petroleum-based resins. The second part of the work was focused on the development of new biobased unsaturated monomers (UM) in order to replace the Sty in UPR formulations. These new UMs should possess low volatility, good compatibility with the resin, and should also permit to obtain UP/monomer mixture with suitable viscosity to be cured. Finally, a new class of UPRs based on citric and tartaric acid were prepared, with potential application in the biomedical field. The new UPs were crosslinked with 2-hydroxyethyl methacrylate, a monomer widely used to produce polymers for biomedical applications.

CHAPTER 1 – **Review of Literature**

1.1 Introduction

1.1.1 Chemistry of Unsaturated Polyesters

From the Greek terms *poly* (many) and *meres* (parts), a polymer can be defined as a macromolecule built up by single repeating units, the monomers[1]. A polymer can be synthesized by two main polymerization processes: step-growth polymerization (successive addition reactions involving monomers with reactive functional groups) and chain-reaction polymerization, also known as addition polymerization (with the sequentially addition of monomers to the growing end of a chain)[1,2].

Step-growth polymers were historically the first synthetic polymers to be investigated. In the end of the 30's, Carothers *et al.* synthesized polyesters from maleic acid and ethylene glycol, being the pioneers in the synthesis of polymers by polycondensation[3]. An important work about polyesters was published latter, by Bjorksten *et al.*, defining polyesters as the polycondensation products of dicarboxylic acids with dihydroxy alcohols[4]. Over the years, the polymers synthesized by polycondensation have been used in several areas of daily life and, currently, their production is well established worldwide. One of the most popular polymers prepared by this process is poly(ethylene terephthalate) (PET)[5].

The polyesterification is an equilibrium reaction and, in order to shift the reaction towards the polymers formation, the by-generated secondary products (frequently water) must be continuously removed. Different approaches can be employed for such purpose, namely the use of a continuous stream of an inert gas, a vacuum system with a collecting trap, or the use of azeotropic distillation using xylene or toluene as the solvent[6,7].

Among the different classes of polyesters, unsaturated polyesters (UPs) are particularly important. UPs present double bonds in their structure, being able to participate in crosslinking reactions in the presence of an unsaturated monomer (UM), usually styrene (Sty). After the crosslinking reaction, thermoset polyesters are obtained and are commonly known as unsaturated polyester resins (UPRs). The beginning of the UPRs' industry dates back to the later 40´s and since then it continued to grow steadily.

UPs are currently synthesized by the reaction of saturated and unsaturated dicarboxylic acids (aromatic or aliphatic) or anhydrides with diols[5]. The generic process to obtain an UPR is schematized in Figure 1.1.

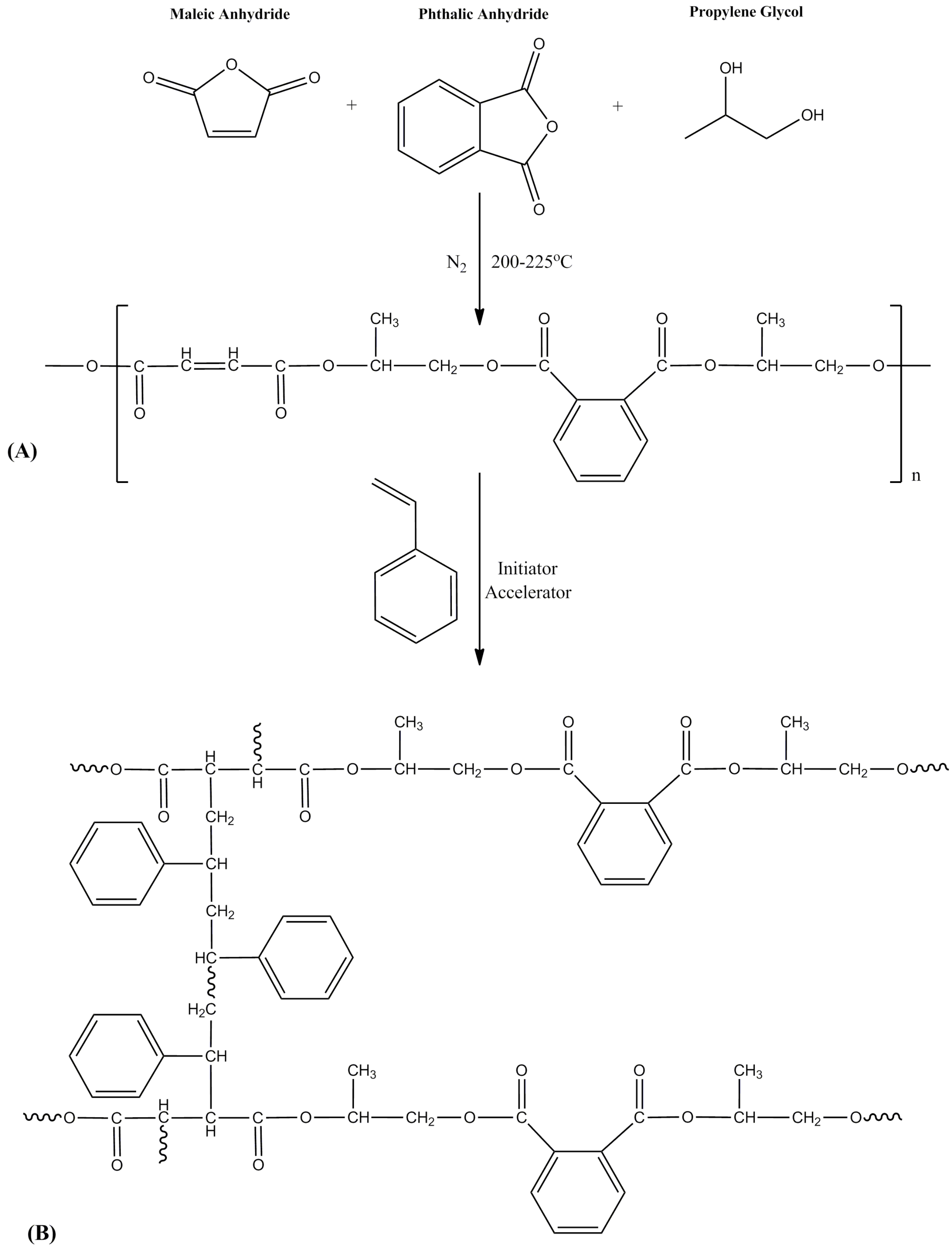


Figure 1.1- Development of an unsaturated polyester resin: (A) synthesis of UP by polycondensation reaction, (B) UPR formation by crosslinking reaction.

The UPs are characterized by low-molecular weights (M_n) ranging of 700 to 3000 g.mol^{-1} and polydispersities (*Đ*) around 2, and their properties depend mainly on the monomers used[3-5]. Propylene glycol (PG) and maleic anhydride (MA) are the most common monomers in the UP synthesis. PG presents in its structure a pendant methyl group, allowing the obtainment of less crystalline materials, with increased compatibility with Sty, than those obtained with ethylene glycol (EG) or diethylene glycol (DEG)[7]. MA is the most important source of carbon double bonds in UPs formulations, since this monomer is highly reactive and has a low cost. Besides MA, fumaric acid (FuAc) can also be used to introduce unsaturations in the polyester backbone. However, due to its lower reactivity and higher costs, it is not widely used in the UPs industry[8]. Besides these monomers, phthalic anhydride (PhA) has also been used in UP formulations for industrial purposes. A balance between the amounts of PhA and MA is crucial for the obtainment of an UP with a suitable amount of double bonds and to yield an UPR with good mechanical performance. In addition to PhA, isophthalic acid (IsAc) has also been used as the aromatic monomer in UPs synthesis and different works have been reported[9-12]. This monomer is frequently applied to improve the resistance to hydrolysis of the final crosslinked network[4,8]. In a 4-8 pH range, the half ester of PhA is easier to hydrolyze than corresponding half esters of IsAc. This feature is due to the so-called anchimeric effect. The location of the carboxyl group in a half ester of PhA may promote the hydrolysis of its neighboring ester, contributing to the poorer hydrolytic stability of the UPRs with this monomer[13].

The selection of different monomers and changes in their ratio in the formulation will allow the design of UPs (and ultimately, UPRs) for specific purposes. Typically, aliphatic components contribute to the flexibility of the final polymers, whereas the aromatic components improve their hardness and stiffness[7,8,14]. The use of diols with longer aliphatic chains improve the tensile strength of the UPs[15].

The chemical structure of the monomers has a key role in terms of the properties of the final UP (and UPRs) properties and applications. However, the performance of the UPRs is also extensively affected by the UM concentration and its nature[8]. Thus, it is not only important the impact of the monomers in the polyester structure but also the detailed understanding about the cure reaction.

1.1.2 Unsaturated Polyester Resins

In the past few years, UPR became very popular in the polymer industry, mainly due to their low cost, good thermal stability, excellent mechanical properties and good chemical resistance[15,16]. Due to these advantages, these resins have been widely employed in coatings, for building and construction, adhesives, for sanitary and domestic applications, in the electronic industries and, more recently, in biomedical applications and tissue engineering [7,9,15,17-19].

UPRs have two main components, the UP and the UM. The UM is generally Sty, but other diluents such as dimethacrylates, alkyl methacrylates, vinyl esters and divinyl benzene can also be used[4,8,20]. The UM is currently used for two distinct purposes: reduce the viscosity of the UP, contributing to a better processability, and promote the crosslinking reaction with the double bonds of the UP structure[4]. Besides these two components, the formulations for the UPRs preparation also contain inhibitors, initiators and accelerators. In UPR synthesis the inhibitor is applied essentially to prevent Sty polymerization during the addition of this monomer to the UP and also to increase the storage time of the final formulation. The most common inhibitors applied in UPRs industry are hydroquinone and *t*-butyl hydroquinone [4,8]. Due to the nature of the cure reactions, a radical initiator is also required[21]. A wide range of organic compounds can be used as initiator, but the organic peroxides are the most used. Among them, it is possible to mention: ketone peroxides, hydroperoxides and diacyl and dialkyl peroxides[8]. Accelerators, also called promoters, have also an important role in the UPRs cure, allowing the decomposition of the initiator at low temperatures. Aromatic tertiary amines (e.g., *N,N*-dimethylaniline, *N,N*-diethylaniline and *N,N*-dialkylanilines) are the most commonly used accelerators[22]. Nonetheless, other accelerators can be used in order to reduce the activation energy involved in initiators decomposition. As example, it is possible to mention the organic salts of cobalt and vanadium[23,24].

The cure of UPRs is a free radical polymerization between the UM and the double bonds present in the polyester chains[25]. When the UP resin formulation is submitted to heating and/or irradiation, the initiator decomposes and release free radicals in the system. Then, the radical crosslinking initiates and long-chain molecules are formed through the reaction of the UM and the UP molecules, by intermolecular reactions. Due to the presence of intramolecular crosslinking between the double bonds of the UP, these long-chain molecules are predisposed to organize in spherical structures, known as microgel (Figure 1.2). According to Lu *et al.*[21] this event, known as gelation, starts at an early stage, even for conversions as low as 3-4%.

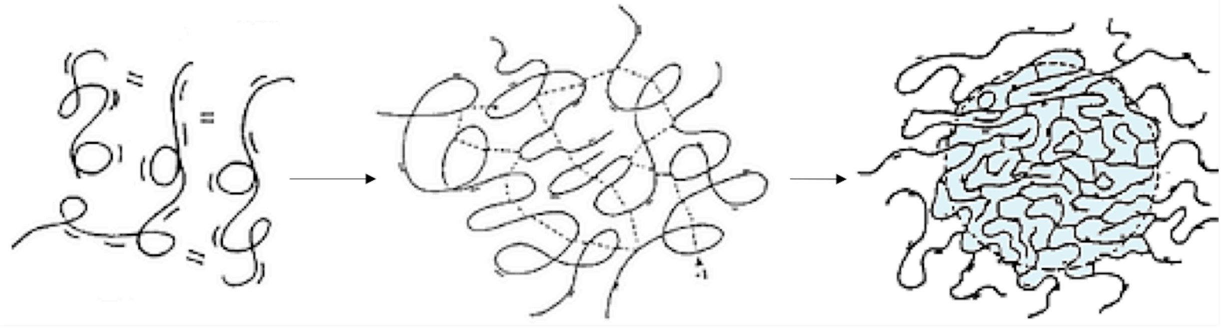


Figure 1.2- Schematic diagram of microgel formation in a cure reaction of UPR, adapted from [25].

The microgel presents pendant C=C bonds inside its structure able to react with the unsaturated monomer. Due to an increase of the intraparticle crosslinking observed in this step, a smaller and compact structure is obtained. In this point, also known as vitrification, the cure reaction is controlled by the diffusion of the reactive species. When high compactness is attained, the unsaturated monomer cannot diffuse into the particle and the cure process ends[26-28].

In this complex crosslinking process, different simultaneous reactions can occur: UM-UP copolymerization, UM homopolymerization and UP homopolymerization[21,22].

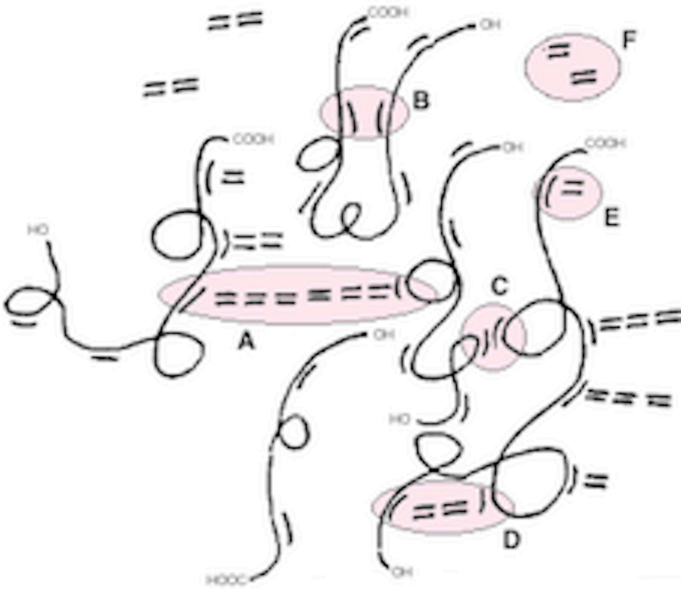


Figure 1 3- Schematic diagram presenting all possible reactions in the UM-UP copolymerization, adapted from [27].

According to Yang and Lee[27], the reactions can be classified in four types (Figure 1 3): (1) intermolecular crosslinking with or without linking through the UM (e.g., Sty), leading to the formation of a macroscopic network through the connection of adjacent UP molecules (A,C);

(2) intramolecular crosslinking with or without linking between the UM (B,D) (in this reaction, the crosslink density increases but no contribute to the macroscopic network is observed); (3) branching on the UP molecule by UM (E) (in this reaction, with a minor effect on the network formation, a small increase of the polyester coil size can be observed); and (4) free unsaturated monomer homopolymerization (F), leading to the formation of a soluble fraction[26,27]. Due to the exothermic nature of the cure reaction, it can be monitored by differential scanning calorimetry (DSC)[21,28-30]. In this study, through the enthalpy of each identified peak, different phenomenological models can be applied and kinetic parameters such as activation energy and reaction order can be determined[31,32].

The field of UPs and UPRs is undoubtedly a branch of polymer science that will deserve the attention in the next years. The tendency will be the development of biobased UPs, making use of monomers obtained from renewable resources, and the replacement of Sty, totally or partially, in the UPRs' formulation. In the next sections, an overview about the renewable resources used in the preparation of UPs will be presented and the strategies regarding the Sty replacement will be discussed.

1.2 Renewable Monomers for the Synthesis of UPs

Since the beginning of human activities, the renewable resources defined as “any animal or vegetable species which is exploited without endangering its survival and which is renewed by biological (short term) instead of geochemical (very long term) activities”[6], are used in everyday life. For centuries, a wide diversity of renewable resources such as natural rubber, wood and vegetable oils, was extensively used by man for different applications. However, due to the petrochemical revolution in the 20th century, the breakthrough of the biopolymers stopped and a new class of materials, the synthetic polymers, has emerged. During this century, a massive variety of synthetic polymers were developed, exhibiting outstanding properties that couldn’t be achieved with the natural polymers[33,34]. Only in the beginning of the 21st Century, a new thrust towards the development of renewable resources marks the renaissance of the biobased polymers. In an age of increasing emphasis on environmental concerns, and due to the scarcity of petroleum, in the last years growing attention has been paid to renewable resources and the concept of biorefinery quickly became one of the most important paradigms of the century[6,33-35]. In biorefinery, biomass feedstock is transformed into a wide range of high quality products such as fuels, power and chemicals, providing an interesting sustainable platform for the design of new biobased polymers able to compete with petroleum-based materials[36-40].

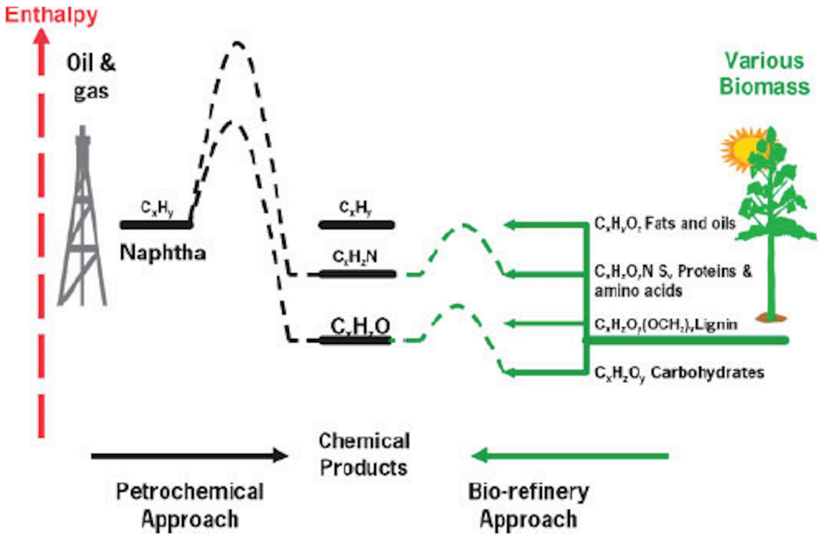


Figure 1.4-Biorefinery approach, reprinted from [41].

In analogy to petroleum refinery (Figure 1.4), in which petroleum is refined to produce different monomers, in biorefinery the multiple biomass feedstocks are also transformed to obtain renewable oil and monomers[34,39]. Among the different available raw materials, lignocellulose is the most abundant and an important biorefinery feedstock, not only due to its competitive price but also because is an inedible source, not competing with the food supplies[37,39,42]. Thus, sugars derived from lignocellulose (namely xylose and glucose, five and six-carbon sugars, respectively) form an important platform to biorefinery and, through their biological, thermal and chemical conversions, a wide range of building blocks for polymer synthesis can be obtained, as it will be presented in the following subsections[36,37,42].

1.2.1 Aliphatic Monomers

With the emergence of the biorefinery concept, a wide range of compounds can be obtained from biomass components, namely from cellulose, being the most important feedstock for the production of monomeric building blocks, suitable to synthesize different polymers such as polyesters, polyethers, polyamides, polyurethanes and polycarbonates[37,42]. Currently, a vast amount of aliphatic acids is available for the synthesis of polymeric materials[33].

Succinic acid (SuAc), or 1,4-butanedioic acid, is a versatile compound currently produced by the direct hydrogenation of maleic acid or by the hydrogenation of MA, followed by an hydration step[43]. Synthesized for the first time in the 16th century from amber distillation, by Georgius Agricula, this aliphatic monomer can be a precursor for other chemical compounds such as 1,4-butanediol (BDO), tetrahydrofuran, succinonitrile, dimethyl succinate, adipic acid, among others[33,37,44]. In the past few years, more attention has been given to the synthesis of SuAc through fermentation processes, using biomass as the feedstock. Currently, this acid is produced through the fermentation of glucose mediated by *Anaerobiospirillum succiniciproducens*, *Actinobacillus succinogenes*, *Mannheimia succiniciproducens* and recombinant *Escherichia coli*, in a process where the amount of by-products (e.g., lactic acid or acetic acid) are residual. However, in the industrial synthesis of biobased SuAc, the separation and isolation of the product from the aqueous fermentation broth remains a problem and the optimization of the fermentation process is still required[43,45]. Nowadays, with an annually global production of about 50 kton, several companies such as Myriant, Reverdia and Bioamber are successfully synthesizing this renewable monomer[33,37].

Itaconic acid (ItaAc), also known as methylene butanedioic acid or methylene SuAc, is one of the most important biobased platform chemicals, being not only used in polymer synthesis, but also in pharmaceutical industry and in agriculture[37,44,46,47]. Identified for the first time in the 19th Century as a product of the thermal decomposition of citric acid, ItaAc has been synthesized since 1960 from the fermentation of sucrose, glucose and xylose using *Aspergillus terrous* and *Aspergillus itaconicus*[44,46,48]. The highest yield of ItaAc production is attained when pure glucose is used as the substrate[49], but efforts have been made to synthesize ItaAc with cheaper substrates, namely molasses, starch, hydrolysates of corn syrup and wood. Another strategy to increase the yield of ItaAc encompasses the use of metabolic engineered microorganism strains[49,50].

Fumaric acid (FuAc), or (*E*)-2-butenedioic acid, was isolated for the first time from the plant *Fumaria officinalis*. Due to the presence of a double bond and two carboxylic groups, FuAc has been extensively applied in the polymers industry, namely in the preparation of UPRs[51,52]. Currently, FuAc is obtained from the isomerization of maleic acid monomer but, in recent years, more attention has been given to the production of this monomer through fermentation processes, being on the list of the top 10 monomers that can be produced from sugar [52-54]. FuAc synthesis through fermentation processes is not new. In fact, the production of this monomer from glucose, sucrose, starch, and molasses by fermentation was explored in a commercial scale during the 1940s, but the production was discontinued due to the low productivity and the low prices of petroleum-based feedstocks[55]. Presently, with the increasing environmental concerns, the interest in FuAc by fermentation processes has been reestablished. Nowadays, FuAc can be obtained from fungi such as *Rhizopus oryzae* and *Rhizopus arrhizus*[54]. However, due to the difficult growth of fungi, other microorganisms have also been used in the industrial production of FuAc, namely some bacteria (*Lactobacillus* ssp.) and metabolically engineered *Saccharomyces cerevisiae*[37,51,54]. In the fermentation process, starch and lignocellulose are the most common substrates[37]. The annual production of FuAc is estimated in 240 000 tons, being the Chinese companies Changmao Biochemistry and Jiangsu Jiecheng Bioengineering the main producers.

Figure 1.5 presents the chemical structures of the described aliphatic acids. Besides the mentioned carboxylic acids, citric, levulinic, gluconic and sebacic acids have also been pointed as important biobased chemicals, being essentially prepared by chemical modification and fermentation processes[37,44,56].

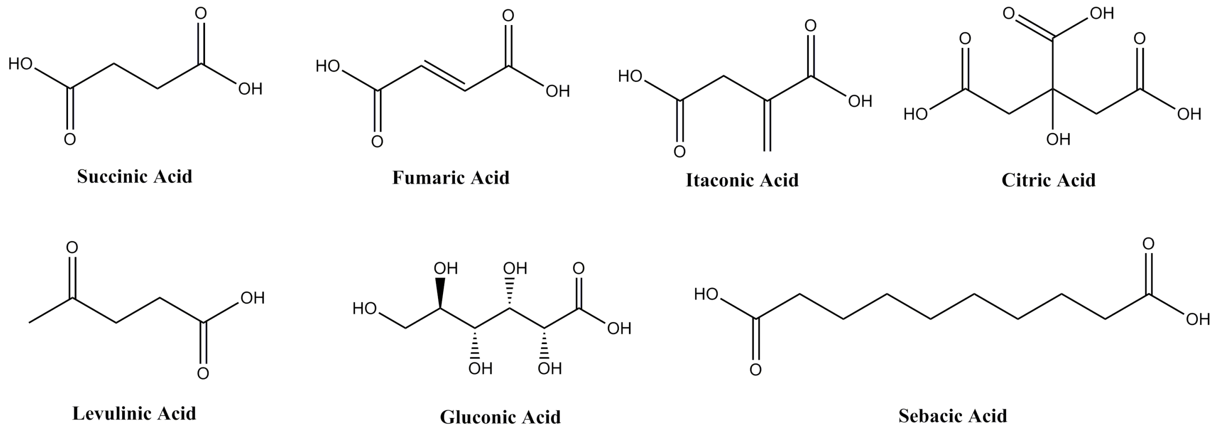


Figure 1.5- Chemical structures of succinic, fumaric, itaconic, citric, levulinic, gluconic and sebacic acids.

Currently, the transformation of biomass into monomers by fermentation of carbohydrates is unquestionably the most developed pathway to produce monomers, or their precursors, from natural resources[56]. In addition to the mentioned carboxylic acids, aliphatic diols such as propylene glycol (PG), 1,3-propanediol (PDO), 1,4-butanediol (BDO) and 1,4:3,6-dianhydrohexitols (DAHs) can also be obtained through these fermentation processes[57].

PG, recognized as an extremely important non-toxic building block for the chemical industry, has a very broad spectrum of applications. With an annual global demand higher than 1 million tons, PG is the common glycol used in the industrial synthesis of UPs, being also applied as a solvent or additive in pharmaceuticals and cosmetic industries, for liquid detergents, as anti-freezing agent, among others. Currently, the industrial production of PG is essentially based on a petrochemical route, where propylene is converted to propylene oxide, being further hydrolyzed into PG[58]. However, various strategies have been proposed for the production of this chemical feedstock by fermentation of renewable resources through the action of microorganisms. The microbial production of PG was first reported in 1954, through the action of *Clostridium thermobutyricum*. Recently, different microorganisms are known by their potential to metabolize sugars and produce PG such as *Clostridium thermosaccharolyticum*, *Saccharomyces cerevisiae*, *Escherichia coli*, *Synechoccus elong*ates, *Thermoanaerobacterium thermosaccharolyticum* and *Corynebacterium glutamicum*. Recently, Ashland and Cargill started together the industrial synthesis of PG from glycerol by fermentation using *E. coli* or *T. thermosaccharolyticum*[59-62].

PDO, one of the oldest fermentation product, was obtained for the first time in 1881, by August Freund, from glycerol fermentation using a mixed culture in which *Clostridium pasteurianum* was the active microorganism. The preparation of PDO from glycerol fermentation gains even more importance because it allows the recovery of a sub-product of the biodiesel industry[57,63]. Several bacteria have been used to convert glycerol in PDO, being the genera *Klebsiella*, *Clostridia*, *Citrobacter*, *Enterobacter* and *Lactobacilli* the most common. Besides bacteria, PDO can also be obtained by fungi such as *Aspergillus niger* and *Aspergillus oryzae*[33,37,57]. The fermentation of glycerol into PDO is an anaerobic conversion. However, renewed attention has been paid to the aerobic processes due to their low cost [57]. Glucose is another substrate very interesting for the obtainment of PDO but, until now, there are no references to microorganisms capable of directly converting glucose in PDO. To overcome this difficulty some solutions have been presented, namely the use of a culture of mixed microorganisms or the use of genetically engineered microorganisms that convert glucose into glycerol, that is subsequently converted in PDO[37,44,57]. Currently, with an annual production of 45 kiloton, PDO is industrially produced by DuPont through the fermentation of glucose with the intermediacy of glycerol, being essentially used in synthesis of poly(trimethylene terephthalate) (PTT) (Figure 1.6)[42].

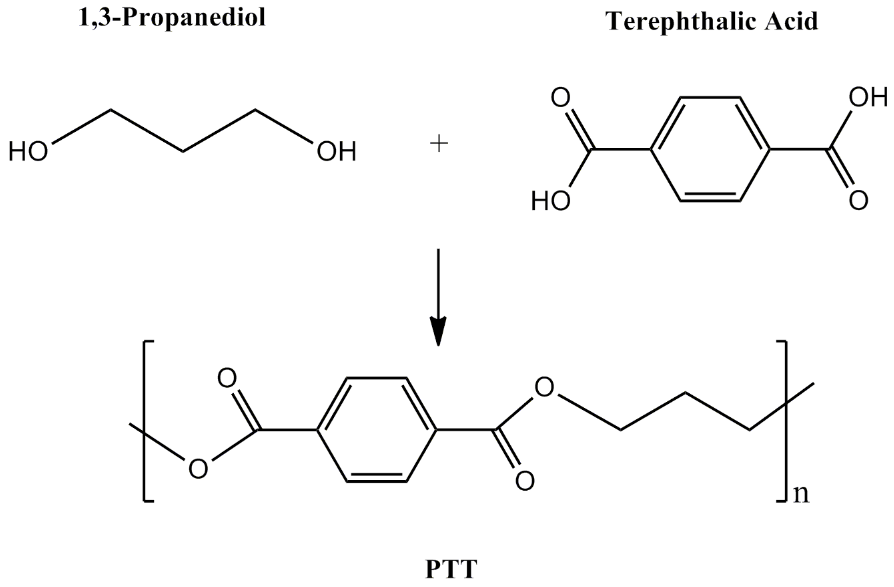
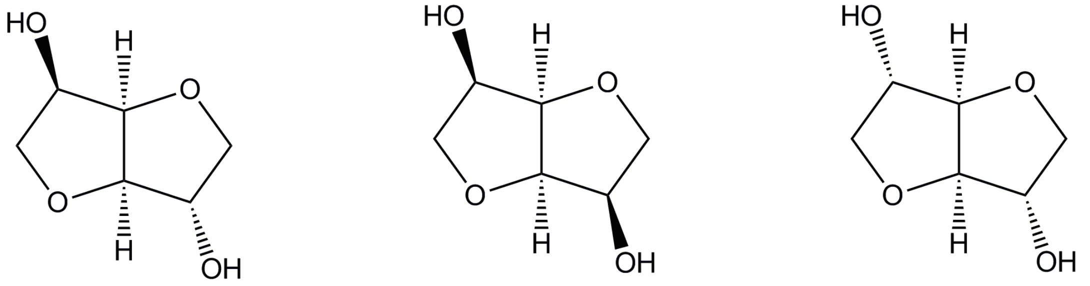


Figure 1.6- Synthesis of poly(trimethylene terephthalate) from PDO[57].

Due to its wide range of applications (e.g. polymer synthesis, food, adhesives, lubricants, laminates, solvents) PDO, previously classified as “specialty chemical”, is now considered as a “commodity chemical”[37,57].

BDO is currently obtained from MA, and it is used not only in the synthesis of polymeric materials but also as a precursor for other compounds, such as tetrahydrofuran (THF)[37,44]. Recently, diverse efforts have been made by some of the biggest chemical companies (e.g. Bioamber and Myriant) to synthesize in an industrial scale the biobased BDO. The process used involves the fermentation of sugars into SuAc that is subsequently converted in BDO through chemical reduction. BDO can also be synthesized by the fermentation of sugars using recombinant *Escherichia coli*[33].

In addition to PDO and BDO, 1,4:3,6-dianhydrohexitols (DAHs) are one of the most promising biomass-based diols in the synthesis of polymeric materials. DAHs are cyclic dihydroxyethers synthesized through dehydration of hexitols, which are obtained from the reduction of hexose sugars[37,64]. Due to the presence of the fused ring system and two hydroxyl groups at the C_2 and C_5 position, three stereoisomers can be obtained: isosorbide (Iso), isomannide (IM) and isoidide (Figure 1.7). In isoidide, both hydroxyl groups are located in the *exo* position whereas IM exhibits an *endo* configuration for these groups. Isosorbide, in turn, presents one hydroxyl group in the *endo* position and the other in the *exo* position[37,64].



Isosorbide **Isomannide** **Isoidide**

Figure 1.7- Chemical structures of DAHs.

Differing only in the configuration of the hydroxyl groups, these stereoisomers present different physical and chemical properties and distinctive reactivity, being isoidide and IM the most and the less reactive, respectively. Iso has an intermediate reactivity[65]. At this moment, Iso is the only stereoisomer that is produced at an industrial scale by Roquette from starch[42].

Nevertheless, due to the scarcity of the precursor of isoidide from vegetable biomass as well as the lower reactivity and high productions cost of IM, the industrial production of these stereoisomers is not available[65]. Polymers containing Iso are commercially applied in coatings, fiber applications and also for medical applications[42,66].

1.2.2 Aromatic Monomers

Currently, diverse biomass-based aromatic monomers have been considered as building blocks for polymers synthesis, namely furan-based monomers, as 2,5-furandicarboxylic acid (FDCA), and lignin derivatives such as vanillin.

FDCA has been presented as one of the most promising aromatic monomer in the synthesis of polyamides, polyesters and polyurethanes, being applied as potential substitute of terephthalic, isophthalic and adipic acids[42,44]. FDCA can be obtained from the catalytic oxidation of 5-hydroxymethylfurfural (HMF), which in turn results from the acidic dehydration of hexoses, mainly fructose (Figure 1.8). The synthesis of HMF from hexoses is still the most challenging step of this process, because of the low yields observed and the instability of HMF under acidic conditions[37,63,67]. The synthesis of FDCA is carried out in two distinct steps: HMF is firstly converted in a dialdehyde derivative, followed by a step of oxidation of the aldehyde groups into carboxylic acid groups[37].

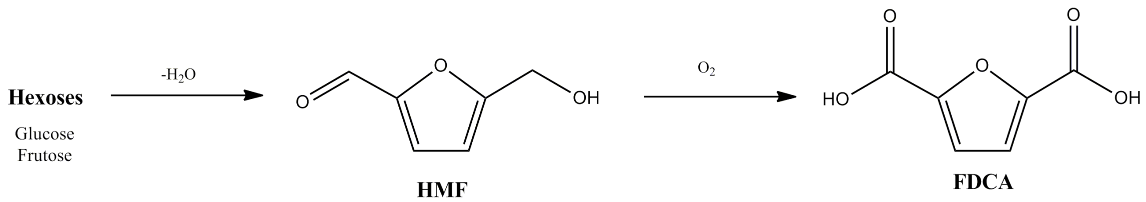


Figure 1.8- Conversion of hexoses into FDCA[37,67].

In the recent years, the oxidation of HMF to FDCA has been developed through a methodology based on a platinum/carbon catalyst. Besides this approach, and to obtain high yields, different oxidation conditions and diverse types of catalysts (as gold nanoparticles) have been used. The bioconversion of HMF to FDCA through enzymes was also reported. At this moment, this biobased dicarboxylic acid is successfully synthesized by Avantium[37].

Lignin, the major component of the vegetable biomass, is found primarily in cell walls of vascular plants[37,68]. With an annual production of 50 million tons, this natural polymer is recognized as a waste product of paper pulping process, being burned and used as a low value biofuel[39,69]. However, due to the huge potential to give a wide range of aromatic chemicals identical to those currently derived from fossil sources, lignin is currently considered one of the most available sources of renewable monomers such as vanillin (Figure 1.9)[33,34,70,71].

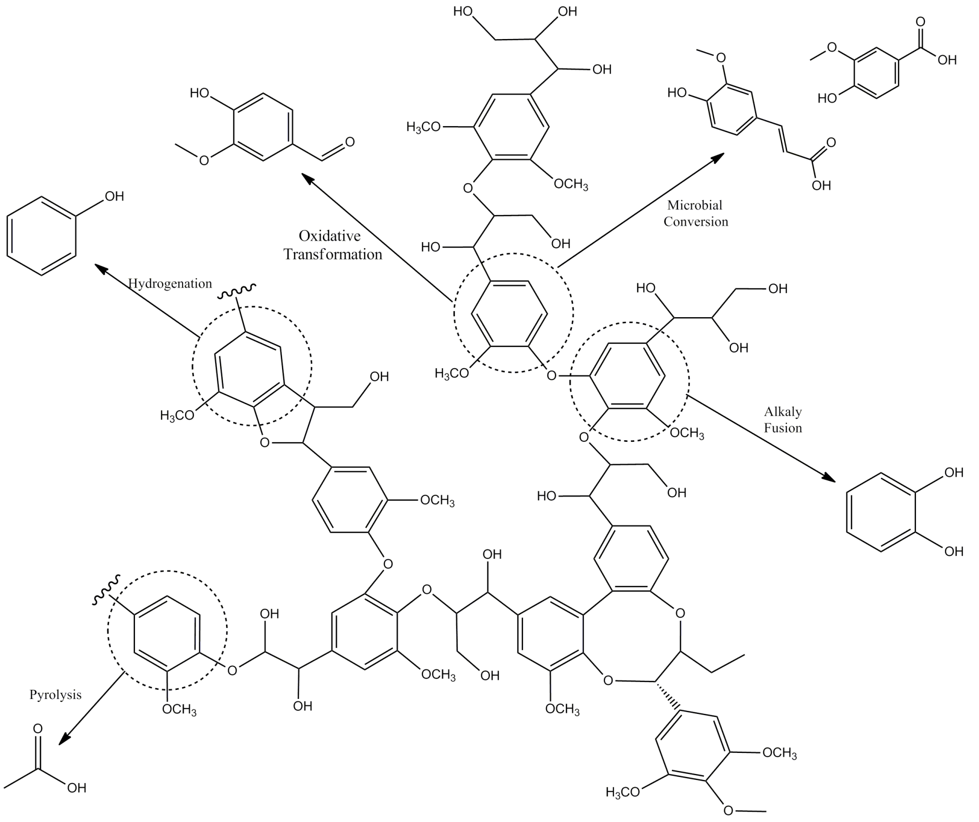
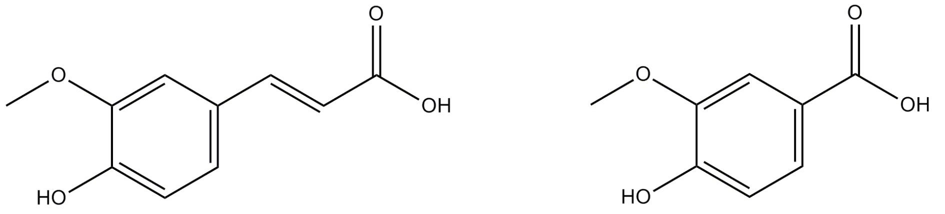


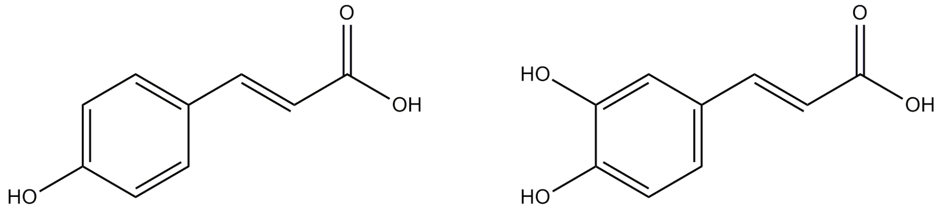
Figure 1.9- Lignin molecule with potential derivative chemicals, adapted from [33].

Vanillin (Van), or 4-hydroxy-3-methoxybenzaldehyde, is an aromatic compound originally extracted from orchid. Commonly applied as flavoring and fragrance, only a small amount of this monomer is produced from lignin by chemical oxidation[37,70]. Currently, new routes have been developed to synthesize Van by biotechnological processes through the application of native fungi, yeast, bacteria and genetically modified microorganisms. Besides lignin, other natural precursors such as glucose and ferulic acid (FeAc) can be applied for the bioconversion of vanillin[72]. FeAc, an abundant derivative of cinnamic acid, can be found in the plant cell walls[73]. Being an important compound in the pharmaceutical industry, namely due to its anti-microbial and anti-oxidant properties, this phenolic hydroxyl acid has received increasing attention for a wide range of applications such as cosmetic, food, and also for renewable resource-based polymers[74]. Indeed, according to Miller[75], FeAc can be selected for the synthesis of polymeric materials improving their thermal and mechanical properties with an increase of melting and glass transition temperatures. Recently, different biotransformations have been reported to metabolize FeAc in different monomers such as Van, vanillic acid (VaAc), 4-vinyl guaiacol, among others, with a relevant interest in the preparation of polymers[37,72,73]. In addition to FeAc and VaAc, also *p*-coumaric and caffeic acids are cinnamic-acid derivatives with a great interest in the synthesis of polymeric materials. Through biotransformation processes, using recombinant *Escherichia coli*, caffeic acid (3,4-dihydroxycinnamic acid or DHCA) can be obtained from *p*-coumaric acid, currently available from agricultural waste such as bagasse and straw[72,74,76]. Due to their structures, both monomers have been used in polymer synthesis leading to materials with good thermal and mechanical properties[37]. The chemical structures of the described materials are represented in Figure 1.10.



Ferulic Acid

Vanillic Acid



p-Coumaric Acid

Caffeic Acid

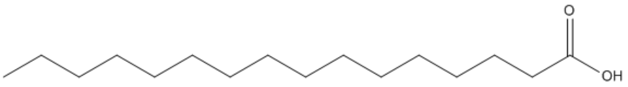
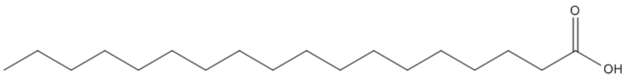
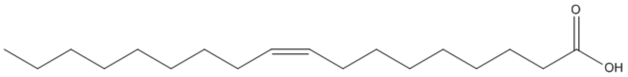
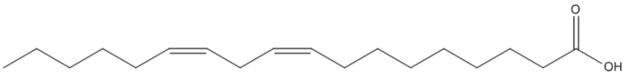
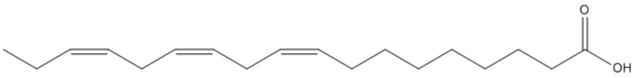
Figure 1.10- Chemical structure of cinnamic acid derivatives.

1.2.3 Vegetable Oils

Presently, the attention given to renewable resources is increasing and vegetable oils have emerged as promising monomers for polymer synthesis. Having already been used as the primary constituent in paints and coatings in the cave paintings, vegetable oils represent currently a promising feedstock for the polymers industry[77,78]. In last decades, vegetable oils have been seen as one of the most viable alternative to petrochemical-based materials, presenting abundant availability, reactive functionalities and competitive cost[38,78,79].

Vegetable oils are mainly composed by triglycerides from esterification of glycerol with three long-chain fatty acids. Fatty acids represent about 95% of the total weight of triglycerides and, with properties depending on the source of the oil, the length of their chains ranges from 12 to 20 carbons, with 0 to 5 double bonds (DB) per molecule[38,80-82]. Chemical and physical properties of vegetable oils depend significantly on the degree of unsaturation in the fatty acid chains[81]. Table 1.1 presents the five most common fatty acids in polymer chemistry.

Table 1.1- Fatty acids commonly used in polymer chemistry[38,82,83].

Nome	Molecular Structure	Structure (C:DB)*	Formula
Palmitic Acid		16:0	$C_{16}H_{32}O_2$
Stearic Acid		18:0	$C_{18}H_{36}O_2$
Oleic Acid		18:1	$C_{18}H_{34}O_2$
Linoleic Acid		18:2	$C_{18}H_{32}O_2$
Linolenic Acid		18:3	$C_{18}H_{30}O_2$

* C corresponds to the number of carbons and DB indicates de number of double bonds in the fatty acids chains.

In the last years, many researchers focused their work on the study of vegetable oil as alternatives to the currently petroleum-based resources in the polymer synthesis, being the soybean, corn, linseed and castor oils the most used vegetable oils for the preparation of these materials[37,79,80,84-86]. However, as a result of their heterogeneous constitution and origin, the use of unmodified vegetable oils as monomers remains a challenge[79].

Triglyceride molecules present several reactive sites such as double bonds, allylic carbons and ester groups, suitable to be chemically modified[38]. With the introduction of polymerizable groups, the reactivity of these molecules is substantially enhanced and, with different functionalities, these monomers can offer a wide range of properties[87].

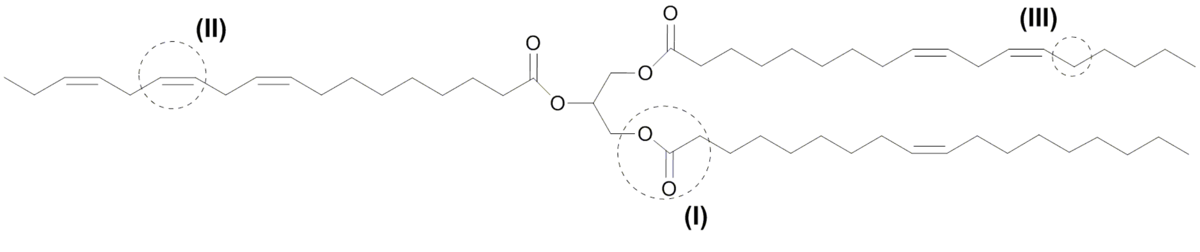


Figure 1.11- Reactive sites of a triglyceride molecule: (I) ester group, (II) double bond and (III) allylic carbon [80].

According to Khot *et al.*[88], polymerizable chemical groups can be introduced in the reactive sites of the triglycerides and unsaturations can also be converted to hydroxyl or epoxy functionalities (Figure 1.11)[88]. Due to the functionalization of the triglycerides, vegetable oils can be involved in polycondensation and ring-opening reactions.

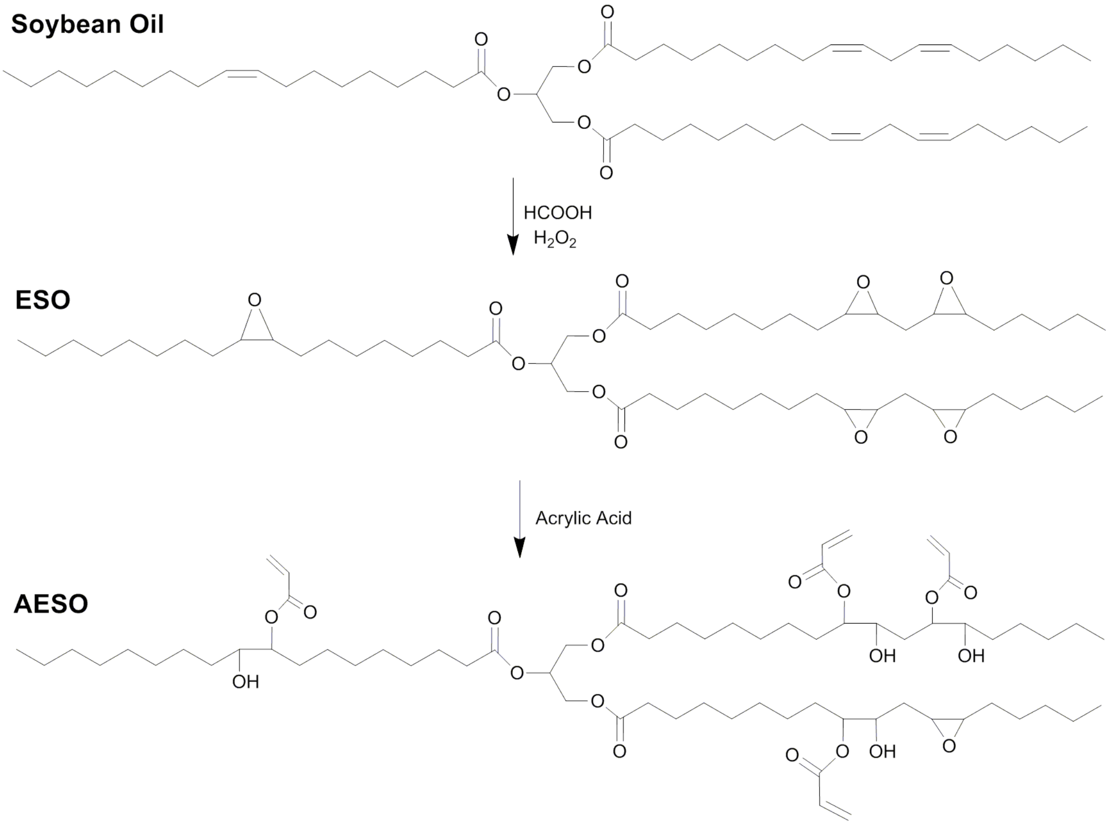


Figure 1.12- Synthesis of acrylated epoxidized soybean oil [89].

The double bonds of the most abundant fatty acids can be easily epoxidized, with a specific catalytic system, using hydrogen peroxide. This reaction is extremely common in the soybean oil giving the epoxidized soybean oil (ESO), whose derivatives are widely used in the industry of polyurethane foams and poly(vinyl chloride) (PVC)[33]. From the reaction of ESO with acrylic acid (see Figure 1.12), is also obtained the acrylated epoxidized soybean oil (AESO), extensively used in polymers and composites. Currently, AESO is commercially available as Drapex 6.8 and Ebecryl 860 (from UCB Chemical Company) [78,88].

1.3 Biobased Unsaturated Polyester Resins

1.3.1 Unsaturated Polyesters (UPs)

The search for a sustainable development based on renewable resources has been the paradigm of the civilization of the 21st century, leading to the emergence of new approaches in the development of polymeric materials. In the last years, and as mentioned before, a wide range of biomass-based molecules and derivatives have been presented as promising building blocks for the synthesis of polymeric materials, leading to the development of polymers with a high biobased content. The aim of these studies for this work is that they propose several formulations incorporating different biobased monomers. In some cases, the UPs are crosslinked without the assistance of the UM.

Isosorbide (Iso) has been recognized as a key feedstock for biobased polyesters. Currently, several authors have reported the successful preparation of Iso-based UPs with high glass transition temperatures (T_g)[37,90]. Jasinska and Koning[91] prepared and characterized water-soluble UPs based on Iso, MA and poly(ethylene glycol) (PEG) with different M_n. The biobased UPs were synthesized by bulk polycondensation, catalyzed by titanium(IV) n-butoxide. Through measurements of iodine number, the unsaturation content of the UPs was determined and the authors found out that part of C=C reacted with Iso or PEG. Consequently, branched structures were also obtained. Thermal properties of UPs were also investigated and the results have shown that an increase in PEG content, essential to form water soluble polymers, led to a significant decrease of T_g values. Nevertheless, biobased UPs with good thermal resistance were achieved, able to be applied in free radical curable coatings.

In addition to Iso, ItaAc has also received serious attention as renewable monomer for the development of UPs and a wide number of studies have been published. Teramoto *et al.*[92] prepared prepolymers based on poly(butylene succinate) (PBuS) with ItaAc or MA units and studied the biodegradability of the materials. The biobased polyesters were synthesized by bulk polycondensation of BDO, SuAc and ItaAc or maleic acid and, after solubilization on chloroform, they were subjected to cure in the presence of benzoyl peroxide (BPO). The crosslinked materials displayed high thermal stability and higher T_g values when compared with the uncrosslinked counterparts. The biodegradability of materials tested by biochemical oxygen demand assay with activated sludge has shown a decrease in the biodegradability after the crosslinking.

Farmer *et al.*[93] described and characterized in detail a set of fully biobased UPs prepared by the melt polycondensation of different diesters of ItaAc, FuAc and SuAc with multifunctional alcohols (PDO, BDO, glycerol and sorbitol). Titanium(IV) butoxide was used as the catalyst (Figure 1.13).

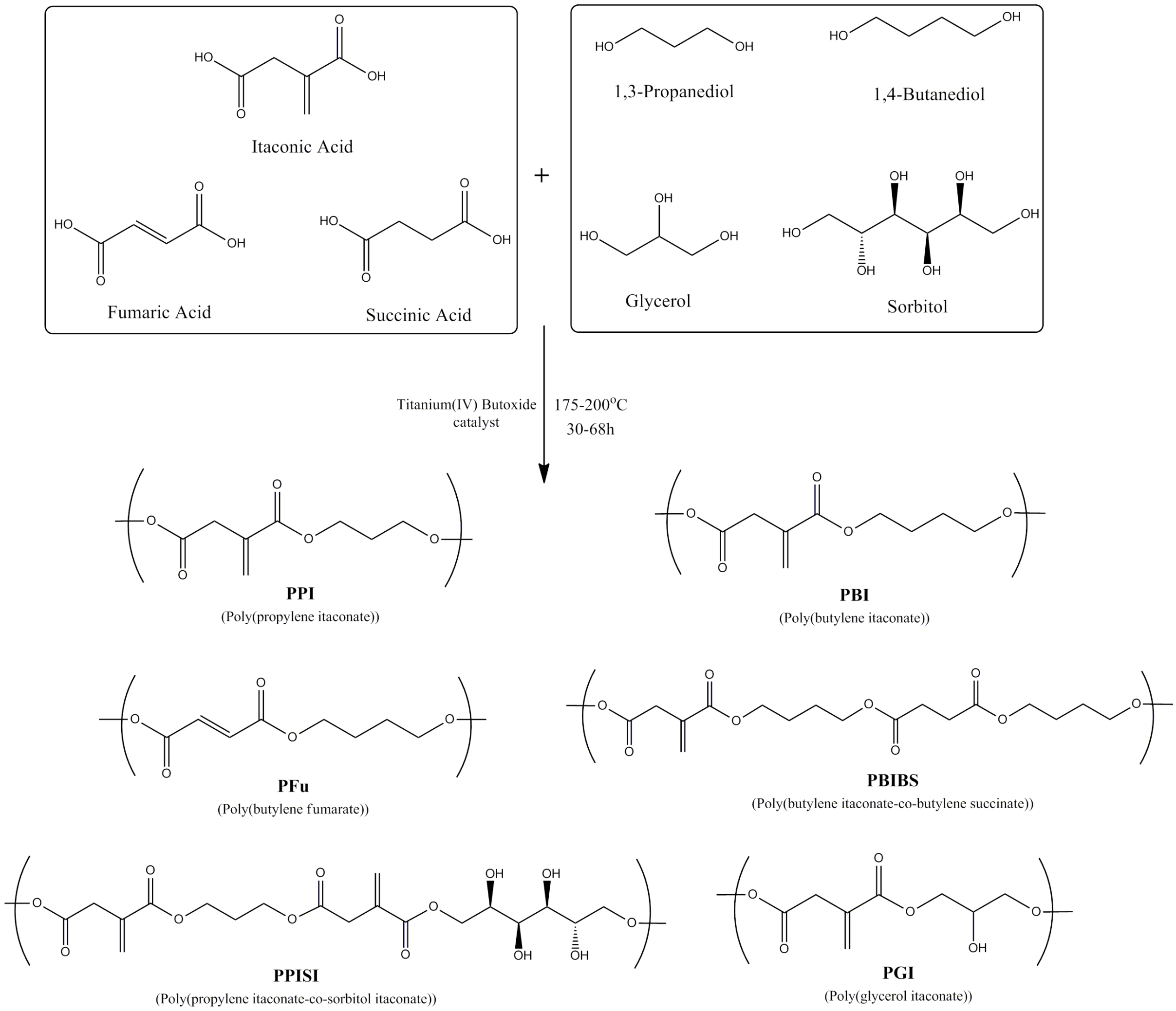


Figure 1.13- Synthesis of UPs from biobased monomers.[93]

The ^{1}H NMR analysis revealed that the double bond of both ItaAc and FuAc moieties were preserved in all UPs. For all the UPs with ItaAc, with the exception of poly(propylene itaconate-co-butylene succinate) (PBIBS), in addition to the itaconate protons the ^{1}H NMR analysis also showed the presence of mesaconate and citraconate moieties, due to isomerization processes (Figure 1.14).

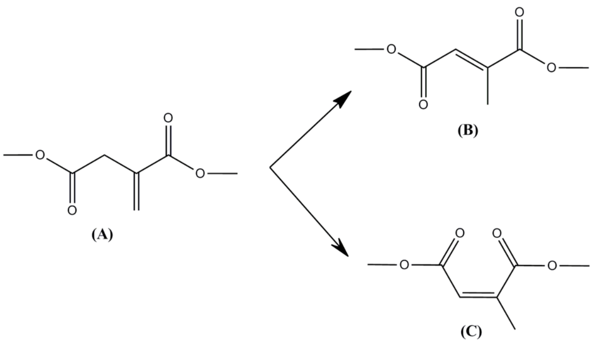


Figure 1.14- Isomerization of itaconate (A) in mesaconate (B) and citraconate (C) moieties[93,94].

For these UPs, branched and crosslinked structures were also obtained. These structures were ascribed to the reaction of the lateral bonds of itaconate moieties with the hydroxyl groups of the diols. Besides chemical analysis, the thermal and mechanical properties of the UPs were also analyzed and showed that the replacement of diols by polyols led to polymers with lower thermal stability, higher T_g values and higher solubility in polar solvents. These results were explained by the formation of highly branched polymeric structures.

Guo *et al.*[95] developed a series of poly(propylene sebacate) polymers (BPEs) from ItaAc, sebacic acid (SeAc) and PDO and studied their ability as shape memory materials for biomedical applications. DEG was also used by the authors to tailor the flexibility of materials. The biobased UPs were prepared by bulk polycondensation in the presence of tetra-*n*-butyl titanate, as catalysts, and after a purification step they were dissolved in chloroform ($CHCl_3$) and subjected to cure in presence of dicumyl peroxide (Figure 1.15).

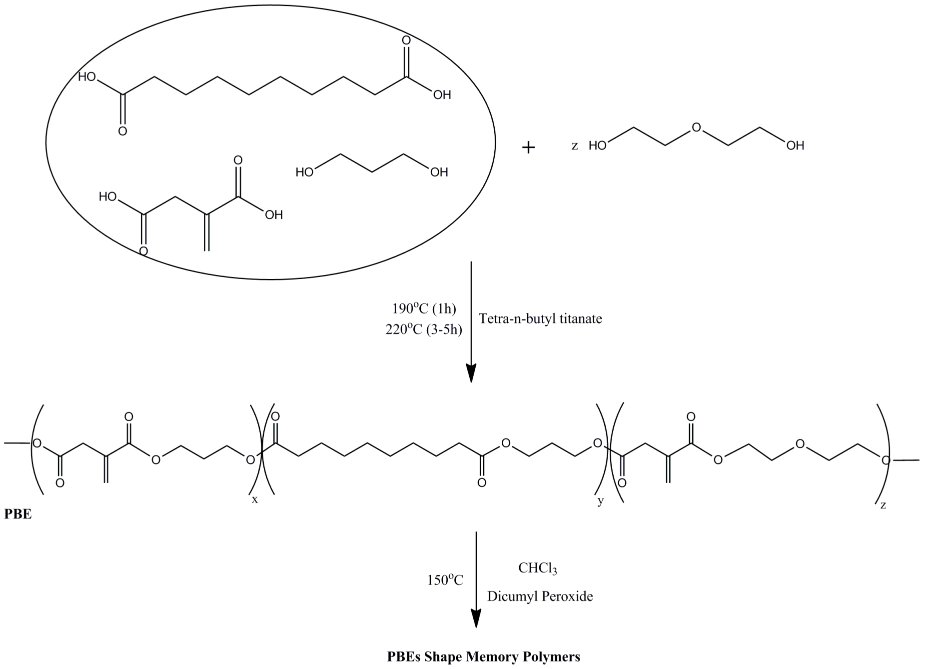


Figure 1.15- preparation of BPEs.[95]

According to the authors, the crosslinked materials presented a semi-crystalline structure and, therefore, their shape memory behavior was closely related with the melting of the crystalline domains. In turn, the melting temperature of the polymers (T_m) was tuned by changes in polymer composition and curing extent. The mechanical properties of the crosslinked UPs were studied and showed to be dependent on the DEG-PDO ratio and on catalyst content. Characterized by promising cell viability and *in vitro* degradation results, the materials also proved to be good candidates to be used in the biomedical field.

Recently, Dai *et al.*[96] developed ItaAc-based UPRs for waterborne UV-curable coating applications. Three different UPs based on ItaAc and different diols (EG, BDO and 1,6-hexanediol (HDO)) were synthesized by polycondensation, with *p*-toluenesulfonic acid monohydrate and dibutyltin dilaurate (DBTL) as pre-polymerization and polycondensation catalysts, respectively (Figure 1.16).

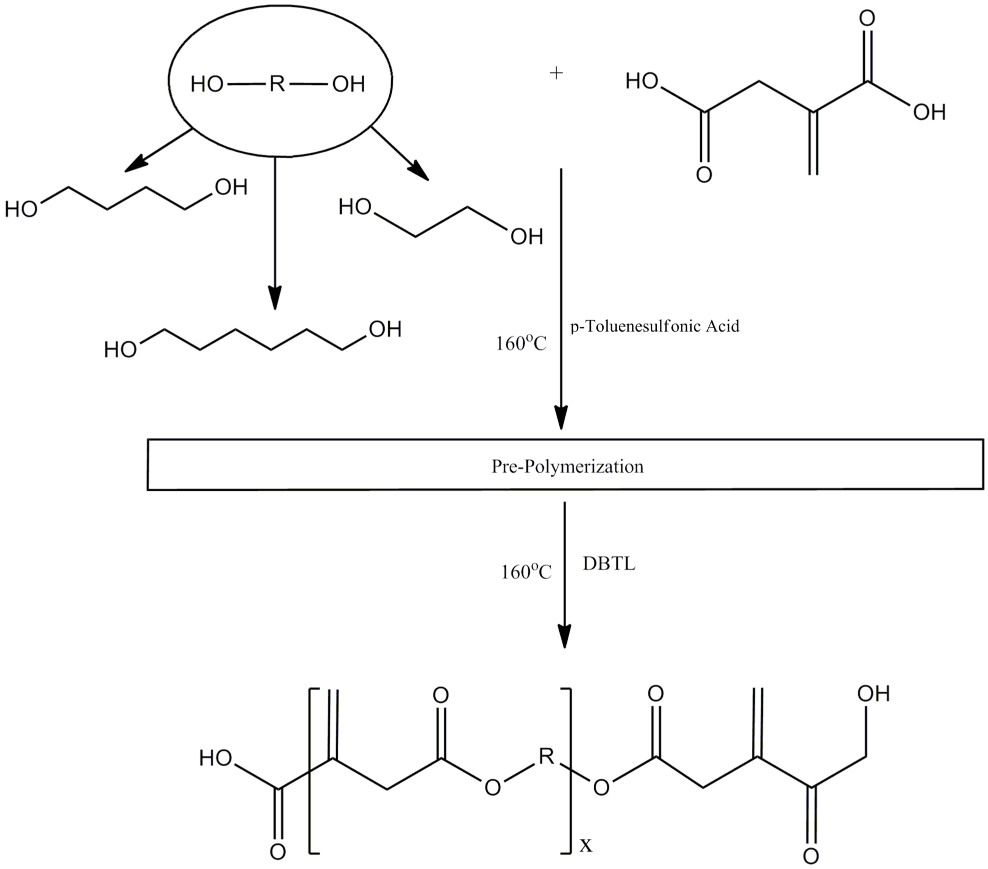


Figure 1.16- Synthesis of ItaAc-based UPs [96].

For the preparation of the coatings, the UPs were emulsified in water, in the presence of sodium hydrogen carbonate, and then subjected to photopolymerization, using the photoinitiator Irgacure 2959. The thermomechanical properties of the coatings were evaluated by dynamic mechanical thermal analysis (DMTA) and the results have shown that, at room temperature, poly(ItaAc-EG) had the highest elastic modulus (E’) value, being lowest E’ obtained for poly(ItaAc-HDO). In the rubbery plateau, the poly(ItaAc-EG) presented the lowest E’ and crosslinking density values. This result was attributed to the incomplete reaction of the double bonds during the cure process. The thermal stability of UPRs was also evaluated and it was found that the degradation temperature for 10 % of weight loss ($T_{10\%}$) increased with increased length of the diols chains. The coating based on poly(ItaAc-EG) exhibited the best properties in terms of water resistance, solvent resistance, and hardness. In what respects the adhesion to substrate, the coating poly(ItaAc-HDO) showed the best result.

In a completely different vein, Chanda and Ramakrishnan[97] reported the development of ItaAc-based polyesters and used the Michael addition reaction as a vehicle to post-polymerization functionalization. Firstly, the UPs were prepared by melt polycondensation using dibutyl itaconate and different diols (1,12-dodecanediol, 1,20-icosanediol, 1,4-cyclohexanedimethanol (CHDM) and PEG-300), in the presence of DBTL as the catalyst. Different UPs were obtained, such as poly(dodecyl itaconate) (PDDI), poly(icosyl itaconate) (PII), poly(CDM-itaconate) (PCDMI) and poly(oligoethyleneoxy itaconate) (PEOI). The ^1H NMR analysis revealed that the *exo*-chain double bond of the ItaAc moieties remained intact, even with the high temperatures of the polycondensation, making the functionalization possible. The functionalization reactions were carried using different thiols and a variety of amines, yielding different UPs derivatives (Figure 1.17). The ^1H NMR analysis showed that the modification was almost quantitative and the M_n of the derivatives ranged from 4000 to 92000 g.mol^{-1}.

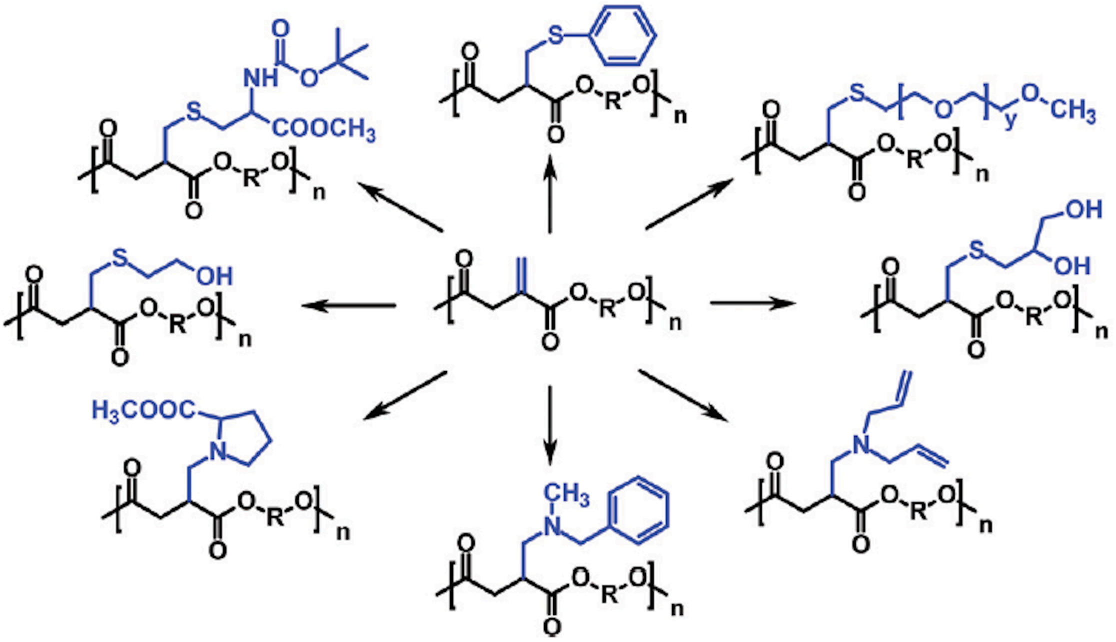
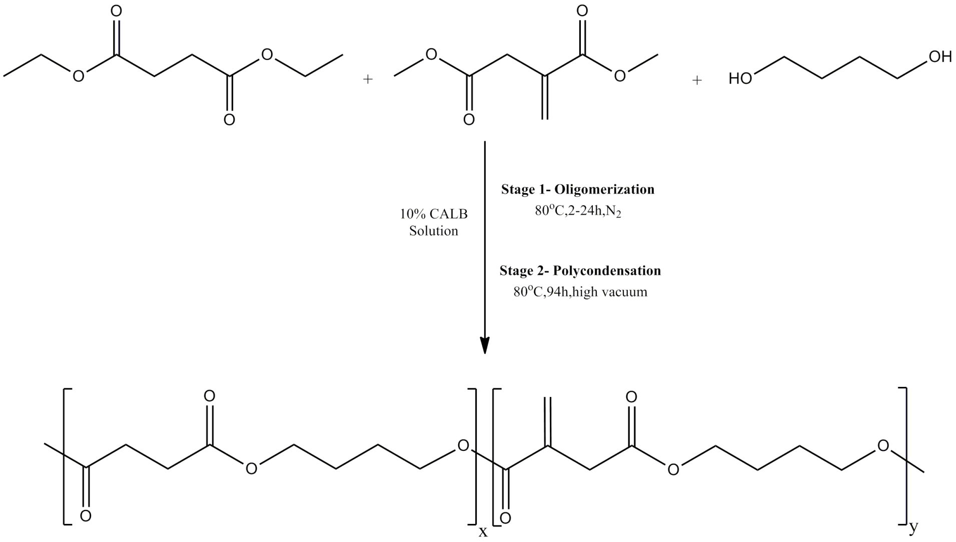


Figure 1.17- Structures of polyesters derivatives prepared using Michael addition, reprinted from [97].

The thermal properties of the synthesized UPs were studied and the results showed that PDDI and PII have phase transition associated with the melting, PCDMI only exhibited a T_g and for PEOI no transitions were identified. The overall results suggest that the post functionalization by Michael addition is a straightforward way to obtain a wide range of materials based on UPs, and whose final properties can be easily changed.

Currently, for industrial purposes, the use of polycondensation reaction, in the presence of organometallic or acid catalysts, is widely used. However, the use of enzymes to catalyze the polycondensation reactions to yield UPs has gained increased interest, namely due to the mild conditions. Barrett *et al.*[98] reported the synthesis of photocurable polyesters using thermal polycondensation reaction and enzymatic polymerization. ItaAc and dimethyl itaconate (DMI) were used as the unsaturated compounds in the thermal polycondensation and enzymatic polymerization (mediated by Lipase B from *Candida Antarctica* (CALB)), respectively. In the first approach, ItaAc was copolymerized with adipic acid (AdAc) and trimethylolpropane (TMP) and with SuAc and sorbitol, yielding branched UPs. In the second approach, DMI was copolymerized with 1,4-cyclohexanedimethanol (CHDM), PEG and 3-methyl-1,5-pentanediol (MPD), leading to the obtainment of linear UPs. The different UPs were then subjected to photopolymerization, in the presence of 2,2-diethoxyacetophenone (DEAP) as the photoinitiator. The results indicate that, for the branched polyesters with TMP, the addition of AdAc contributed to resins with superior mechanical properties. In the case of the UPs synthesized from DMI, it was found that the formulation with CHMD was a brittle material, whereas those containing PEG showed a high flexibility. For the UPs obtained by enzymatic polymerization, the best results in terms of mechanical properties were obtained for the crosslinked networks UP made from DMI, MPD, and AdAc. Overall, the materials showed interesting and easily tunable properties and have shown to have low cytotoxicity, making them good candidates to be used in biomedical applications.

Jiang *et al.*[99] also reported the enzymatic condensation of biobased UPs, using CALB as the biocatalyst. DMI, dimethyl succinate (DSA) and BDO were enzymatically co-polymerized, in a two-stage method (Figure 1.18).



PBSI

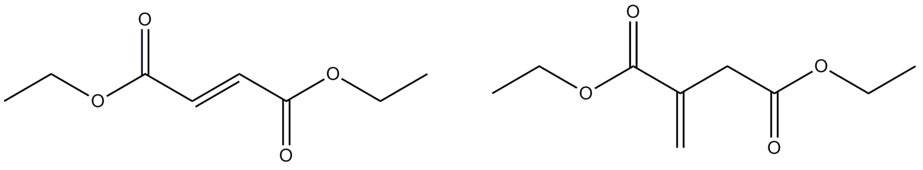
Figure 1.18- Enzyme-catalyzed polymerization of poly(butylene succinate-*co*-itaconate) (PBSI) [99].

UPs, with different feed molar amounts of DMI, were prepared using diphenyl ether (150 wt.% relatively to the monomers) as the solvent. The best result in terms of molecular weight ($M_{n,GPC}$=13300 g.mol^{-1}) and yield (90%) was obtained with a formulation having 15% molar of DMI in the feed. When the molar amount of DMI in the feed was higher than 35% no product was obtained. The NMR analysis showed that the C=C bonds of itaconate in PBSI were preserved during the reaction. The results provided by the thermal analysis (DSC and thermogravimetric analysis (TGA)) indicated that the amount of DMI had almost no impact on the T_g (-35 to -38 ºC) and decomposition temperature (*ca.* 400 ºC), but significantly influenced the T_m that decreased almost linearly as the amount of DMI increased in PBSI.

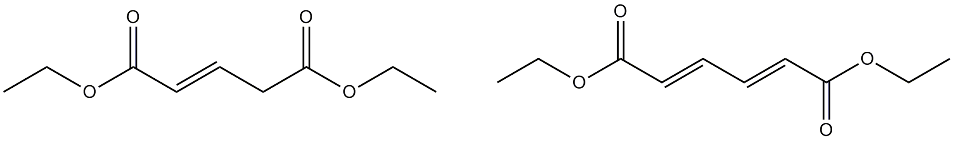
The same research group[100] reported the synthesis of PBSI, making use of three different CALB-catalyzed methods: two-stage melt polymerization, azeotropic polymerization using cyclohexane/toluene as solvent, and two-stage solution polymerization in diphenyl ether. The authors found that, for the three synthetic routes, when the dicarboxylic acids (ItaAc and

SuAc) were used instead of their dialkyl esters derivatives (DMI and DSA), the yields of reaction were very low and only oligomeric species were obtained. This fact was attributed to the poor solubility of the dicarboxylic acids in the reaction media and to their high T_m (significantly above the reaction temperature used) that impaired a good accessibility of CALB to the dicarboxylic acids. Regarding the polymerization making use of the dialkyl esters, it was found that the azeotropic polymerization was the most suitable method, allowing the obtainment of high molecular weight PBSI (~5000 $g.mol^{-1}$), with amounts of itaconate up to 50 % mol. The X-ray and DSC analysis performed on the PBSI revealed a decrease in the crystallinity degree as the amount of itaconate increased in the polymer. Crosslinked structures based on PBSI were obtained by hot pressing at 150 ºC, in the presence of dicumyl peroxide, and were characterized in terms of their thermomechanical properties. As expected, increasing crosslinking densities led to PBSI with higher T_g. All the crosslinked materials presented high Young´s modulus and tensile strain and low rupture strain, being brittle materials.

Naves *et al.*[101] reported the enzymatic condensation, by azeotropic distillation in cyclohexane/toluene, of Iso or isomannide (IM) with diethyl adipate and unsaturated diesters (Figure 1.19) (diethyl fumarate (FU), diethyl itaconate (IT), diethyl *trans*-glutaconate (GL) and diethyl *trans*-*β*-hydromuconate (HM)) in the presence of CALB.



Diethyl Fumarate **Diethyl Itaconate**



Diethyl trans-Glutaconate **Diethyl trans-β-Hydromuconate**

Figure 1.19- Chemical structures of FU, IT, GL and HM.

The UPs based on Iso presented low M_n values, but higher isolated yields when compared with their IM counterparts, fact that was ascribed to the lower reactivity of the latter. It was also observed that FU and IT were, respectively, the diesters with the highest and lowest reactivity towards polycondensation. The *exo*-chain double bonds in IT can hamper the access of CALB to the carboxyl group, lowering the reactivity of the monomer. The highest M_n was obtained for the UPs prepared from FU (from 10500 to 16000 g.mol^{-1}), and a decrease in the values was observed when long aliphatic chains were incorporated. The UP based on Iso, FU and DA showed to be thermally stable until 390 ºC, and presented a T_g of 39 ºC. The enzymatic transesterification reaction was also studied with less sterically hindered diols, namely BDO and HDO. The products of reaction have shown to have molecular weights very close to those presented by the UPs from Iso and IM. Towards the MALDI-TOF analysis it was possible to confirm the presence of double bonds within the polymeric structures, making them good candidates to participate in crosslinking reactions.

Another field of research that is currently being subject of renewed interest is that related with the preparation of photoresponsive UPs based on renewable monomers. This class of materials is characterized by the presence of photosensitive functional groups, incorporated in the polymer backbone or as pendant groups, which are able to undergo [2+2] cycloaddition reactions when exposed to UV light[102]. Upon exposure to UV radiation, the photo-activated double bonds of monomers dimerize with the adjacent molecules and cyclobutane derivatives are obtained[103-105].

Cinnamic acid derivatives are currently one of the most promising biobased compounds able to undergo [2+2] cycloaddition reactions and form photoreversible covalent crosslinks in polymeric materials, as cyclobutane rings, upon exposure to wavelength $\lambda > 260$ nm. For $\lambda < 260$ nm, this reaction is reversible and a dynamic switching between the alkenes and the cyclobutane rings can be achieved (Figure 1.20)[105,106].

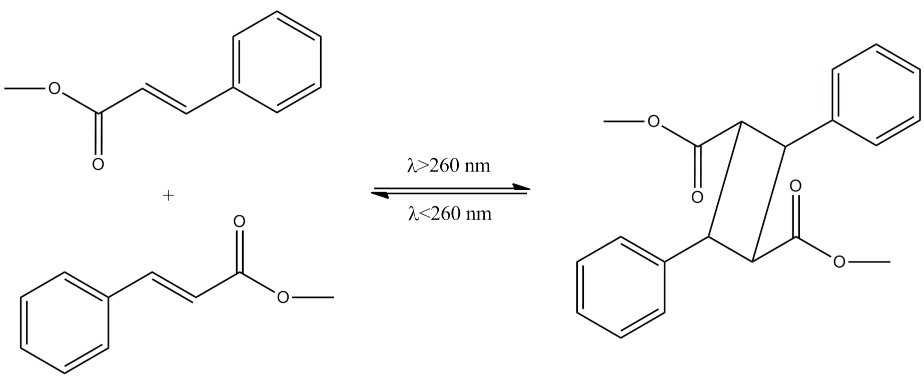


Figure 1.20- Photodimerization of the cinnamic acid derivatives [105].

Photo-induced [2+2] cycloaddition reactions play an important role in the field of polymeric materials and the photoresponsive materials can be used in a variety of applications, namely shape memory polymers, fluorescent coatings, printing formulations, polymeric liquid crystals, biomedical applications, among many others[103,105-109].

In the last few years, an extensive number of studies concerning the synthesis of photoresponsive polyesters have been reported, and the arsenal of UPs sensitive to light radiation is steadily growing. Currently, cinnamic acid derivatives are among the most selected photoresponsive compounds for the synthesis of these type of polyesters, namely the 4-hydroxycinnamic acid (4HCA) and the caffeic acid (DHCA)[110]. The polyesters bearing this kind of monomers can undergo [2+2] cycloaddition and, consequently, form tridimensional structures without the presence of any reactive solvent. Additionally, since the monomers have an aromatic ring in their structure, their presence in the polymer chain will contribute to an enhancement of the thermomecanical properties of the final polymers.

Dong *et al.*[110] synthesized biobased poly(3,4-dihydroxycinnamic acid-*co*-lithocholic acid) through polycondensation reaction between DHCA and lithocholic acid (LCA). According to the authors, hyperbranched copolymers were obtained and, for LCA molar contents above 30 %, good solubility in chloroform, THF, DMSO and acetone were achieved. Due to the presence of a flexible aliphatic chain (with a carboxyl end group), the presence of LCA in the polymeric structure reduced its rigidity, which allowed an improved solubility. Moreover, with the presence of LCA, the synthesized copolymers also presented lower T_g values when compared to the homopolymer of DHCA. The thermal stability of materials showed higher values for the copolymers with high amounts of LCA.

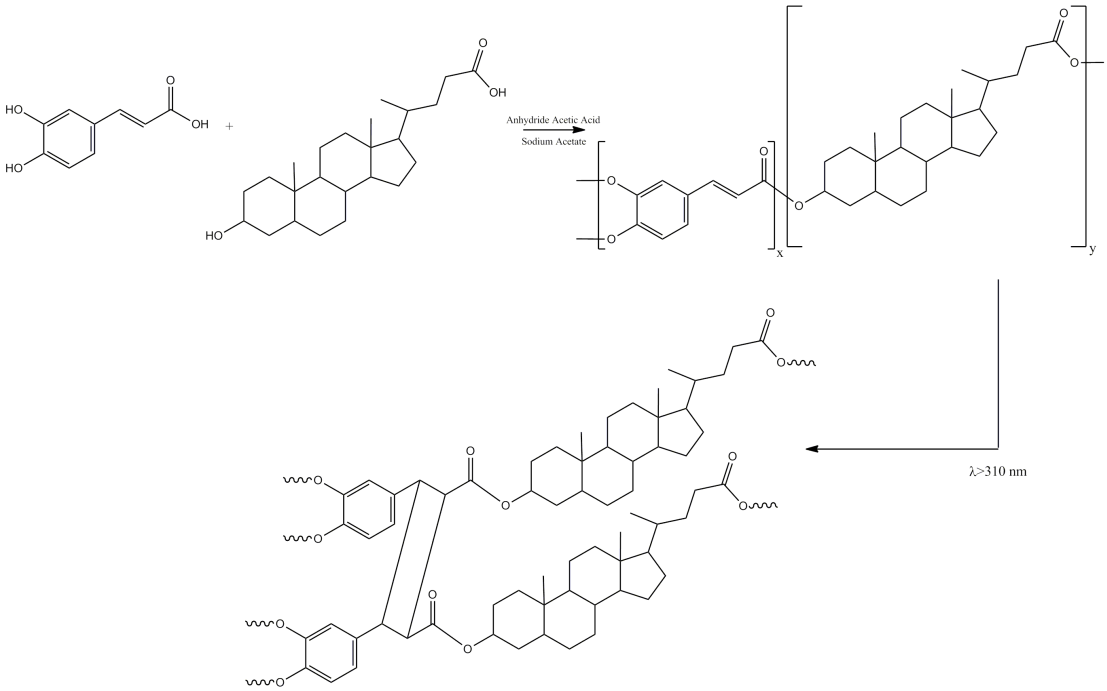


Figure 1.21- Synthesis and photocuring reaction of poly(DHCA-*co*-LCA)[110].

After characterization, the copolyesters were photocrosslinked using a glass filtered high-pressure lamp (λ> 310 nm) (Figure 1.21). The detailed study of the photoreactivity of the materials showed that, with different UP composition, the photoreactivity of the copolyesters could be tailored. The hydrolytic stability was also evaluated in alkaline and in phosphate buffered saline solution (PBS) and it was showed that the stability increased with increasing contents of LCA. In addition, it was also observed that the synthesized copolyesters exhibited high fluorescence emission intensity. Thus, the investigation of these authors led to the development of new branched, biodegradable copolyesters with good thermal stability and fluorescence performances. These features make them good candidates for a wide range of applications. Later, the same authors reported the synthesis of biobased UPs (Figure 1.22) by polycondensation reaction of DHCA with 10-hydroxycapric acid (HDA), a renewable monomer obtained from castor oil, and investigated the impact of different amounts of the monomers in the polymers' performance[111].

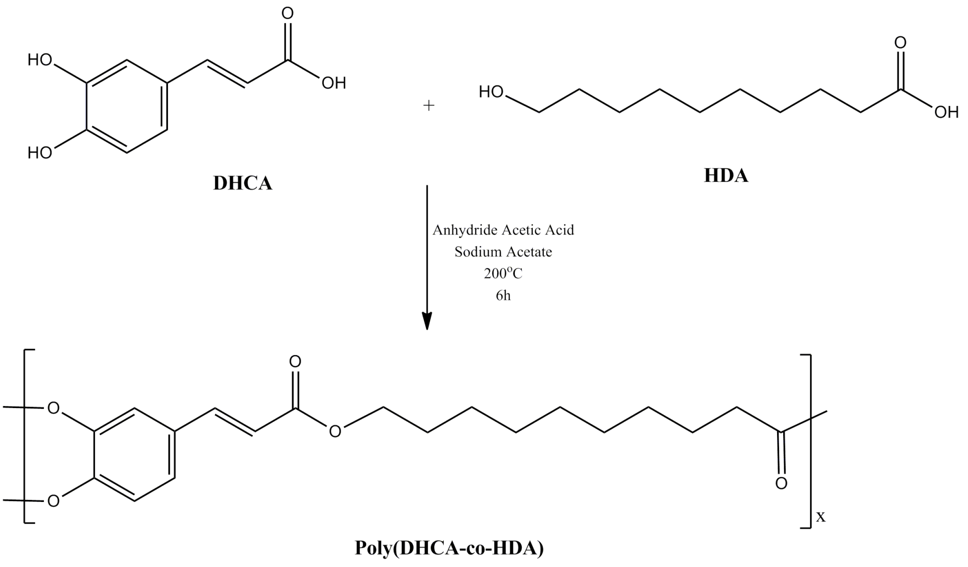


Figure 1.22- Synthesis of poly(DHCA-co-HDA)[111].

After purification, biobased UPs with low molecular weight values and *Đ* ranging from 1 to 2 were obtained. With increasing amounts of HDA, a decrease in the T_g value was observed, due to the increased flexibility promoted by the long aliphatic chain of HDA. Additionally, polymers with higher elongation at break but lower tensile strength were obtained. The copolyesters were crosslinked by irradiation of UV light (λ> 320 nm) and their mechanical properties were also studied. As expected, crosslinked copolymers showed high tensile strength but lower elongation at break when compared to uncrosslinked UPs. The hydrolytic stability of the synthesized materials was also studied and the results showed that, after irradiation, the degradation rate was decreased with increasing amounts of HDA.

Recently, several studies have been reported concerning the preparation of copolymers based on cinnamic acid and lactide or lactic acid (LA). These copolymers will gather the good properties of poly(L-lactide) (*e.g.*, biodegradability and biocompatibility) with those provided by the presence of the cinnamic acid derivatives (*e.g.*, photoreactivity and enhanced thermomechanical properties).[112-114]. Matsusaki *et al.*[112] reported the synthesis of biobased polyesters (Figure 1.23) from different amounts of 4HCA and D,L-lactic acid (DLLA) in bulk and using acetic anhydride as solvent.

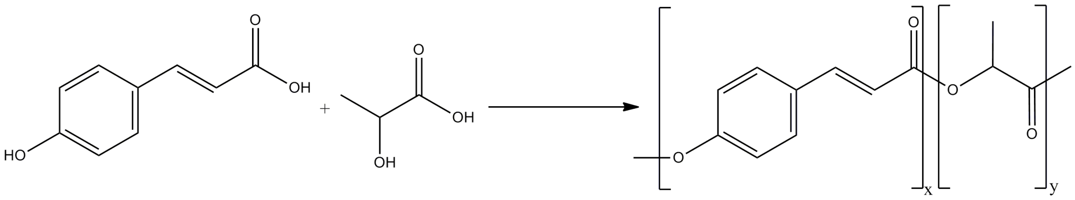


Figure 1.23- Synthesis of poly(4hydroxycinnamic acid-co-D,L-lactic acid)[112].

The copolymers obtained by bulk polycondensation presented high solubility in a wide range of organic solvents for all the molar percentages of 4HCA tested contrarily to those obtained from the solution polymerization. In the latter case, the polymers were only soluble in some of solvents (*viz.* acetone, tetrahydrofuran, dichloromethane, chloroform and acetonitrile) and for molar contents of 4HCA below 20 %. The results provided by UV and ^{1}H NMR spectroscopic analysis showed that for the bulk polycondensation method some of the 4HCA double bonds disappear. The copolymer containing 20 % and 80 % molar amount of 4HCA and DLLA, respectively, was subjected to photocrosslinking with irradiation $\lambda > 290$ nm. The crosslinked material revealed to have lower degradation rates when placed in PBS (pH=7.4), at 37 °C, when compared with films made from the PDLLA homopolymer.

Later, Du *et al.*[115] synthesized liquid-crystalline polymers for tissue engineering, from polycondensation of ferulic acid (FeAc), 4-hydroxybenzoic acid (4HBA) and DLLA. Thermal properties of polyesters were investigated and the results have shown that an increase in LA content led to a significant decrease of T_g values and a decrease on the T_m. In respect to thermal stability, the incorporation of FeAc or 4HBA in the PLLA chain led to more thermally stable materials. A slight increase in the LA content contributed to a better the solubility in chloroform and biodegradability, while maintaining their liquid-crystalline properties. It was also found that the copolymers are able to be photocrosslinked, but their liquid-crystalline properties are lost.

Thi *et al.*[113] conjugated 3,4-diacetoxycinnamoyl chloride (DACC), a derivative of DHCA, to the terminal hydroxyl group of PLLA, yielding a 3,4-DACC-terminally conjugated PLLA (Figure 1.24).

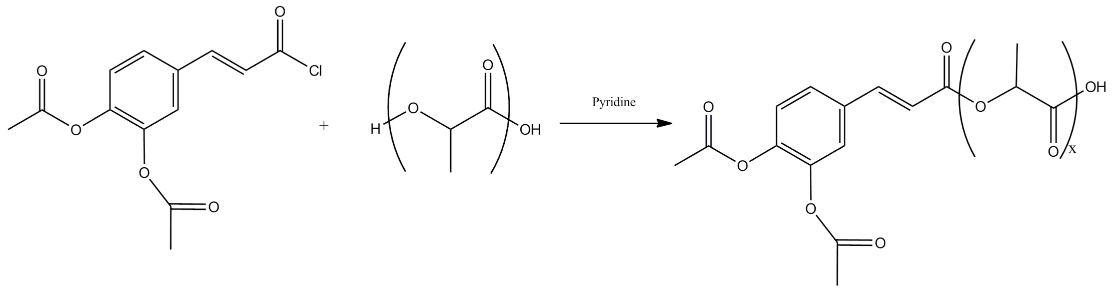


Figure 1.24- Synthesis of DACC-PLLA[113].

The thermal stability of the polymers was evaluated and it was shown that the incorporation of DACC in the PLLA contributed to an increase in the thermal stability. The DACC-PLLAs were able to be crosslinked under UV light (λ> 280 nm). In a very interesting approach, the authors conjugated a fluorescent dye onto the surface of the DACC-PLLAs films by means of the [2+2] cycloaddition. After the photoreaction, the film exhibited fluorescence proved by confocal fluorescence scanning microscopy. Taking this result into account, the authors believe that this type of polymers could be useful to conjugate fluorescent target molecules, making them good candidates to be used in the biomedical field.

Nagata and Sato[116] synthesized biodegradable polyesters by polycondensation of 4,4-(adipoyldioxy)dicinnamic acid (CAC) with α,ω-dihydoxy-terminated poly(L-lactide)s (PLLA diols) with different M_n. The obtained CAC/PLLA materials were photocrosslinked (λ > 280nm) and, an increase in the photocuring times, led to materials with high gel content, high tensile strength and high tensile modulus. In turn, the elongation at break of the copolymer suffered a decrease. Improved properties were observed for the copolyester with the PLLA chain with molecular weight of 3000 g.mol^{-1}. The hydrolytic degradation of the cured polyesters was also studied and showed to be slower than for PLLA materials. Later, following the same line of research, Nagata and Inaki[114] synthesized and characterized photosensitive PLLAs having a pendant cinnamate group. The synthesis was carried out between PLLA diols with different molecular weights and a diacyl chloride of 5-cinnamoyloxyisophthalic acid (ICA). The obtained polyesters (ICA/PLLA) showed increasing values of T_g, T_m and crystallinity as the molecular weight of the PLLA diol increased. ICA/PLLA polyesters were photocured (λ> 280nm) and the results revealed the improvement of the tensile strength and Young's modulus when compared with the uncured materials. Nevertheless, the properties were inferior to those presented by pure PLLA.

1.3.2 Unsaturated Polyester Resins (UPRs)

Nowadays, most commercially available UPRs are derived from petroleum-based resources, but, as mentioned above, there is a great interest in developing such materials making use of biobased UPs (see Section 1.3.1), that are afterwards crosslinked with Sty or another UM. In this subsection are presented the relevant works that present the preparation of UPRs making use of partially or totally biobased UPs.

An interesting study in this field comprises the work of Gonçalves *et al.*[9] in which biobased UPs for microstereo-thermal-lithography application were prepared. The UPs were synthesized via polycondensation reaction between dicarboxylic acids (SuAc, adipic acid (AdAc), sebacic acid (SeAc) and isophthalic acid (IsAc)), glycols (PG and DG) and the unsaturated fumaric acid (FuAc) (Figure 1.25). The influence of the chemical composition in the thermal and mechanical properties was extensively evaluated.

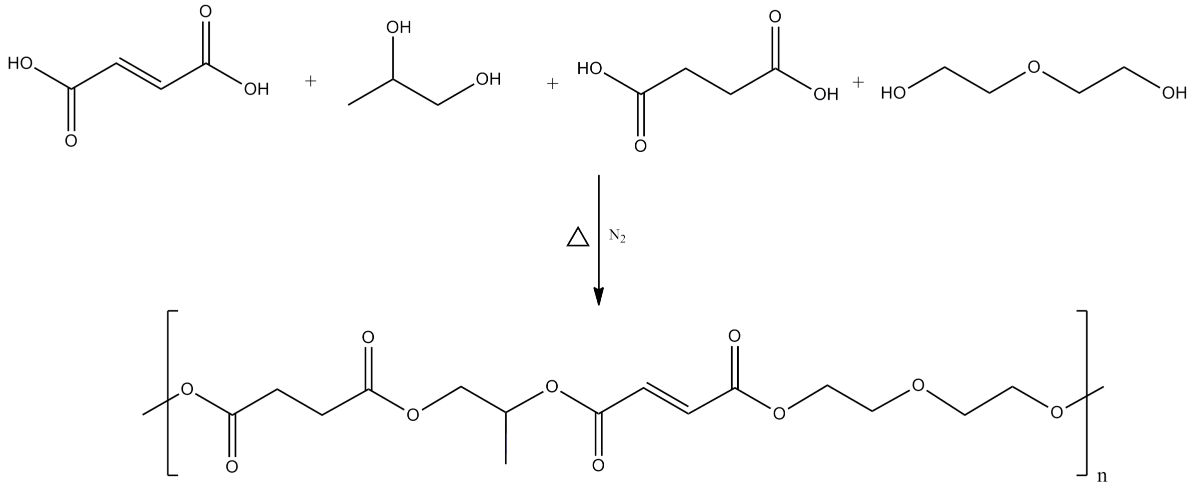


Figure 1.25- Synthesis of biobased UPs, with SA as the dicarboxylic acid [9].

According to the authors, the UP with IsAc and high content of FuAc presented the lowest thermal stability of all synthesized polyesters. On the other hand, for UPs with the biobased monomers SuAc, AcAc and SeAc, instead of IsAc, it was observed an increase in thermal stability with increasing number of carbons in the main chain. Besides thermal stability, also thermomechanical properties were evaluated and showed that UPs with the aliphatic dicarboxylic acids presented the lowest T_g, decreasing with the increased of the carbons in the main chain. The highest T_g value was observed for the UP with IsAc and with a high content of FuAc. The UPs were then dissolved in Sty and the ensuing formulations, especially the UPs without IsAc, showed to have suitable viscosities for microstereo-thermal-lithography technique. By this technique, scaffolds with controlled structure were obtained and proved to be able to promote cell adhesion and proliferation.

In a different vein, Jasinska and Koning[117] developed UPRs based on Iso for coating applications. The polycondensation reaction of Iso, SuAc and MA was performed following the same procedure presented in their previous report (Figure 1.26)[91]. The ^1H NMR and MALDI-Tof-MS analysis showed the presence of branched structures resulting from the Michael addition of Iso end groups and the unsaturated bonds present in the main chains of UPs. The UPs presented high thermal stabilities and high T_g values, with good properties for coatings applications.

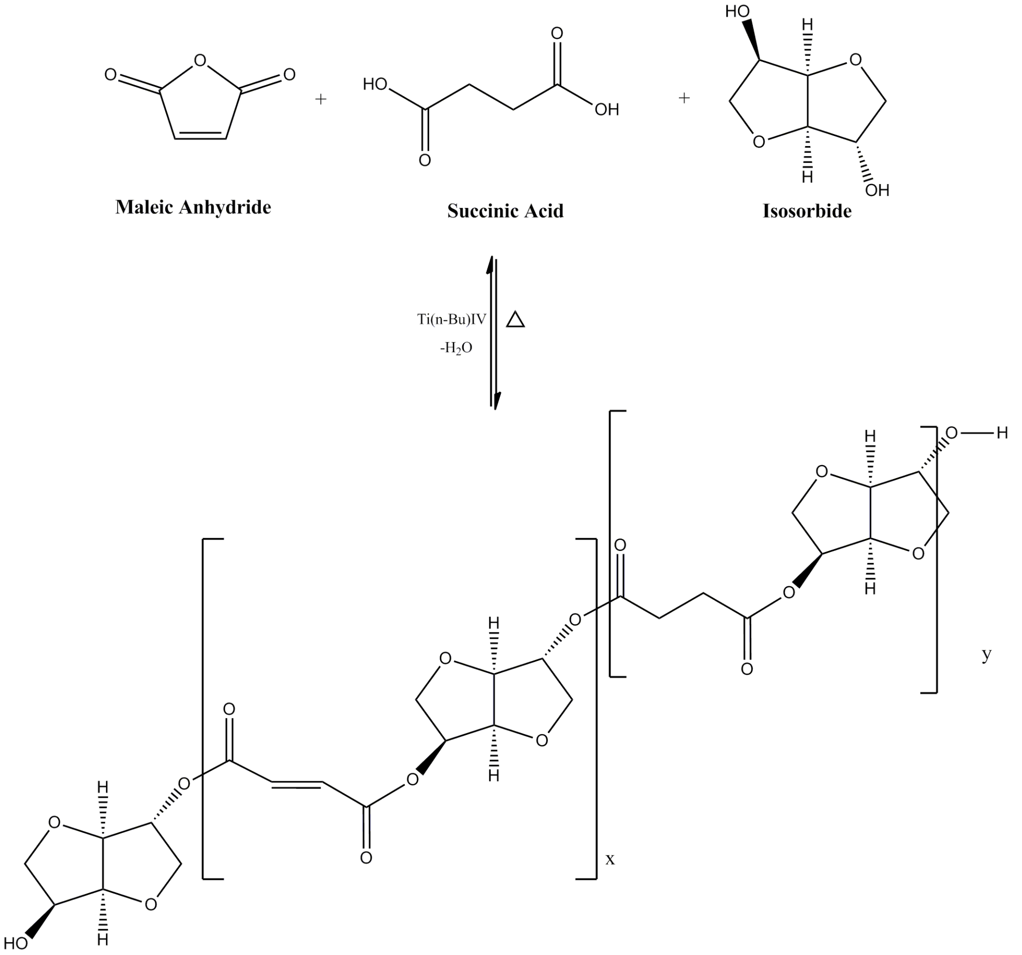


Figure 1.26- Synthesis of poly(isosorbide maleate-co-succinate)s [117].

Instead of the Sty, the authors used 2-hydroxyethyl methacrylate (HEMA), *N*-vinyl-2-pyrrolidinone (NVP), methacrylamide and acrylic acid (AcAc) for the crosslinking reaction that was carried out in the presence of 2-butanone peroxide as initiator and cobalt (II) 2-ethylhexanoate as accelerator. UPRs with high T_g (in the range 50-105 ºC) values were obtained, being the highest value observed for the resin with AcAc. In addition, comparing these UPRs with the respective UPs, it was observed that the former have lower thermal stability despite their crosslinked nature, which was explained by the presence of side bonded oligomers in the crosslinked networks. Moreover, the UPRs also have shown to be thermally stable until 200 ºC.

Other interesting study used Iso, SuAc and ItaAc to synthesize biobased UPs that were subsequently used to prepare UPRs with shape memory properties[90]. Poly(isosorbide itaconate) and poly(isosorbide itaconate-co-succinate)s (Figure 1.27) were obtained from the polycondensation of the corresponding monomers carried out under microwave irradiation at 140 ºC, in toluene, being catalyzed by sulfuric acid (H_2SO_4). Different amounts of monomers were used and their impact in the T_g and molecular weigh of the materials were evaluated.

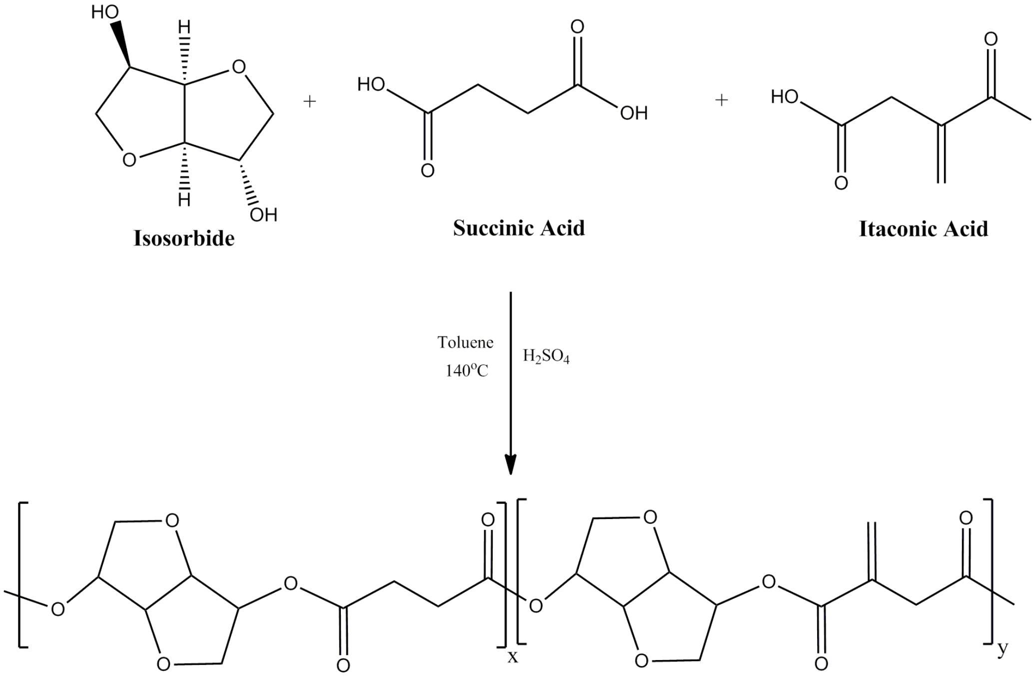


Figure 1.27- Synthesis of biobased UP from isosorbide, succinic and itaconic acids [90].

In the synthesized biobased UPs, higher M_n and higher yields were achieved with increasing amount of SuAc. Moreover, through ^1H NMR analysis, it was also observed a higher incorporation of SuAc, when compared with ItaAc, proving its higher reactivity. After characterization, the biobased copolyesters were crosslinked with dimethyl itaconate (DMI) as the only reactive monomer, in the presence of the free radical initiator 2,2'-azobis(2,4-dimethylvaleronitrile). In the UPRs, the T_g values varied from 57 ºC to 65 ºC, increasing with increased amount of SuAc. Furthermore, all the UPRs have shown to have shape memory effect at T_g.

Iso was also used by Sadler *et al.* as a structural monomer to improve the stiffness of a biobased UPR[118]. UPs based on Iso, EG, MA and different saturated diacids were synthesized by azeotropic distillation, catalyzed by *p*-toluenesulfonic acid (PTSA). According to the authors, the polar nature of Iso decreases significantly the solubility of UPs in Sty and, because of this fact, hydrophobic moieties were added to the formulation. The authors have found that the solubility of the UPs in Sty was improved when suberic or sebacic acids were used. The UPRs were then obtained from the crosslinking reaction of UPs with Sty in the presence of methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate. The thermomechanical properties of the UPRs showed that both E' and T_g values of resins increased with decreasing the carbon length of aliphatic acids. An increasing amount of Iso also led to UPRs with improved thermomechanical properties.

Recently, a similar study was carried out by the same research group[119], which developed UPRs with monomers from renewable sources and compared their properties with a fossil-based commercial UPR (Hexion 713–6150®). The polycondensation reactions of Iso, DEG PhA and MA were performed following the same procedure presented in their previous report[118]. The thermomechanical properties of the UPRs crosslinked with Sty were evaluated by DMTA and the results have shown that, for the UPs with 15 wt.% of Iso, the obtained UPR presented values of T_g and E', at 25 ºC, higher than those observed for the commercial resin. However, for higher amounts of Iso, no improvements on the thermomechanical properties were observed. The results proved to be promising in the development of new biobased UPRs with improved performances.

Fonseca *et al.*[120] also used Iso to prepare new UPRs with high biobased content (Figure 1.28). The polyesters were synthesized by an uncatalyzed bulk polycondensation using combinations of biobased unsaturated monomers (FuAc and ItaAc) with a saturated dicarboxylic acid (SeAc) and biobased glycols (Iso, PG and PDO). DEG was also used, being the only petroleum-based monomer in the work.

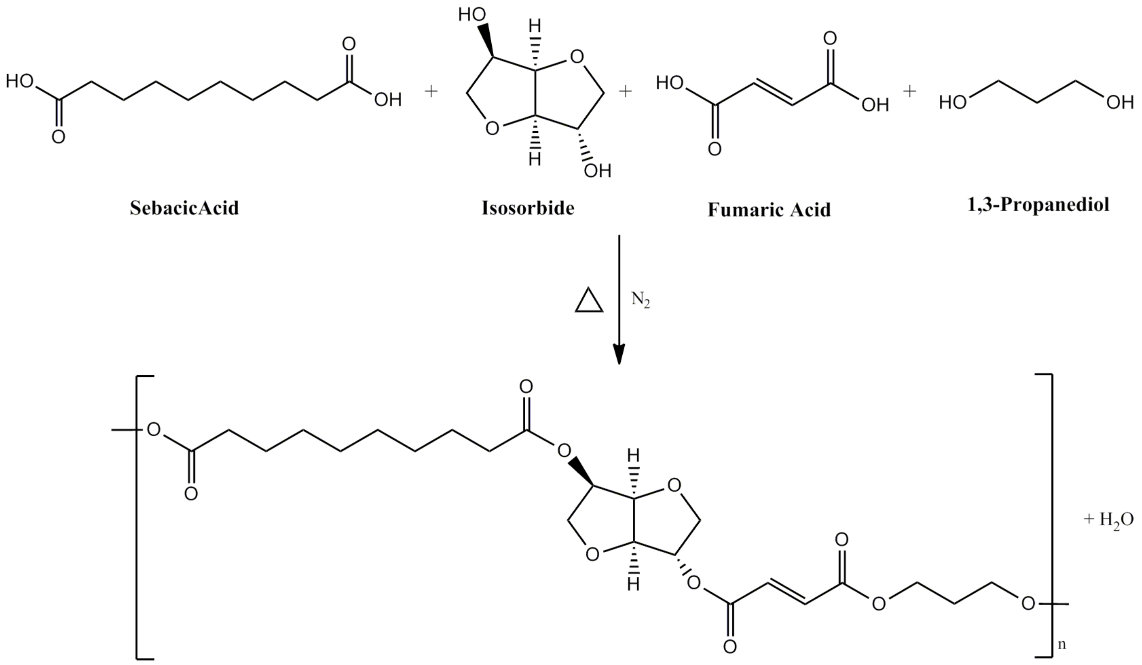


Figure 1.28- Synthesis of biobased UP with high biobased content from Iso, PDO, SeAc and FuAc[86].

In the synthesized biobased UPs, lower M_n and higher $Đ$ values were observed for ItaAc containing UPs when compared to that with FuAc. In some cases, the $Đ$ value was higher than 2, indicating the presence of a branched structure. The data also revealed that changes in the composition led to minor differences in the thermal stability of the UPs. The biobased UPs were then crosslinked with different amounts of HEMA, using benzoyl peroxide (BPO) as the initiator. The authors observed that UPRs with high gel content values were obtained, being this value dependent on the M_n of the UPs and on the HEMA content. The thermomechanical properties of the resins were evaluated and showed the presence of two transitions (β and α), corresponding to the motion of the different domains in the resins. After the swelling and *in vitro* hydrolytic degradation tests, the UPRs proved to be interesting candidates for biomedical applications.

An interesting study was also recently carried out by Sousa *et al.* [121] in which a novel class of UPRs based on 2,5-furandicarboxylic acid (FDCA) were developed. The UPs (Figure 1.29) were synthesized by bulk polycondensation, with no catalyst, between the renewable monomers FDCA, SuAc, FuAc and PDO.

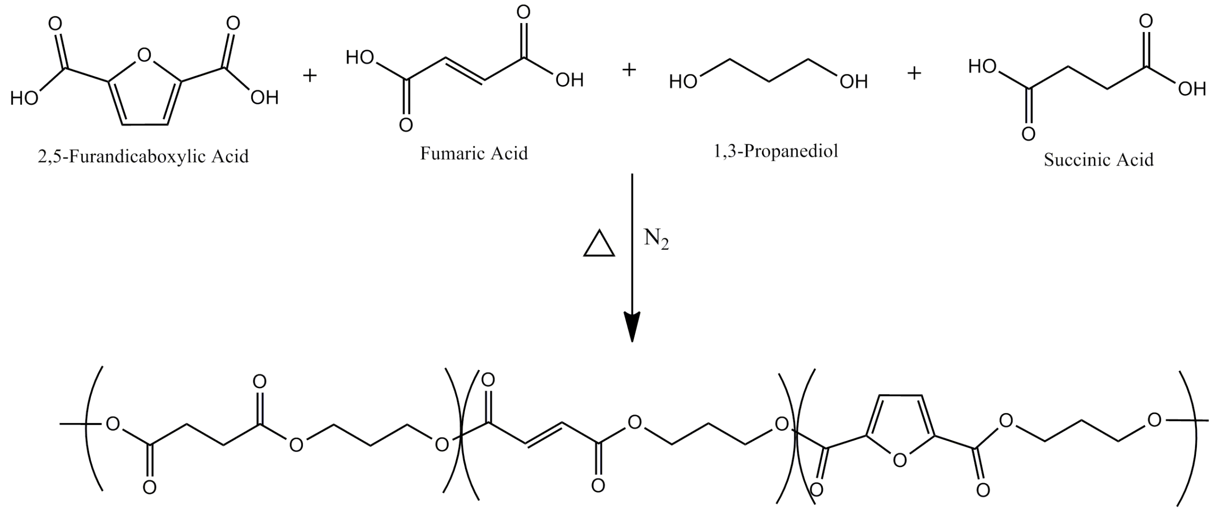


Figure 1.29- Synthesis of FDCA-based UPs[87].

The UPs were then crosslinked with HEMA in the presence of BPO as the initiator. The UPRs presented high gel contents (> 93 %), and it was found that the swelling capacity and the water contact angle (WCA) values were highly dependent on the FDCA content. Whereas the swelling capacity increased with the increasing content of this monomer, the opposite relationship was observed for the WCA. The thermogravimetric analysis was carried out and showed that the UPRs were characterized by similar thermal stability, but lower than the corresponding UP. This fact was explained by the early thermal degradation of oligomers species or small segments of poly(HEMA) that are side bonded to the 3D network. The thermomechanical properties were also evaluated and showed the presence of two transitions: a γ transition (occurring nearly at the same temperature for each UPR) that was ascribed to the vibration of the hydroxyl groups in oligo(HEMA) or poly(HEMA) segments, and the α transition, corresponding to the T_g of the samples, which proved to be dependent on the FDCA content. For the resins under study, the highest T_g values were observed for the formulation with the highest FDCA content.

A similar work was recently published by Dai *et al.* [122] who prepared biobased UPs from FDCA, ItaAc, SuAc and PDO (Figure 1.30), following their crosslinking reaction with guaiacol methacrylate (GM), as UM.

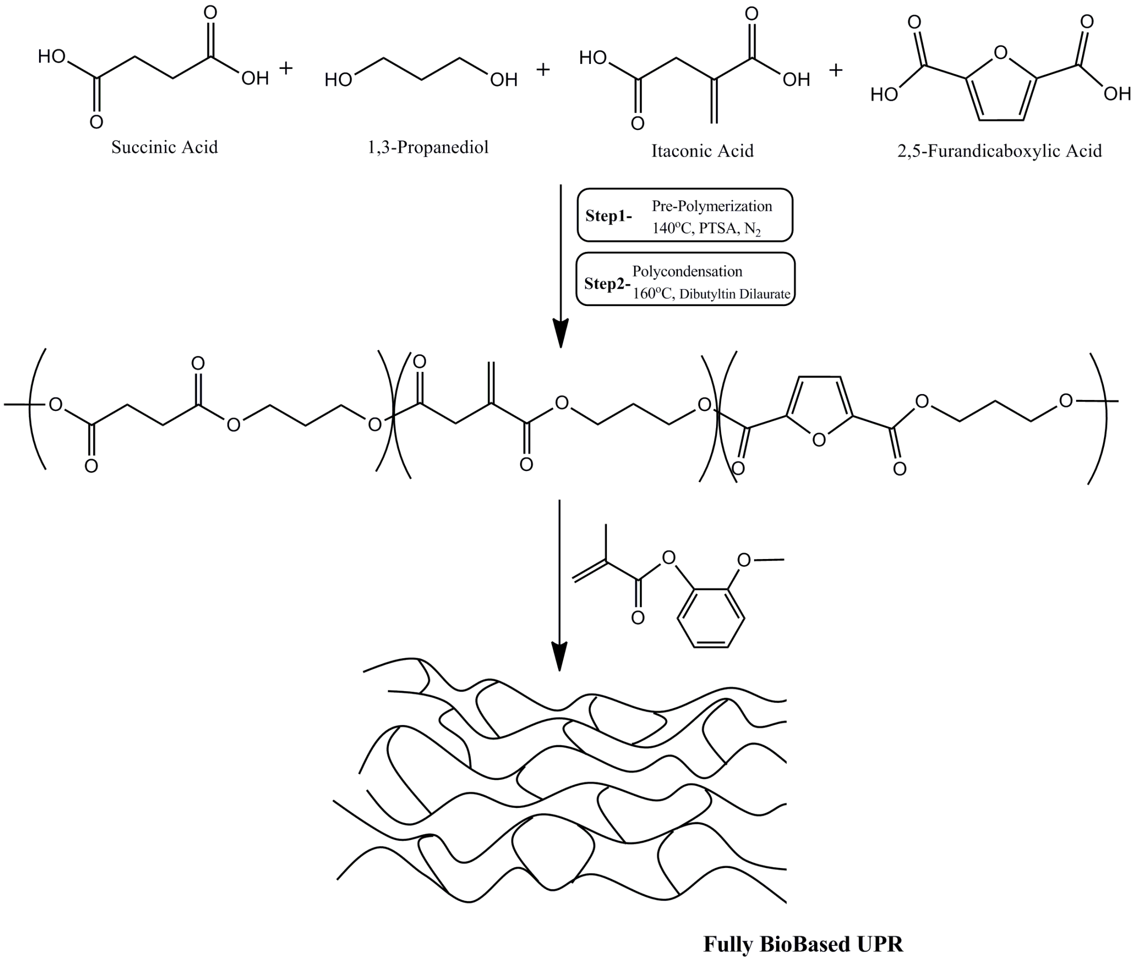


Figure 1.30- Overall strategy for the development of a fully biobased UPR.[122]

According to the thermogravimetric analysis, all the developed UPRs presented high thermal stability, with the highest values observed for the materials with FDCA in their composition. An increasing amount of FDCA up to 15 % mol led to UPRs with improved flexural strength. The augment in the quantity of SuAc also contributed to a decrease in the flexural strength of the UPRs. The DMTA data showed that increasing amounts of FDCA did not translate in a steady increase of the T_g and E’ of the samples. For the UPRs with 15% mol of FDCA, it was found that the incorporation of increasing amounts of SuAc led to UPRs with higher T_g and E´ values. The authors stated the properties presented by the FDCA-based UPRs make them interesting candidates to replace the fossil-based UPRs in their main applications.

As mentioned in Section 1.2.3, vegetable oils are currently one of the most important renewable feedstock of the chemical industry. In the last years, many researchers focused their work on the study of vegetable oil-based UPRs. A vast variety of oils like palm, linseed, soybean and castor oil have already been used for the synthesis of biobased UPRs or have been mixed with commercial UPRs formulations to enhance their ‘green’ content. Lai *et al.*[123] synthesized UPRs based on palm oil and evaluated the swelling properties of the cured polyesters. A palm oil monoglyceride (POMG) was initially synthesized by an alcoholysis method, followed by reaction with MA using different ratios of POMG:MA. The obtained palm oil-based UPs were further crosslinked using Sty (35 wt.%), cobalt naphthalene and MEKP and the swelling properties of the UPRs in different solvents were evaluated. According to the authors, the content of MA have a significant impact on the swelling properties of materials. An increase in the amount of MA led to more dense and compact crosslinked samples, decreasing the sorption ability in hexane. On the contrary, for toluene, ethanol and methanol, the sorption increased with increasing amounts of MA. A very similar study by Mahmoud *et al.*[124] focusing on the synthesis of palm oil-based UPRs was also reported. A monoglyceride was obtained from the reaction of palm oil with glycerol followed by the addition of different ratios of MA to the mixture. The biobased UPs dissolved in Sty (30 wt.%) were UV-cured with Irgacure 184, and the impact of different ratios of monoglyceride/MA on the properties of UPRs was exhaustively studied. It was found that the UPRs with the highest gel content were obtained for the formulation containing 3 eq. of MA relatively to the monoglyceride monomer. Due to its highly cohesive crosslinked network, this UPR also showed the best mechanical properties (high pendulum hardness, high tensile strength and high tensile toughness).

In another study, Mustapha *et al.*[125] used different amounts of epoxidized palm oil (EPO) to mix with a commercial UPR (with 45 wt.% of Sty) and studied the thermal and mechanical properties of the cured biobased resins. The commercial UPR presented a higher crosslinked density when compared with the samples crosslinked from the EPO/UPR mixture. As a result, for the EPO based UPRs, materials with lower E’ and T_g values were obtained. It was also found that the different solubility of EPO/UPR mixture in Sty led to a phase separation and, consequently, the tan δ curves were broader for the cured EPO/UPR samples. Nevertheless, the obtained results also suggested that the addition of EPO slightly improved the impact properties of resins. Thus, with an EPO-rich rubber phase strongly linked to the main phase, resins with rough surface were obtained.

Recently, Liu *et al.*[126] combined highly functionalized castor oil with a commercial UPR, containing 35 wt.% of Sty, and studied the impact of addition of the renewable resources in the UPR performance. Castor oil pentaerythritol glyceride maleate (COPERMA) was synthesized (see Figure 1.31) and mixed with the UPR, followed by cure reaction with tert-butyl peroxy benzoate as initiator. The properties of the resulting materials were extensively studied.

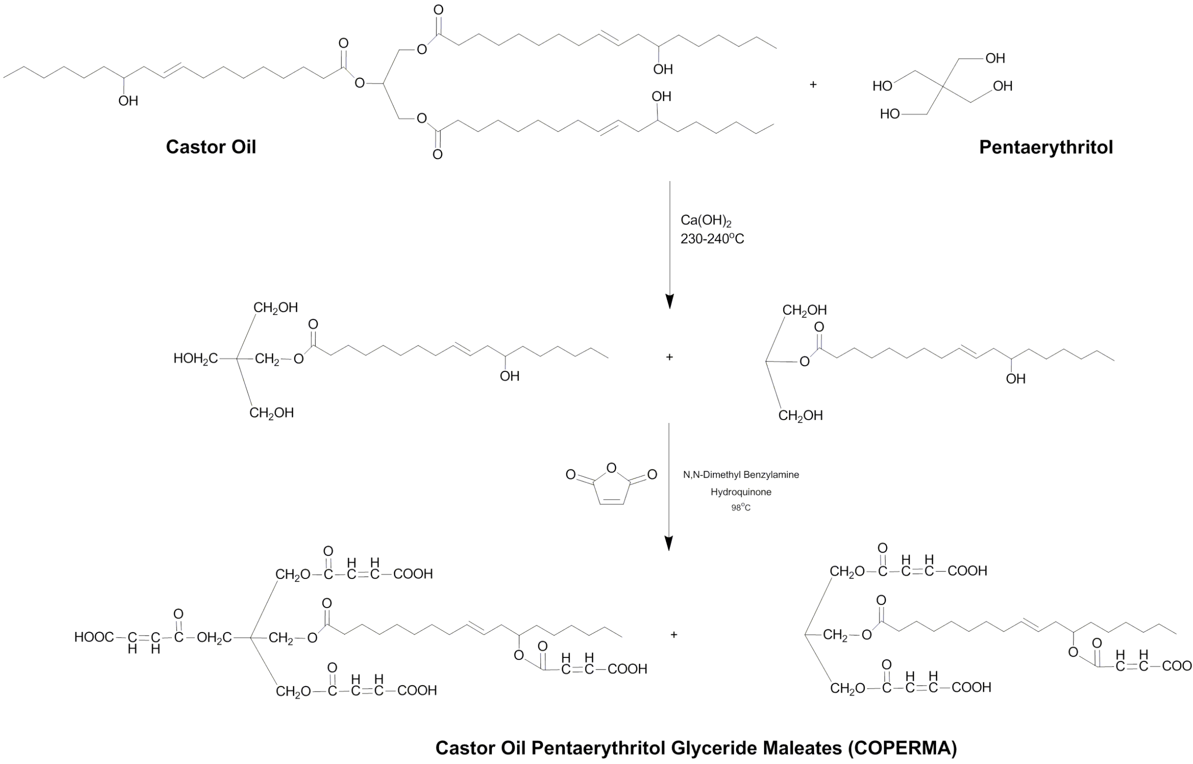


Figure 1.31- Synthesis of COPERMA from castor oil triglyceride[126].

According to the authors, high thermal stabilities were observed for commercial and COPERMA-based resins, with a maximum weight loss near the 400 ºC. In addition to thermal analysis, mechanical properties were also evaluated. With the incorporation of COPERMA in the polymeric matrix, a slightly increase in the crosslinking density could be observed. Thus, in the presence of this maleinated product, the biobased resins showed higher T_g values as well as improved tensile and flexural moduli. Moreover, it was also observed similar strength and stiffness for the commercial petroleum-derived and biobased UPRs. The overall results indicated that the thermomechanical properties were similar, and in some cases slightly better than those of the fossil-based UPRs.

Miyagawa *et al.*[127] reported the preparation of UPRs using a mixture of fossil-based UPs (with 34 wt.% of Sty) with functionalized linseed oil (epoxidized methyl linseedate, EML) up to 25 wt.%. After cure with 2-butanone peroxide and cobalt naphthalene, as initiator and accelerator respectively, the thermomechanical properties of the resulting materials were studied. Due to lower crosslinking density, both E' and T_g values of biobased UPRs decreased with increasing amount of EML. Additionally, increasing the amount of EML led to a broadening of the loss modulus (E'') curve, indicating that the UP/EML formulations had some degree of heterogeneity.

Besides linseed and castor oil, soybean oil (SO) has also been widely used for the preparation of monomers and polymers. Following a similar approach to their previous work, Miyagawa and *et al.*[128] developed UPRs making use of a mixture of a fossil-based UP (*Polylite* 32570-00) with epoxidized methyl soyate (EMS), diluted in Sty (34 wt.%). The results showed a decrease in the E' and in the heat deflection temperature as the amount of EMS increased in the formulation. This fact was attributed to the decrease of the crosslinking density with increasing amounts of EMS. In addition, lower T_g values were also achieved. In turn, the Izod impact strength value did not change its value with the increasing amounts of EMS, even with the presence of EMS-rich rubber phase for resins containing 20 wt.% of this compound. According to the authors, this can be ascribed to the weak chemical bonding between the main phase and the EMS-rich phase and consequent lower energy dissipation. Can *et al.*[129] also synthesized UPRs based on SO. A soybean oil monoglyceride (SOMG) was synthesized by the reaction between the oil and glycerol at high temperatures. The SOMG was next esterified with MA leading to the formation of SOMG maleate half esters (Figure 1.32).

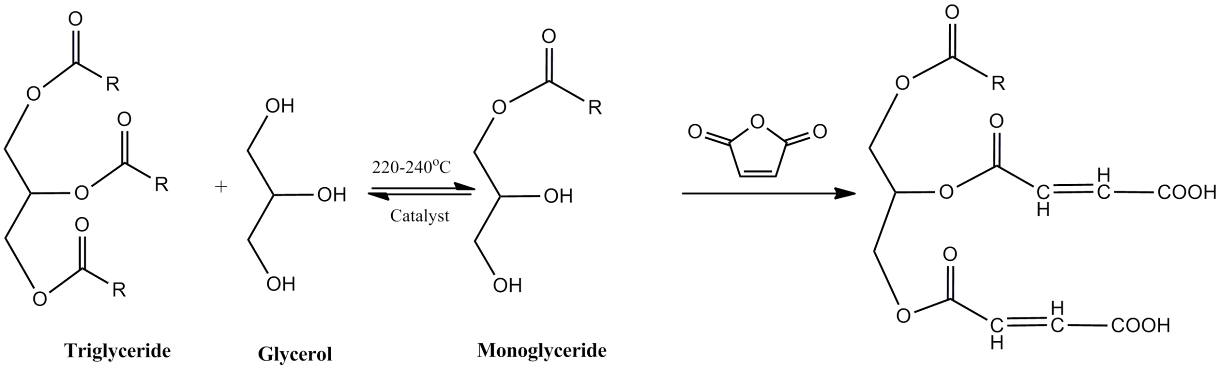


Figure 1.32- Synthesis of SOMG maleate half ester.

Through radical copolymerization with Sty, biobased UPRs were obtained and their mechanical properties showed values of surface hardness, T_g and E' similar to commercial UPRs, these materials can be seen as reliable alternatives to the fossil-based UPRs. In addition, the polar carboxylic acid groups in polymeric structure contributed to an enhancement of the interfacial adhesion of the UPR with fillers such as glass fibers.

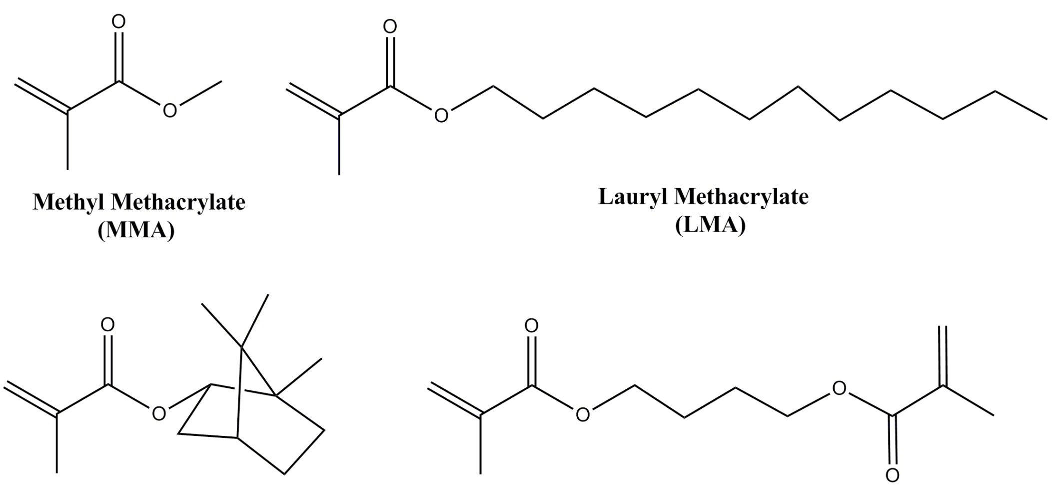
SO was also used by Li *et al.*[130] to obtain biobased UPRs. A soybean oil monoglyceride mixture (SOMG) was firstly obtained by transesterification between glycerol and SO and, in the second step, this mixture was made to react with PG, MA and PhA. The obtained polyester was chemically characterized by FTIR and ^{1}H RMN. With increasing amounts of SO, UP with high molecular weights were obtained. In addition, it was also confirmed that no side reactions between SO and MA occurred. The mechanical properties of the UPRs were next evaluated in the second work of Li *et al.*[131]. According to the authors, with an increasing weight content of monoglyceride, higher impact strength and tensile elongation were achieved but lower flexural and tensile strength were obtained. For monoglyceride contents higher than 20 wt.%, the presence of fatty acid chains hampered the crosslinking between UP and Sty. Nevertheless, with a weight content of monoglyceride between 15 and 20 %, resins with good impact strength, tensile strength and flexibility were obtained.

1.4 New Biobased Reactive Monomers as Potential Styrene Substitutes

As already mentioned, the application of UPs as a structural material requires the addition of an UM (or reactive solvent), not only to reduce the viscosity of the unsaturated polyesters but also to promote the crosslinking reactions. Sty is by far the most common UM used in industry of UPRs, making 30 to 40 % in weight of the final material, mainly because of its availability and low cost. Additionally, the UPs crosslinked with Sty lead to UPRs with excellent physical and mechanical properties[3,16,132].

In spite of being widely used, Sty has some disadvantages being the most relevant its high toxicity and its high volatility during the processing of UPRs [3,133]. For this reason, and due to the constant increasing interest in sustainable developments, significant efforts have been dedicated to the replacement of Sty by less volatile and less toxic monomers issued from renewable resources.

Cousinet and *et al.*[134] studied the applicability of some biobased methacrylate derivatives as Sty substitutes in UPRs. For such purpose, the authors evaluated the compatibility of the different monomers (Figure 1.33), *viz.,* methyl methacrylate (MMA), isobornyl methacrylate (IBOMA), lauryl methacrylate (LMA) and butanediol dimethacrylate (BDDMA) with the UPRs in terms of miscibility and viscosity.



Methyl Methacrylate (MMA)

Lauryl Methacrylate (LMA)

Isobornyl Methacrylate (IBOMA)

Butanediol Dimethacrylate (BDDMA)

Figure 1.33- Chemical structure of MMA, IBOMA, LMA, and BDDMA.

The mechanical properties of the resin with BDDMA, the only biobased UM with low volatility which completely dissolved the UP, were evaluated and it was found that the UPRs showed high stiffness but poor resilience due to the presence of a very dense and tight network. In order to improve the thermomechanical properties, mixtures of BDDMA with the other monomers were also used as reactive solvents. In the case of MMA, a homogeneous network was obtained for all ratios of monomers with a large range of mechanical behaviors. With an increase of MMA, improved ductility and resilience were attained. When IBOMA is added to BDDMA-based UP systems the resulting network was significantly looser. Heterogeneous materials were achieved due to a phase-separation of an IBOMA-rich phase and, consequently, materials with poor mechanical properties were obtained. For formulations with UP, BDDMA and LMA, E’ and T_g values were shifted to lower temperatures. This fact can be ascribed to the presence of longer fatty acids chains of LMA that contributes to an increase of free volume in polymeric matrix. In addition, this UPR presented high strain at break but low flexural and impact strengths compared with UP-BDDMA resins. Thus, of all systems based on methacrylate derivatives, the MMA/BDMMA mixture proved to be promising in replacing Sty.

Due to their abundance, low cost and essentially due to their low volatility, fatty acid-based materials with methacrylate function have been reported for several authors as promising monomers to replace the Sty in UPRs. Wu and Li[135,136] used pure acrylated epoxidized soybean oil (AESO) to replace Sty in two different commercially available UPRs for fiber-reinforced composites. One of the UP was based on PG, IsAc and MA (PG-IsAc-MA), whereas the other one was only based on PG and MA (PG-MA). In their studies, different weight ratios of AESO-UP were studied: 50/50, 60/40 and 70/30. According to the authors, in both studies, the fiber-reinforced resins with 60 wt.% of AESO presented the best flexural and tensile properties similar those with Sty. However, for the resin PG-IsAc-MA[135], the final composite with this AESO content showed high water absorption. Only the resin with 50 wt.% of AESO originate composites with lower and similar water absorption to those with Sty. For PG-MA resins[136], the thermomechanical properties of the composites were also evaluated by DMTA and the results have shown that the resin with 60 wt.% of AESO had the highest E', the highest tan δ_{max} but the lowest T_g value of the AESO-based composites. Notwithstanding, the results of both works showed that AESO could be a promising monomer for Sty replacement in UPR fiber-reinforced composites.

In a different approach, the same research group[137] developed thermally cured coatings using a mixture of an UP with AESO. Different UPs were used, namely poly(ItaAc-EG), poly(ItaAc-BDO), poly(ItaAc-HDO) and an UP prepared from ItaAc, BDO and glycerol; poly(itaconic acid-1,4-butanediol-glycerol (PIBG). The gel content of the crosslinked mixtures was determined and compared to that of crosslinked AESO, and the results show that the mixtures have higher values of gel contents because of their high crosslinking density. The AESO-based thermosetting resins presented higher E' and T_g values, being also characterized by high tensile strengths and modulus and low values of elongation at break. The UPs with glycerol (PIBG) led to AESO-based materials with much higher tensile strength and modulus when compared to those without this monomer. An improvement of the tensile properties was observed with an increasing content of PIBG, due to the increased intermolecular forces resulting from the higher amount of hydroxyl groups in the structure. Besides the mechanical performance, the coating properties of the resins such as solvent resistance, pencil hardness and flexibility were also evaluated and good results were obtained.

Carbohydrates are the most abundant renewable resources and provide a wide range of raw materials such as cellulose, hemicellulose, starch and lignin that can be used as building blocks in polymers based on renewable resources[44,56]. In 1960, vinyl levulinate (VL), a derivative of levulinic acid, obtained from the sugars of hemicellulose and starch, was used as an internal plasticizer of PVC. Presenting a low volatility and being odorless, VL was used as substitute of Sty in UPRs by Cousinet and *et al.*[133]. The mixture of VL with a commercial UP presented low viscosity and was crosslinked in the same conditions used for the crosslinking of the same UP with Sty. The results showed that the UPRs based on VL have lower T_g values and lower E' values when compared to those UPs crosslinked in the presence of Sty. This result was attributed to residual VL in the UPR, whose presence was confirmed by DSC and NMR spectroscopy. Additionally, UPRs based on VL also presented lower flexural modulus and flexural strength than the ones with Sty but both resins showed comparable impact strength. Although UPRs with VL have inferior performance, the mechanical properties of these resins can be improved with addition of fibers or fillers, leading to materials able to be applied for industrial applications. VL can also be combined with other biobased vinyl esters or methacrylates with improved reactivity, being a reliable alternative to replace Sty.

Guaiacol is another renewable resource obtained from lignin that, due to its aromatic character, has potential to be used as Sty substitute. As described in Section 1.3.2, the new biobased UPs prepared by Dai *et al.* [122] were dissolved in guaiacol methacrylate (GM), with a weight ratio of UP-UM of 60/40, and subjected to cure in the presence of *tert*-Butyl peroxybenzoate (TBPT). According to the authors, UPRs with good properties were obtained and showed to be dependent on the UPs composition.

In addition to aforementioned works, some authors have also reported their studies focused on alternatives to St replacement namely in vinyl ester (VE) resins. However, it is also expected the successful application of these Sty substitutes in the UPRs formulations.

La Scala *et al.*[138] selected four different fatty acids (lauric, stearic, oleic and linoleic) to obtain methacrylated fatty acid (MFA) based monomers, able to replace Sty in VE resins. The biobased monomers were prepared by the reaction of the carboxylic acid of the fatty acids with the epoxide group of glycidyl methacrylate, catalyzed by AMC-2 (Figure 1.34).

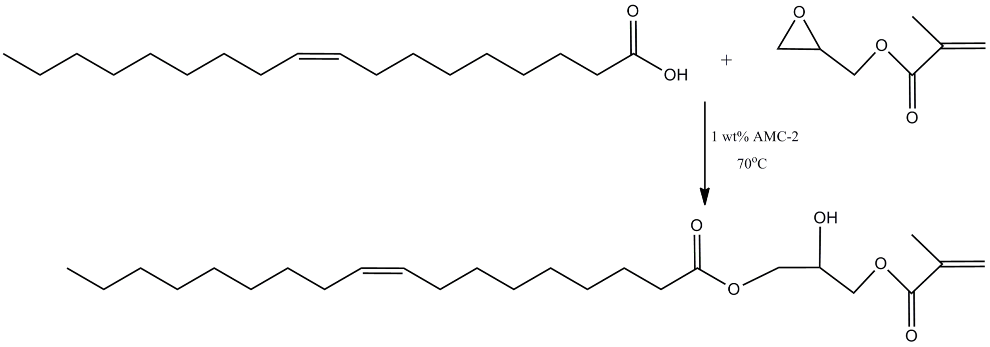


Figure 1.34- Reaction scheme route to obtain methacrylated fatty acid monomer from fatty acids[138].

VE resins comprising 35 and 45 wt.% of MFAs and blends of MFAs and Sty were prepared. When only MFAs were used as reactive monomers, lower T_g and E’ were achieved. The most promising results were observed for short saturated MFA with lauric acid (MLA), leading to resins with high T_g and E' values. For VE resins with MLA and Sty, better properties were obtained than those with MFA as the only reactive diluent.

Later, Stanzione and *et al.*[139] synthesized new UMs by esterification between methacrylic anhydride and vanillin, guaiacol and eugenol (Figure 1.35) and studied these methacrylated monomers as alternative to Sty in VE resins.

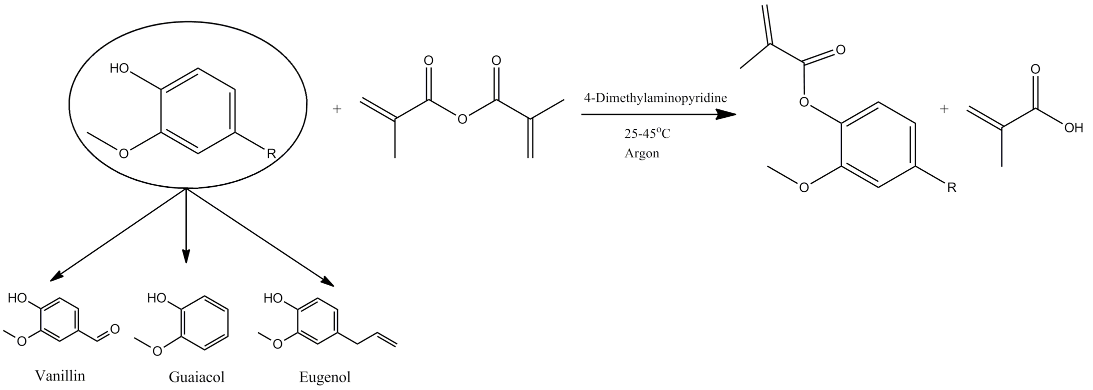


Figure 1.35- Synthesis of methacrylated monomers from methacrylic anhydride and lignin-derivative compounds [139].

Despite presenting higher viscosities, resins with methacrylated guaiacol (MG) and methacrylated eugenol (ME) showed T_g values comparable to that of VE resins with Sty. These results suggest that MG and ME monomers can be used to replace Sty in industrial applications, without compromising the properties of the final resins.

An interesting study in this field comprises the work of Sadler *et al.*[140] in which two biobased monomers with the methacrylate functionality where studied as UM for Sty replacement (Figure 1.36).

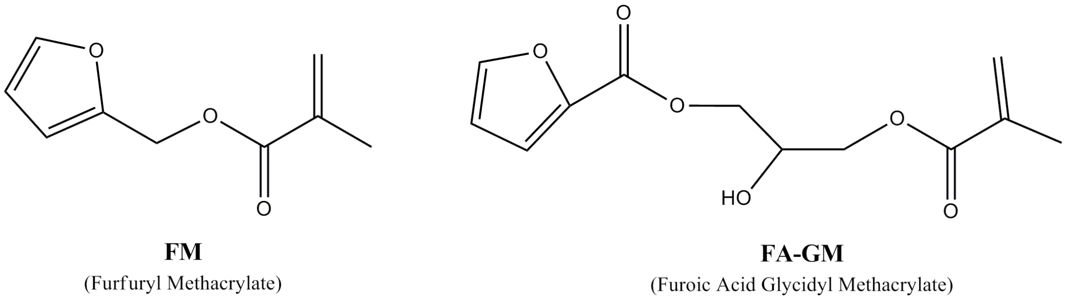


Figure 1.36- Biobased monomers to Sty replacement in VE formulations.[140]

After the cure reaction, the final resins from FM and FA-GM presented higher crosslinking densities and similar values of E', at high temperatures, when compared to that crosslinked with Sty. According to the authors, these new compounds are promising candidates to be used in VE formulations, especially for a partial replacement of Sty.

In summary, due to their intrinsic properties, UPRs are definitely one of the most promising families of polymers. For the last decades, the use of renewable resources to produce biobased materials have been attracting ever-increasing attention but, so far, the main challenge remains in the replacement of the current fossil-based polymers, without jeopardizing the thermal and mechanical properties of the final materials.

The final properties of the polyesters can be easily tuned by changing the nature of the monomers, the composition ratio and the polymerization processes allowing the preparation of materials tailored for a specific application. The wide number of works reported in literature about use of renewable resources in UPs and UPRs is indicative of the potential of these materials in the scientific activity and also for industrial applications.

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CHAPTER 2 – **Increasing The Biobased Content Of A Commercial UPR**

Due to the success of the work developed in this chapter, a new biobased unsaturated polyester resin is currently on the market, being commercialized under the trade name ERIS 140.

Several Portuguese and Spanish media published the news and the work was also discuss in the TV show on Porto Canal channel (Portugal).

CONFIDENTIAL

This chapter is presented separately for confidentiality reasons.

CHAPTER 3 – **Going Greener: Synthesis of Fully Biobased Unsaturated Polyesters for Styrene Crosslinked Resins with Enhanced Thermomechanical Properties**

Parts of this chapter have been accepted for publication:

C. S. M. F. Costa, A. C. Fonseca, J. Moniz, M. Godinho, A. C. Serra, J. F. J. Coelho. "Going Greener: Synthesis of Fully Biobased Unsaturated Polyesters for Styrene Crosslinked Resins with Enhanced Thermomechanical Properties" *eXPRESS Polymer Letters* **2017**.

3.1 Abstract

The main goal of this work was the development of fully biobased unsaturated polyesters (UPs) that upon crosslinking with unsaturated monomers (UM) could lead to greener unsaturated polyester resins (UPRs) with similar thermomechanical properties to commercial fossil-based UPR. After the successful synthesis of the BioUPs, those were crosslinked with styrene (Sty), the most commonly used monomer, and the influence of the chemical structure of the UPs on the thermomechanical characteristics of UPRs were evaluated. The properties were compared with those of a commercial resin (Resipur®). The BioUPRs presented high gel contents and contact angles that are similar to the commercial resin. The thermomechanical properties were evaluated by dynamic mechanical thermal analysis (DMTA) and it was found that the UPR synthesized using propylene glycol (PG), succinic acid (SuAc) and itaconic acid (ItaAc) presented very close thermomechanical properties compared to the commercial resin.

3.2 Introduction

The last years have an increasing demand on renewable-based polymeric materials and, in UPRs industry, one of the major challenge remains in the use of renewable resources, without compromise the properties of the materials.

In the market, a considerable number of available renewable monomers for the synthesis of UPs and UPRs[1-3] is available and, in the last years, some authors have focused their work on the development of UPRs partially based on these raw materials[4-7]. The work of Gonçalves *et al.*[4] reports the preparation of different UPRs for microstereo-thermal-lithography (μSTL). The UPs were prepared using some biobased monomers such as fumaric acid (FuAc), SuAc, adipic acid (AdAc), sebacic acid (SeAc) and PG. The obtained UPs were characterized by good thermal stability and a glass transition temperature (T_g) that has shown to be dependent on the chain lengths of the diacids. In another study, Fonseca *et al.*[8] prepared UPRs with high biobased content using the biobased monomers FuAc, ItaAc, SeAc, PG, 1,3-propanediol (PDO) and isosorbide (Iso). After the crosslinking reaction of BioUPs with 2-hydroxyethyl methacrylate (HEMA), the UPRs presented high gel content and good thermal stability. The thermomechanical properties of the resins revealed the presence of two main transitions, α and β, corresponding to the motion of different domains in the resins. Recently, Sousa *et al.*[9] developed UPRs based on 2,5-furandicarboxylic acid (FDCA), with a biobased content of 50 wt.%. The UPs were synthesized by bulk polycondensation between FDCA, SuAc, FuAc and

PDO, with no catalyst or purification steps. The BioUPs were crosslinked with HEMA, showing good thermal stability and high T_g values. Despite the relevance of these works in the development of BioUPRs, until now very few groups developed UPRs that comprised the use of monomers from renewable sources (with a biobased content lower than 20 wt.%) and compared their properties with a fossil-based commercial UPR. Sadler *et al.*[5,10] focused their work on the development of UPRs with Iso and compared their properties with two commercial resins, *viz.* Hexion 713–6150® and Viapal 450®. The developed Iso containing UPRs did not have properties (elastic modulus, glass transition temperature) to replace the commercial ones in their main applications. Therefore, the further development of UPR formulations with higher biobased content is highly desirable.

In this work, fully biobased UPs were prepared using different combinations of a set of renewable monomers (*viz.*, FuAc, ItaAc, SeAc, AdAc, SuAc, PG, Iso, PDO and 1,4-butanediol (BDO)). The monomers were carefully selected according to their structure envisaging the standard thermomechanical properties expected for an UPR. After the crosslinking with Sty, the properties of the new UPRs were compared with a commercial product that is commonly used in very demanding markets (e.g. synthetic marble and marine industry). In addition, the bulk polymerization method employed for the synthesis of the UPs does not require the use of toxic solvents as other available processes (e.g. azeotropic distillation [11,12]).

It should be pointed out that, to the best of our knowledge, it has never been reported the synthesis of an UP totally based on renewable monomers to afford UPRs (crosslinked with Sty) that have thermal and mechanical properties similar to those of a commercial UPR.

3.3 Experimental Section

3.3.1 Materials

FuAc (99 %), SeAc (94.5 %), PG (99 %), Iso (98 %), Sty (>99 %) and tetrahydrofuran (THF, >95 %) were purchased from Sigma-Aldrich. AdAc (>99 %) and PDO (>98 %) were purchased from TCI Europe. SuAc (99 %), ItaAc (99 %), BDO (>99 %) and potassium hydroxide solution (1N, in ethanol) were purchased from Acros Organic. Cobalt Octoate (CoO) was purchased from AGAMI, phenolphthalein was obtained from Riedel-de-Häen, methyl ethyl ketone peroxide (MEKP) from Algarplás and hydroquinone (HQ, >99 %) was purchased from Analar. Deuterated THF (THF-d_8, 99.5 %) was purchased from Eurisotop. All the reactants were used as received, unless otherwise stated.

3.3.2 Synthesis of the UPs

The BioUPs were synthesized by uncatalysed bulk polycondensation reaction. The monomers and the radical inhibitor HQ (0.01 % of the total weight) were charged in a four head reactor equipped with a mechanical stirrer, a nitrogen inlet and a condenser connected to a round-bottom flask. The polycondensation reactions were carried out at 205 °C. The end of the reaction was set when the acid value (AV) reached a constant value of 30 mg KOH.g^{-1} (determined according to ISO 2114 – 00). Table 3.1 presents the molar amounts of monomers, as well as the reaction times used in the different polycondensations.

Table 3.1- Reaction conditions for the synthesized BioUPs.

Formulations	$n_{\text{saturated acid}}$ (mol)	$n_{\text{unsaturated acid}}$ (mol)	n_{glycols} (mol)	t (h)
Commercial UP	0.33	0.14	0.53	------
BioUP_1	0.33 (SuAc)	0.14 (FuAc)	0.53 (PG)	12.0
BioUP_2	0.33 (AdAc)	0.14 (FuAc)	0.53 (PG)	12.0
BioUP_3	0.33 (SeAc)			10.5
BioUP_4	0.33 (SuAc)	0.14 (FuAc)	0.53 (PDO)	5.0
BioUP_5			0.53 (BDO)	8.0
BioUP_6			0.53 (Iso)	7.0
BioUP_7	0.33 (SuAc)	0.14 (ItaAc)	0.53 (PG)	5.0

n: molar amounts of monomers, in mol; t: reactions time, in hours (h).

3.3.3 Preparation of the UPRs

The BioUPs (BioUPs) were dissolved in 32 wt.% Sty. The initiator MEKP (2 wt.%) and accelerator CoO (1 wt.%) were added under continuous stirring until a homogeneous mixture was obtained [13]. The formulations were cured in a Teflon mold (16 x 7 x 0.5 mm) at room temperature for 24 hours and post-cured at 80 ºC for 3 hours [14,15].

3.3.4 Characterization Techniques

Chemical Structure Identification

ATR-FTIR analysis of UPs was carried out with a Jasco FT-IR-4200 spectrometer, from Jasco Inc. equipped with a Golden Gate Single Reflection Diamond ATR. Data collection was performed with 4 cm^{-1} spectral resolution and 64 accumulations.

^1H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer, from Bruker using a 5 mm TIX triple resonance detection probe, in THF-d_8, at room temperature. Tetramethylsilane (TMS) was used as the internal reference.

Molecular Weight Distribution

The molecular weight (M_n) and polydispersity (*Đ)* of the BioUPs were determined using high performance size exclusion chromatography HPSEC; Viscotek with a refractive index (RI) detectors. The column set consisted of one Viscotek Tguard column (8 µm), one Viscotek T2000 column (6 µm), one Viscotek T3000 column (6 µm) and one Viscotek LT4000L column (7 µm), from Malvern. HPLC pump was set with a flow rate of 1 $mL.min^{-1}$. The system was also equipped with an online degasser. The tests were carried out at 30 ºC using an Elder CH-150 heater. The samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2 µm pore, before the injection (100 µL). Tetrahydrofuran (THF) was used as the eluent. Conventional calibration was done with narrow polystyrene standards (M_n ($g.mol^{-1}$) = 1980; 4290; 10050; 30300; 52220 and 96000).

Thermal Properties

The thermal stability of samples was evaluated by TGA, using a TA Instruments Q500 thermogravimetric analyzer (thermobalance sensitivity: 0.1 μ g). The equipment was calibrated within a temperature interval ranging from 25 ºC to 1000 ºC, at a heating rate of 10 $ºC.min^{-1}$, running tin and lead as melting standards. The samples were analyzed using open alumina crucibles, in the temperature range 25 ºC to 600 ºC and at a heating rate of 10 $ºC.min^{-1}$, under dry nitrogen purge flow of 100 $mL.min^{-1}$.

The differential scanning calorimetry (DSC) studies were performed in a TA Instruments Q100 model, equipped with a RCS90 cooling unit, from TA Instruments. The heat flow and the heat capacity were calibrated at 5 $ºC.min^{-1}$ using indium and sapphire standards, respectively. The samples were analyzed in aluminum pans with an ordinary aluminum lid loosely placed. A heating rate of 5 $ºC.min^{-1}$ and a dry nitrogen purge flow of 50 $mL.min^{-1}$ were used in all measurements. The samples were heated at 5 $ºC.min^{-1}$ from -80 ºC to 200 ºC, after performing a cycle in which the samples were heated from room temperature to 120 ºC and cooled to -80 ºC to erase their thermal history.

The viscoelastic properties of the UPs and UPRs were measured by DMTA with a Tritec 2000 DMA, from Triton Technology, Ltd. BioUPs were analyzed in the single cantilever bending geometry using stainless steel material pockets. The properties of BioUPRs were analyzed in the dual cantilever bending geometry. All DMTA measurements were carried out in a -150 °C to 200 °C temperature range, at frequencies of 1 and 10 Hz, using a heating rate of 5 ºC.min^{-1}. The T_g of the UPs and UPRs was determined from the maximum of tan δ, at 1 Hz.

Kinematic Viscosity

The kinematic viscosity of synthesized UPs was determined by Gardner- Holdt Bubble Viscometer. The sample is placed into a standard viscosity tube and is thermostated at 25 ºC. The viscosity of the sample is determined by comparison to the standard bubble viscometer tubes (or Gardner-Holdt tubes) with standard viscosity marked alphabetically, in which an air bubble rises with the same speed as it does in the tube of the sample being tested. The standard tube with the same viscosity as the sample has a letter that can be converted to the kinematic viscosity, in Stokes (St)[16]. The viscosity of all polyesters was determined in a solution of 2:1 by weight of the UP in 2-ethoxyethanol (adapted from [17]).

Gel Content

The degree of curing of UPRs was determined by the gel content test (according to ASTM D2765 - 16). The gel content was determined by Soxhlet extraction using THF as solvent. The samples were weighed and placed in the Soxhlet's extractor for 8 hours. After that, the samples were dried until constant weight. Gel content was calculated according to the Equation 1:

$$Gel\ Content = \frac{w_f}{w_o} \times 100 \qquad \text{(Equation 1)}$$

where w_0 and w_f represent, respectively, the weight before and after extraction.

Water Contact Angles

The water contact angles (WCA) were measured on the surface of the cured BioUPRs. The analyses were carried out in a Contact Angle System OCA, equipped with Dataphysics SCA20 software. For the measurements, a 10µL drop of distilled water was dispensed, at a rate of 0.5 µL.s^{-1}, and the final WCA was determined as the average of four different drops deposition measurements.

3.4 Results and Discussion

3.4.1 Polycondensation of UPs based on Renewable Monomers And Their Chemical Structure Identification

In this work, new BioUPs were synthesized using bulk polycondensation in the absence of any catalysts. Different biobased glycols and dicarboxylic acids were considered to replace the common petroleum-based feedstocks (Figure 3.1). The stringent selection of monomers was based not only on their reactivity, but also on the expected properties that they could impart to the UPR (*e.g.* flexibility, toughness).

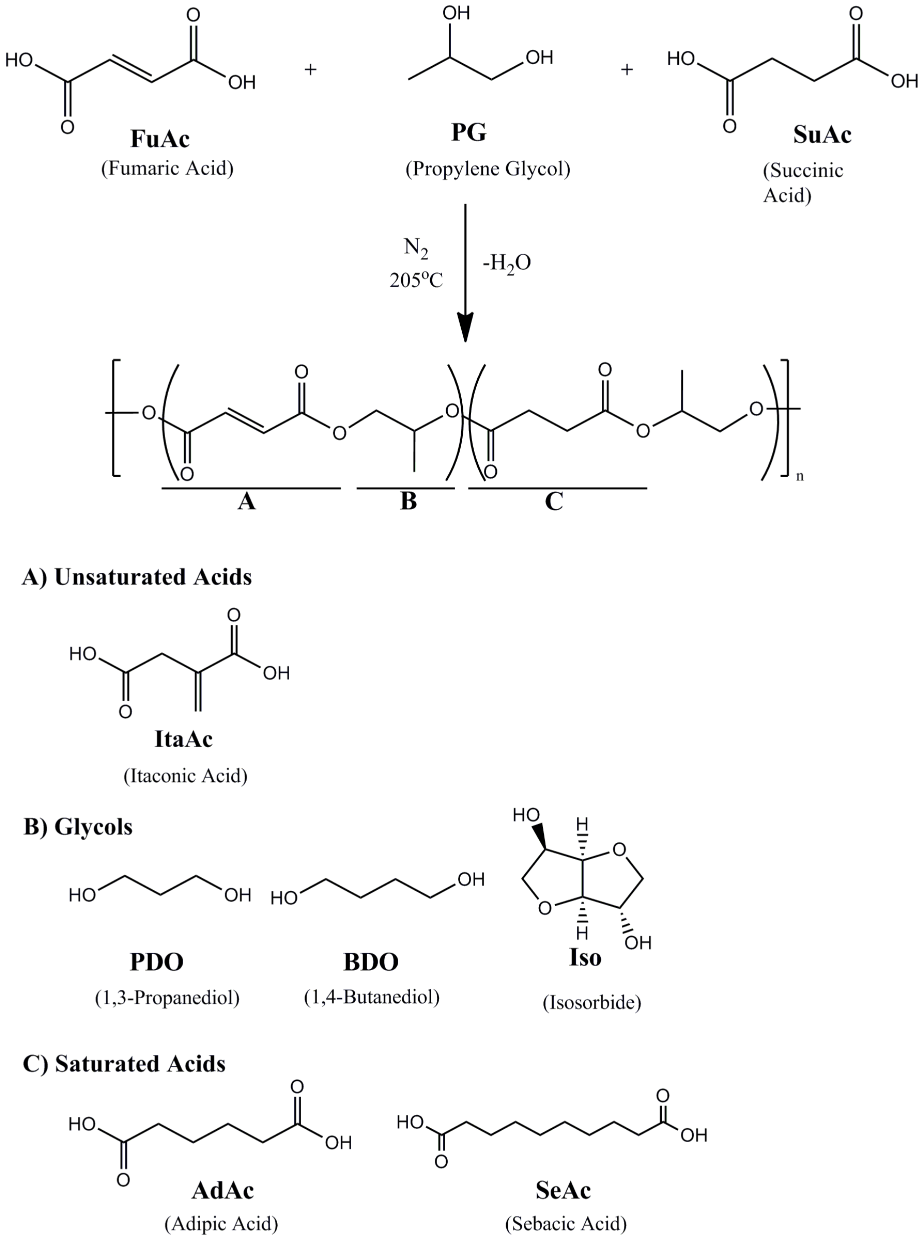

Figure 3.1- Synthesis of BioUPs. The remaining structures (A, B, C) correspond to the different monomers used to prepare the different UPs.

SuAc, AdAc and SeAc can be considered as potential candidates to replace PhA. The different chain lengths enables the design of UPs that, after crosslink, originate materials with different flexibilities and tensile strength[18]. Concerning glycols, our study intended to evaluate the influence of their structures and level of incorporation in the UPs in the final properties of the UPRs. Typically, the most used diol is PG, which is already commercially available from natural sources[19-22]. The other diols used were PDO, BDO and Iso. The latter, due to its cyclic structure, should contribute to improve the rigidity of the final UPRs. FuAc and ItaAc were studied as biobased sources of doubles bonds and the influence of the position of their double bond in the final properties of UPs and UPRs was evaluated.

The chemical structure of the BioUPs was evaluated by ATR-FTIR and ^{1}H NMR. The FTIR spectra of all formulations can be seen in Figure A. 1.

All the BioUPs presented similar FTIR spectra, being possible to identify the band corresponding to the stretching vibration of carbonyl group of the ester linkage[23], at 1722 cm^{-1}, and a band in the region 1280-1240 cm^{-1}, related to the stretching vibration of the C-O-C and C-O groups of the same linkage[24]. The band at *ca.* 1650 cm^{-1} can be ascribed to the stretching vibration of C=C bond in FuAc [25]. The bands at *ca.* 2980, 2930 and 2860 cm^{-1} are due to the vibrational modes of the CH stretching[24].

Table 3.2 summarizes the main bands observed in the BioUPs prepared in this work.

Table 3.2- Main IR bands and respective assignments of the synthesized BioUPs.

Formulation	Infrared Bands (cm^{-1})		
	$\nu_{C=O,\ ester}$	$\nu_{C\text{-}O,\ ester}$	$\nu_{C=C}$
BioUP_1	1722	1249	1644
BioUP_2	1725	1250	1645
BioUP_3	1727	1253	1642
BioUP_4	1729	1249	1643
BioUP_5	1725	1255	1643
BioUP_6	1721	1255	1644
BioUP_7	1726	1250	1642

Further insigths onto the chemical structure of BioUPs were obtained by ^{1}H NMR spectroscopy. Figure 3.2 presents the ^{1}H NMR spectra of BioUP_1, BioUP_2 and BioUP_3, synthesized with different saturated biobased diacids. The integration area of the peaks is indicated in brackets in all spectra.

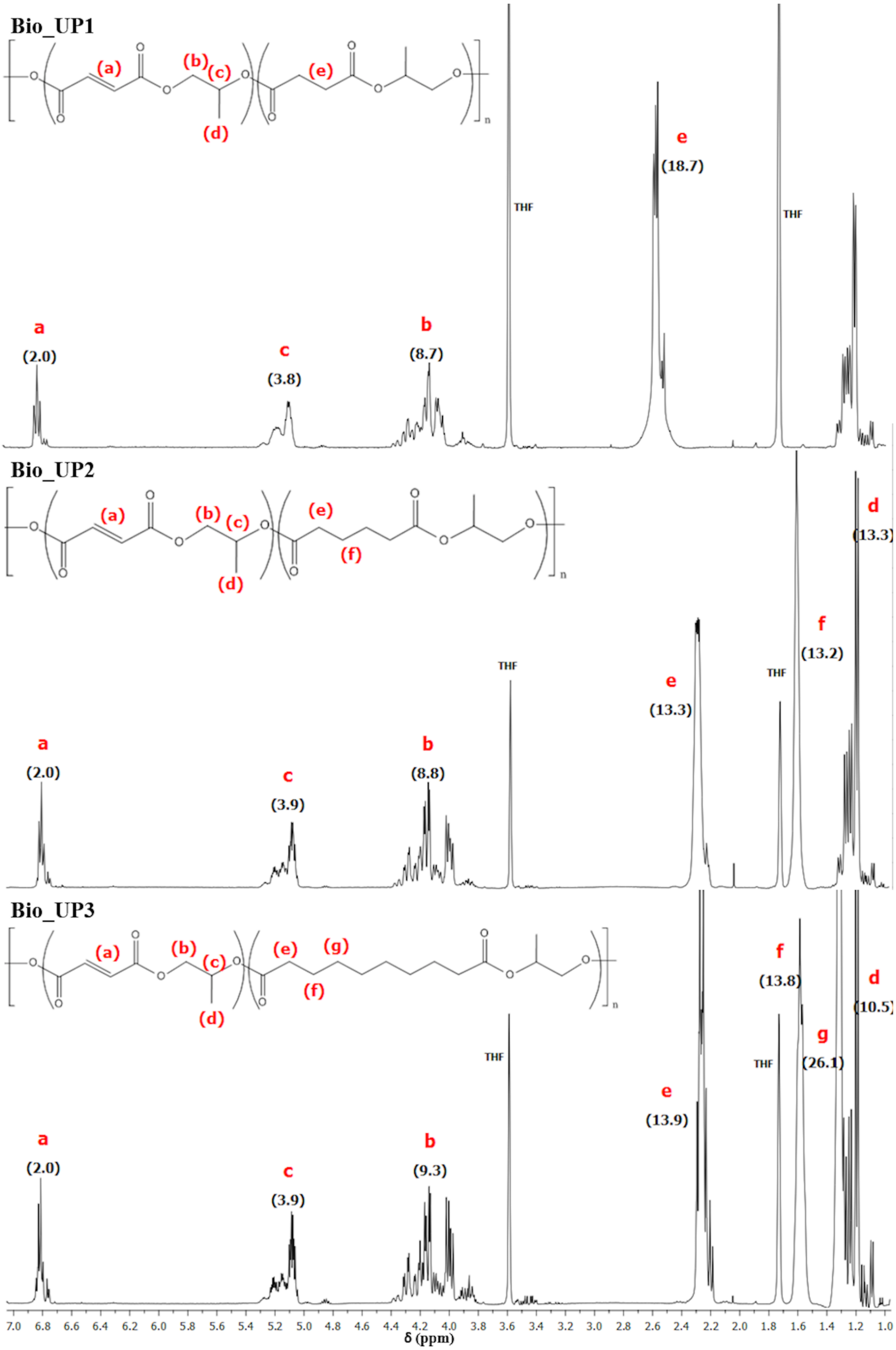

Figure 3.2- ^{1}H NMR spectra of BioUP_1, BioUP_2 and BioUP_3. The integration area of the peaks is indicated in brackets in all spectra.

In all spectra (Figure 3.2), it is possible to identify the peaks belonging to the -C**H₃** protons of PG, at 1.25-1.30 ppm (d)[4]. The signals of the -C**H₂** protons belonging to this diol are seen at 3.7-4.3 ppm (b) and the -C**H** proton at 5.10 ppm (c). The signals between 6.5 and 7.0 ppm (a) correspond to the protons of the double bonds of FuAc moieties[26]. As expected, the presented spectra exhibit distinct peaks for the saturated dicarboxylic acid moieties. In the spectrum of BioUP_1, it is possible to distinguish the protons of the -C**H₂** due to the SuAc structure at 2.4-2.8 ppm (e)[4]. The BioUP_2 presents the signals of AdAc at 2.29 ppm (e) and 1.62 ppm (f), corresponding to the $-CH_2\mathbf{CH_2}C{=}O$ and $-\mathbf{CH_2}CH_2C{=}O$ protons, respectively[4]. Furthermore, the characteristic peaks of SeAc can be identified in the spectrum of BioUP_3 with the $–\mathbf{CH_2}CH_2CH_2C{=}O$ protons at 1.32 ppm (g), $–CH_2\mathbf{CH_2}CH_2C{=}O$ protons at 1.59 ppm (f) and $–CH_2CH_2\mathbf{CH_2}C{=}O$ protons at 2.27 ppm (e)[27].

The chemical composition of formulations containing different biobased glycols (BioUP_4 - BioUP_6) were also studied by ^{1}H NMR spectroscopy. The corresponding spectra is presented in Figure 3.3. As expected, both UPs spectra show the characteristic resonances attributed to the -**H**C=C**H**- of FuAc at δ~6.8 ppm (a) and the SuAc units at 2.5-2.7 ppm (e)[28]. For BioUP_4, the proton resonances are in accordance with the anticipated chemical structure, with the $O\mathbf{CH_2}$ protons of FuAc-PDO and SuAc-PDO at 4.27 (b) and 4.13 ppm (d), respectively, and $OCH_2\mathbf{CH_2}$ protons at 2.00-1.93 ppm (c)[9]. The BioUP_5 spectrum shows peaks at 3.5 ppm (b') and 1.53 ppm (c'), corresponding to unreacted BDO (see Figure A.2). This unexpected result was confirmed by repeating the polymerization two times and showed the low reactivity of this monomer. Also, the ^{1}H NMR spectrum of BioUP_6 revelead the presence of some unreacted Iso (see b' and c' in Figure A.3). The presence of unreacted Iso in the final product can be ascribed to lower reactivity during the polycondensation, caused by the presence of steric hindered endo-hydroxyl groups in its structure[6,8,28].

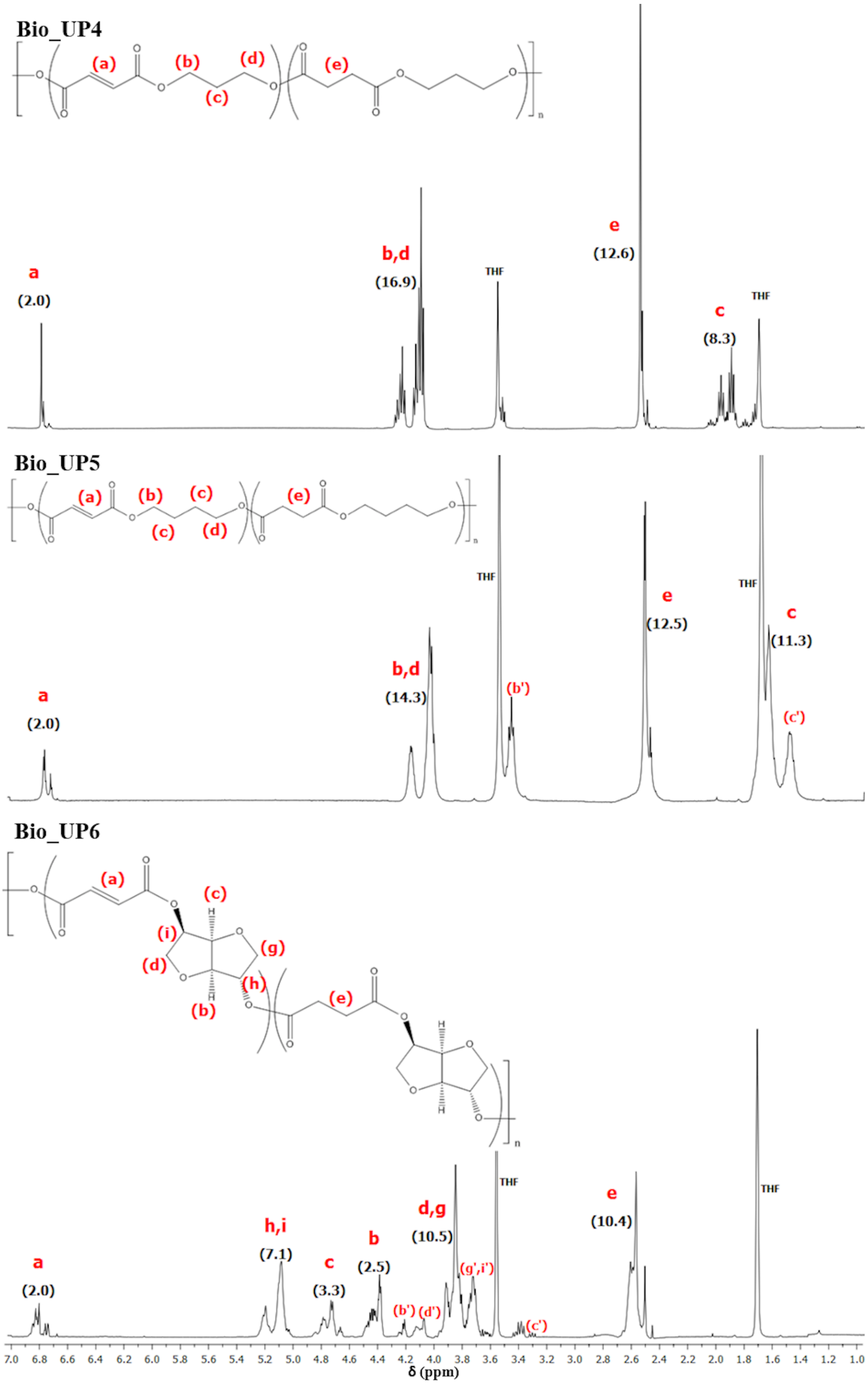

Figure 3.3- ^{1}H NMR spectra of BioUP_4, BioUP_5 and BioUP_6. The integration area of the peaks is indicated in brackets in all spectra.

Figure 3.4 presents the ^{1}H NMR spectra of BioUP_7, with itaconic acid. As expected, when compared to the ^{1}H NMR spectrum of BioUP_1, the main difference concerns the resonances corresponding to the protons of ItaAc.

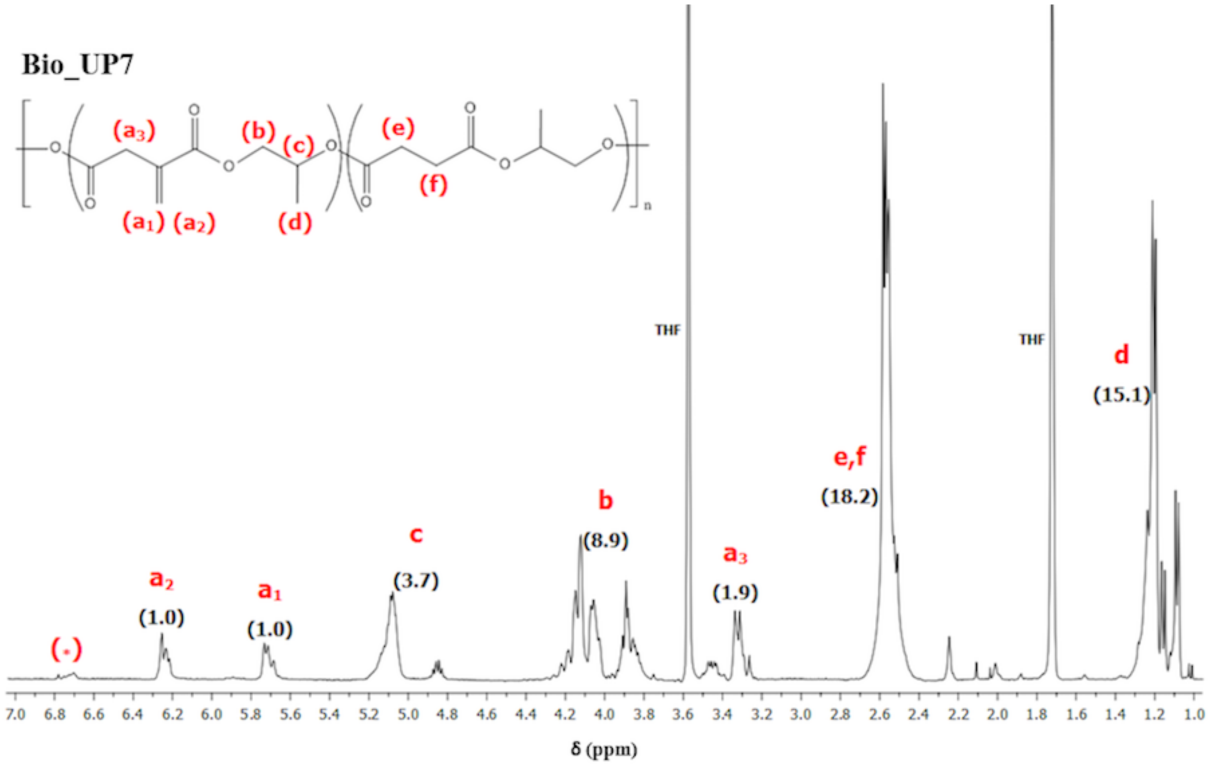

Figure 3.4- ^{1}H NMR spectra of BioUP_7. The integration area of the peaks is indicated in brackets in all spectra.

The resonances ascribed to the unsaturated diacid can be identified at 6.3 ppm (a_1), 5.7 ppm (a_2) and 3.35 ppm (a_3)[28-30]. It should also be pointed out the presence of the protons characteristic of mesaconate moieties at ca. 6.71 ppm (*). Indeed, according to the literature, at high temperatures (180- 200 ºC), the itaconate can isomerizes in citraconate and, specially, in metaconate moieties[29,30].

The relative molar amount of the incorporated monomers in the UPs structure was evaluated taking into account the integral values of the peaks corresponding to the different monomers in the structure. The results are shown in Table 3.3.

Table 3.3- Comparison between the feed amounts of the different monomers and their relative percentages in the final structure of the UPs, determined by ^{1}H NMR.

Formulation	Composition	Initial Molar Ratio (%)	Final Molar Ratio (%)
BioUP_1	SuAc/FuAc/PG	33/14/53	49/11/40
BioUP_2	AdAc/FuAc/PG	33/14/53	40/12/48
BioUP_3	SeAc/FuAc/PG	33/14/53	41/12/47
BioUP_4	SuAc/FuAc/PDO	33/14/53	38/12/50
BioUP_5	SuAc/FuAc/BDO	33/14/53	41/13/46
BioUP_6	SuAc/FuAc/Iso	33/14/53	38/14/48
BioUP_7	SuAc/ItaAc/PG	33/14/53	49/11/40

The data presented in Table 3.3 reveal some differences between the molar amount of the monomers in the feed and their incorporation in the final structure of the UPs. Regarding the saturated acids, it is possible to observe that SuAc was more incorporated than SeAc and AdAc, whereas these last monomers present similar incorporation. The presented results also suggest that, in general, PG is relatively less incorporated than PDO, probably due to its lower boiling point (188 ºC) when compared to the boiling point of PDO (215 ºC). On the other hand, the PG can also suffer from some steric hindrance, which might difficult its incorporation in the UP. In addition, Iso and BDO showed intermediate incorporation values. Indeed, despite its higher boiling point (235 ºC), BDO presented lower incorporation than PDO namely due to the high amount of unreacted monomer at the end of the reaction (20 %). It is also interesting to note that the incorporation of FuAc and ItaAc is very similar (BioUP_1 *vs* BioUP_7), suggesting that the position of C=C in the UM does not affect their incorporation in the UP structure.

Different combinations of biobased monomers (Table 3.1) were used in the preparation of the UPs and the end of reaction was set when the AV reached a constant value. Typically, the UPs used in the preparation of commercial UPRs have AV ranging from 25 to 50 mg KOH.g^{-1} and[31] this was the range that was found for the BioUPs prepared in this work. Table 3.4 summarizes the values of AV, molecular weight (M_n), the polydispersity (*Đ*) as well as the Gardner viscosity values of the BioUPs.

Table 3.4- Molecular weight (M_n) and polydispersity ($Đ$) of the synthesized BioUPs.

Formulation	AV (mg KOH.g^{-1})	M_n (g.mol^{-1})	$Đ$	Viscosity (St)
BioUP_1	31	4062	1.85	4.85
BioUP_2	32	4401	2.50	4.00
BioUP_3	32	4170	2.38	1.91
BioUP_4	29	2708	1.40	**
BioUP_5	25*	n.d.$^{1)}$		**
BioUP_6	31*	< 1980	n.d.$^{2)}$	7.56
BioUP_7	32	3999	1.82	2.31

n.d.: not determined; $^{1)}$ n.d. due to insolubility in the eluent for the SEC analysis; $^{2)}$ n.d. because the chromatogram falls outside the calibration curve.
* UP dissolved only under heating

** solid mixture

According to Table 3.4, the BioUPs are characterized by M_n ranging from 2700 to 4400 g.mol^{-2}, and $Đ$ between 1.4 and 2.5. These results are in the range of values reported in the literature for UPs [32-35]. Besides M_n, the viscosity of the UPs is also a very important characteristic related to commercial applications; UPs with lower viscosity allow the use of a lesser amount of reactive solvent (e.g., Sty). Also, this fact contributes to better cure performances, since allow a higher mobility of the polymeric chains[36]. As expected, the value of viscosity of the different formulations can be easily tuned by varying the monomers in the UPs. Comparing the polyesters with saturated acids, BioUP_1, with SuAc, provides the polyester with higher viscosity, whereas the lowest value was observed for BioUP_3, with SeAc. This result can be explained by the high flexibility of the polymeric chains provided by the diacid with longer aliphatic chains[4,10]. For these formulations, similar values of M_n were achieved and, consequently, this parameter does not have a significant effect on the viscosity of UPs. Regarding the UPs with different glycols, it was not possible to determine the M_n for the UP containing Iso (BioUP_6) due to its low value. The low M_n for this sample can result from two factors: 1) The *endo* isomer of isosorbide is known to suffer steric hindrance, contributing to a lower reactivity; 2) The *endo* hydroxyl groups have the capacity to establish strong hydrogen bonds during the polycondensation which is translated in an imbalance between the –OH/–COOH ratios [6,37]. Interesting to note that, despite its low M_n, BioUP_6 is the polyester with the highest viscosity. In the case of Iso, it is reported that the oxolane ring has the ability of establishing inter-chain hydrogen bonds, causing additional chain interactions [10] and, consequently, higher viscosities are expected. For the formulations with PDO and BDO (BioUP_4 and BioUP_5, respectively) it was not possible to determine the Gardner viscosity since UPs were immiscible with 2-ethoxyethanol used in the test. The results presented in Table 3.4 also revealed that BioUP_3 and BioUP_7 have viscosities very close to the commercial polyester (2.38 St).

3.4.2 Thermal Properties of BioUPs

The thermal stability of the BioUPs was evaluated by TGA, in a 25-600 °C range, under nitrogen atmosphere. The relevant temperatures taken from the thermogravimetric curves are summarized in Table 3.5.

Table 3.5- Characteristic temperatures of the UPs taken from TGA. $T_{5\%}$: temperature corresponding to 5% of mass loss; $T_{10\%}$: temperature corresponding to 10% of mass loss.

	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
Commercial UP	216	246
BioUP_1	242	283
BioUP_2	256	313
BioUP_3	292	327
BioUP_4	258	303
BioUP_5	221	264
BioUP_6	190	240
BioUP_7	202	245

The UPs present only one stage of weight loss between 300-450 ºC, which can be ascribed to the degradation of the ester linkages[4] (see Figure A.4). Regarding the effect of the incorporation of saturated acids (BioUP_1 *vs* BioUP_2 *vs* Bio_UP3), the values of $T_{5\%}$ and $T_{10\%}$ presented in Table 3.5 reveal that the stability of the UPs increases with the number of carbons in the backbone and hence the formulation with SuAc is the less thermal stable. Such behavior has already been reported in literature[4]. On the other hand, the replacement of PG by Iso (BioUP_1 *vs* BioUP_6) led to a decrease of thermal stability, being BioUP_6 the less stable BioUP. This result was somewhat unexpected since in literature it is reported an increase in the thermal stability of the UPs upon inclusion of Iso[8]. However, it was observed that BioUP_6 has a lower M_n than BioUP_1 (see Table 3.4). Thus, it is our belief that the lower stability might be ascribed to the earlier degradation of low M_n oligomers presented in

BioUP_6. Also, the replacement of FuAc by ItaAc led to a significant decrease in the thermal stability. Furthermore, only BioUP_6 and BioUP_7 presented lower $T_{5\%}$ and $T_{10\%}$ than the commercial UP.

The thermal transitions were evaluated by DSC and DMTA. Figure 3.5 presents the heat flow curves (from the second heating cycle) of the different UPs.

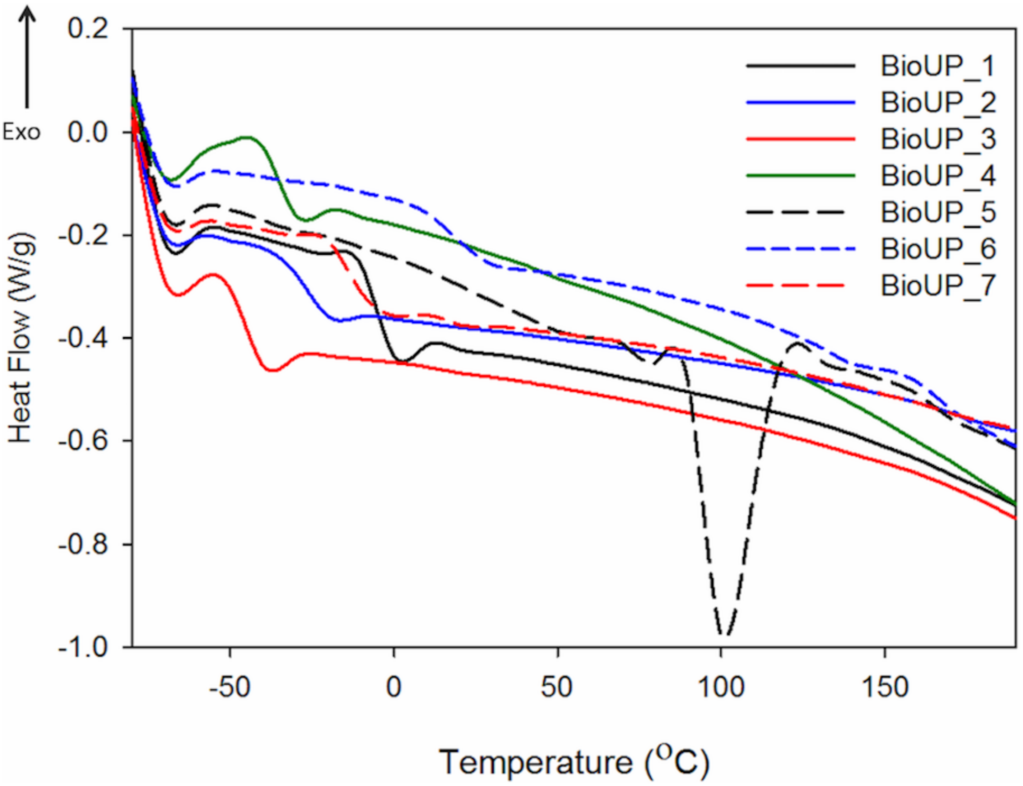

Figure 3.5- Heat flow curves (from the second heating cycle) of the BioUPs.

The different BioUPs, with the exception of BioUP_5, present only one thermal transition corresponding to the T_g, indicating that they have an amorphous character. In the BioUP_5 curve, it is clearly seen an endothermic peak corresponding to the melting (107 ºC), with an associated enthalpy of 82 $J.g^{-1}$. In this specific case no T_g is detected. This result suggests the predominance of the crystalline domains over their amorphous counterparts, impairing the free movements of the latter, which translates in the absence of a T_g[29]. A similar result was obtained for an UP prepared from FuAc and BDO by Farmer *et al.*[29]. The T_g of the BioUPs was also determined by DMTA. Table 3.6 presents the values of T_g obtained with both techniques.

Table 3.6- T_g of the BioUPs obtained from DMTA and DSC.

Formulation	T_g (˚C)	
	DMTA	DSC
Commercial UP	22.8	10.4
BioUP_1	22.3	-2.87
BioUP_2	-2.9	-26.7
BioUP_3	-29.4	-43.2
BioUP_4	-23.2	-38.4
BioUP_5	*	n.d.
BioUP_6	34.9	18.5
BioUP_7	4.4	-12.8

* Broad peak in the T_g region

Regarding the results summarized in Table 3.6, some differences can be observed in the T_g values of the polyesters, which can be explained by their composition. Comparing BioUP_1, BioUP_2 and BioUP_3, it is possible to see that, when the chain length of saturated acids is increased, a decrease of the T_g is observed. According to the literature this fact could be due to the presence of saturated acid with longer chains, which translates to higher chain mobility[4]. Concerning the influence of the glycols, it is also possible to observe that the substitution of PG by PDO leads to lower T_g values. This result can be ascribed to the presence of the methyl pendant group in PG that induces some movement restriction of the polymer chain[29]. On the other hand, BioUP_6 is the formulation with the highest T_g value. This fact can be explained by the cyclic structure of Iso providing additional stiffness to the polymer backbone. For BioUP_5, the DMTA revealed the presence of a very broad peak in the T_g region, which can be explained by a high level of heterogeneity in its composition. Regarding the effect of the unsaturated monomers, it can be seen that Bio_UP7 (with ItaAc) has lower T_g value than BioUP_1 (with FuAc). The UP with ItaAc has pendant double bonds that can contribute to increase the free volume between the polymeric chains with a concomitant decrease in the T_g value [35]. In spite of the differences between the T_g values determined by the two techniques (DSC and TGA) [38], the T_g values follow the same trend.

3.4.3 Development and Characterization of BioUPRs

UPRs have a wide-range of industrial applications and the replacement of the fossil-based UPs by their biobased counterparts could enlarge the potential markets for these materials. In order to obtain the UPRs, the synthesized UPs were dissolved in Sty, the most widely used reactive solvent used for industrial applications, and the mixture was thermally cured in the presence of an initiator and an accelerator[10,39]. BioUP_5 and BioUP_6 were not soluble in Sty and, because of that, no UPRs were obtained from these UPs. As already indicated, the polyester with BDO presents high crystallinity (see Figure 3.5), which could limit its solubility in Sty[29]. The low solubility of Iso based UP can be ascribed to the high polarity of this particular monomer, as described by Sadler *et al.*[5].

Table 3.7 presents the gel content and the water contact angles (WCA) for the commercial resin and the obtained BioUPRs.

Table 3.7- Gel content and WCA on the resins.

	Gel Content (%)	WCA (°)
Commercial UPR	99.9	82.6±2.9
BioUPR_1	97.9	107.7±0.1
BioUPR_2	98.1	92.9±0.5
BioUPR_3	98.9	93.7±0.4
BioUPR_4	99.6	71.1±1.3
BioUPR_7	99.2	87.9±1.1

The results suggest that the BioUPRs have high gel content values, which are very similar to the value obtained for the commercial UPR. The results indicate that the composition of the UPRs can be changed without jeopardizing the extent of the crosslinking reactions.

The WCA is also a very important characteristic related to commercial application of UPRs, in particular when used in synthetic marble and components of boats. According to the results presented in Table 3.7, only the resins BioUPR_1, BioUPR_2 and BioUPR_3 present clearly hydrophobic surfaces, with WCA higher than 90º. BioUPR_7 is the one that present a value closer to the commercial resin. The obtained results suggest that all the UPRs proposed in this work meet the industrial requirements regarding the degree of crosslinking and the WCA, being this conclusion more evident for the formulation BioUPR_7.

The thermal stability of the UPRs under study was also evaluated by TGA under nitrogen atmosphere, in between 25 and 600 ºC. Figure 3.6 gives a global view of the thermal behavior of commercial UPR and each BioUPR. The relevant temperatures obtained from the thermoanalytical curves are summarized in Table 3.8.

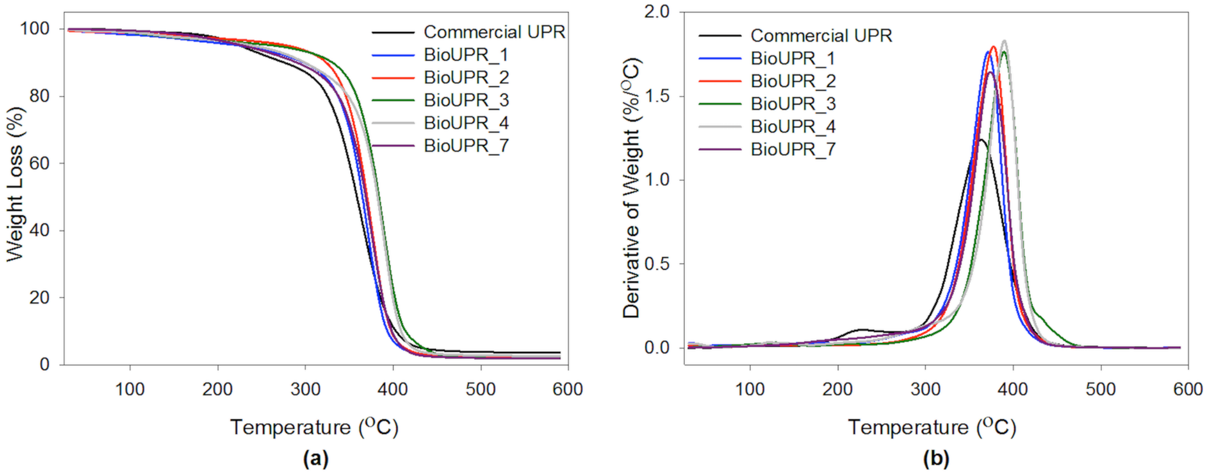

Figure 3.6- Thermogravimetric curves of the commercial UPR and BioUPRs.

Figure 3.6 shows that both BioUPRs present similar weight loss pattern, with one main degradation stage (between 280 and 350 ºC). This stage can be ascribed to the degradation of the tridimensional network[9]. In turn, two different weight loss stages can be identified for the commercial resin, at around 200 ºC and 330 ºC. In the light of the available information in literature, this first weight loss can be correlated with the degradation of small oligomers side bonded to the tridimensional network[6].

The relevant temperatures taken from the thermogravimetric curves are summarized in Table 3.8.

Table 3.8- Characteristic temperatures of the resins taken from TGA curves. $T_{5\%}$: temperature corresponding to 5 % of mass loss; $T_{10\%}$: temperature corresponding to 10 % of mass loss.

	$T_{5\%}$ (˚C)	$T_{10\%}$ (˚C)
Commercial UPR	226	275
BioUPR_1	256	298
BioUPR_2	264	324
BioUPR_3	279	331
BioUPR_4	239	297
BioUPR_7	230	290

The results present in Table 3.8 indicate that, based on their $T_{5\%}$ and $T_{10\%}$ values, the BioUPRs are more stable than the commercial resin. Moreover, regarding the effect of the incorporation of saturated acids, it is also possible to observe that the stability of the UPRs increases with the number of carbons in the backbone, being the UPR with SeAc more stable with higher values of $T_{5\%}$ and $T_{10\%}$. The results also suggest that the replacement of PG by PDO in UPRs contributes to the decrease of their thermal stability. The same trend was observed for the BioUPs. Additionally, comparing the BioUPRs with the respective counterpart, it was possible to observe that the former have high thermal stability, with the exception of BioUPR_3 and BioUPR_4.

The thermomechanical properties of the commercial and BioUPRs were studied by DMTA, at two frequencies (1, 10 Hz), in a temperature range of -150 to 200 ºC. The T_g of the UPRs was determined from the maximum of the tan δ curve, at 1 Hz. The DMTA traces of the UPRs, at 1 Hz, are presented in Figure 3.7.

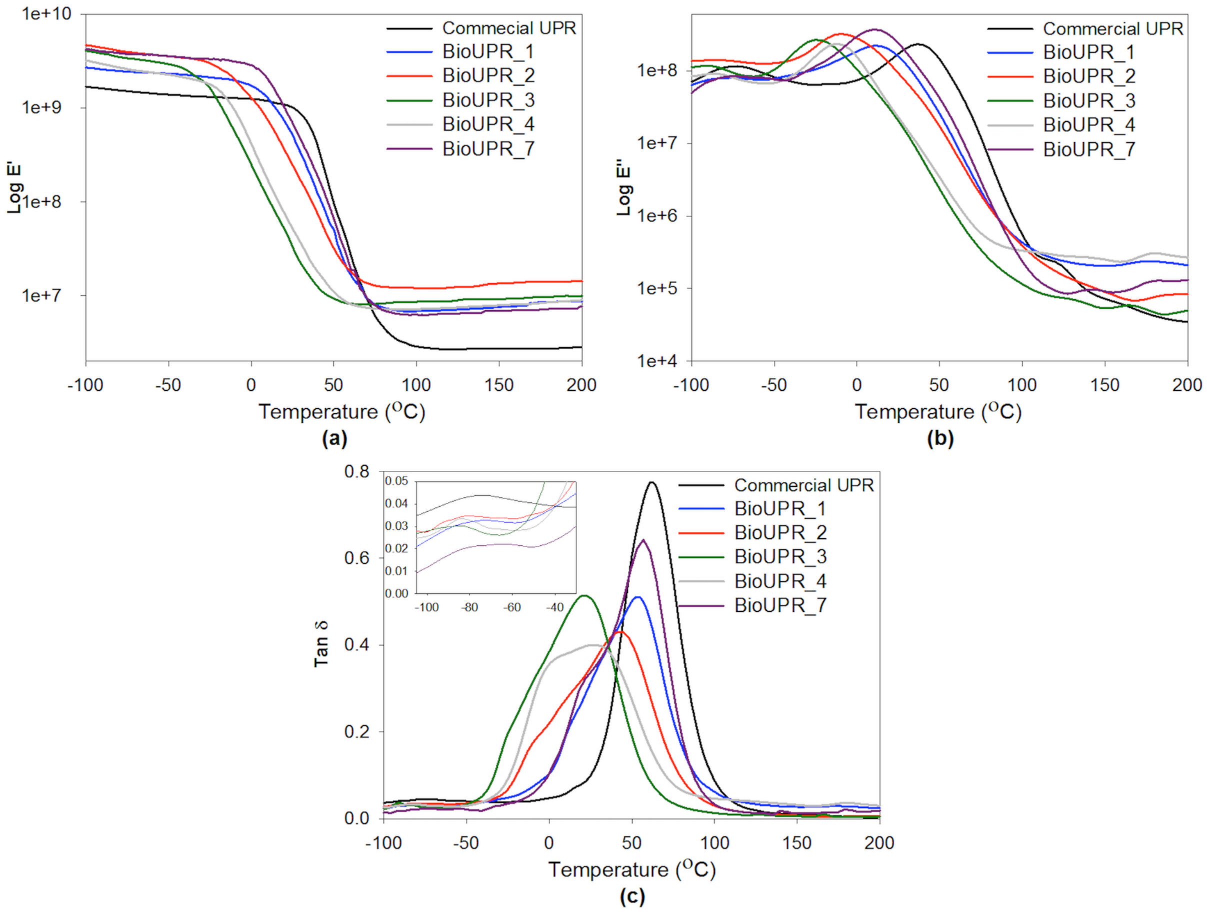

Figure 3.7- DMTA traces of the commercial and BioUPRs in terms of E’ (a), E’’ (b) and tan δ (c).

According to the results presented in Figure 3.7 it is possible to observe that the changes in the monomers used had a significant impact on the thermomechanical properties. Figure 3.7 (a) shows the E’ trace of the studied resins. In the glass region, with lower E’ value, the commercial resin is less rigid than the BioUPRs. This trend is also observed for high temperatures, in the rubbery plateau. As expected, in the glass transition region, a sharp decrease in the E’ is observed for the UPRs under study, being more pronounced for the commercial resin. In this resin, the segmental motions starts nearly at the same temperature and, as a consequence, the temperature range at which the E’ decreases is narrower. It should be mentioned that, in the temperature range of 0-80 ºC, BioUPR_1, BioUPR_2 and BioUPR_7 are very close to the commercial resin. This fact is very important since this is the normal working range temperature for these materials in industrial applications (namely for coatings and reinforcement materials). The E’’ profile (Figure 3.7 (b)) presents two different peaks for the all resins under study that can be ascribed to a secondary transition, at lower temperatures, and to the main transition. The latter occurs at different temperatures for the different materials, indicating that the composition of the BioUPRs influences their ability to dissipate energy. Moreover, in the same temperature ranges, two peaks in tan δ curve are expected. Figure 3.7 (c) presents the tan δ traces for all resins under study. At high temperatures, it is possible to identify the α transition, corresponding to the T_g. The UPRs present different T_g values, and a shoulder can also be observed in all biobased resins ($T_{shoulder}$, in Table 7). This fact might be ascribed to the presence of two different phases that start to move at different temperatures [9,40]. At negative temperatures, it is also possible to identify a peak that is presented in the same region for all resins and does not seem to be dependent on the UPs composition. According to the literature, this transition (γ transition) can be explained by the motions of the aromatic group in poly(styrene) or oligo(styrene) moieties[40,41]. Moreover, it is also possible to observe that the tan δ traces are relatively broad. This feature could be interesting for same applications that require similar properties in wide range of temperatures. It is also worth to note that tan δ peaks have different amplitudes. According to the tan δ traces, the Resipur® is the resin with the highest capacity to dissipate energy, followed by BioUPR_7.

In Table 3.9 are summarized the main values obtained from DMTA data.

Table 3.9- Thermomechanical parameters of the studied UPRs.

Formulation	$E'_{25°C}$ (MPa)	$E''_{25°C}$ (MPa)	T_γ (°C)	$T_{shoulder}$ (°C)	T_g (°C)
Commercial UPR	100×10^1	102	-75.4	----	62.9
BioUPR_1	523	163	-76.3	13.3	53.4
BioUPR_2	240	83.3	-82.5	-10.7	45.6
BioUPR_3	32.7	16.3	-84.3	-24.6	21.8
BioUPR_4	51.8	21.0	-84.1	-1.00	27.1
BioUPR_7	657	232	-74.5	19.2	58.0

Looking at the values presented in Table 3.9, some conclusions can be drawn regarding the influence of composition in the elastic and viscous properties of the materials, at 25 ºC. Concerning the influence of the diacids, it is clear that the BioUPRs made from UPs with diacids with shorter chain lengths are more rigid ($E'_{BioUPR\_1}>E'_{BioUPR\_2}>E'_{BioUPR\_3}$). BioUPR_1 also presents the highest E'' value of these three formulations, corresponding to a higher capacity of the material to dissipate energy as heat due to viscous molecular motions. These results indicate that the use of diacids with shorter chain length leads to a more cohesive crosslinked network, which is translated in a higher rigidity (higher E') and also in a higher amount of energy that is released when the chains start to move (higher E''). One can also see that the replacement of PG by PDO (BioUPR_1 *vs* BioUPR_4) led to a significant decrease in the E' values. This result was somewhat unexpected. PG has a pendant methyl group in its structure which increases the free volume between the polymeric chains and, consequently, provides a less compact polymeric matrix [42]. Thus, it should be expected resins with lower E' values. Nevertheless, for the resins under study, it seems that the pendant group of this glycol restrains the movements of the chains and higher E' values are observed. Accordingly, Bio_UPR1 has a lower value of E''. It should be mentioned that BioUPR_7 is the BioUPR that presents the E' and E'' values closer to the commercial UPR. Moreover, it should be also mentioned that Bio_UPR7 was a T_g value very close to the Resipur®, which suggests that this Bio_UPR is a reliable candidate to replace the commercial resin in its common applications.

3.5 Conclusions

In this work, different UPs were prepared with monomers currently obtained from renewable resources in order to produce BioUPRs with different characteristics, as similar as possible to those of a commercial resin, Resipur®.

The BioUPs were successfully synthesized with biobased monomers by bulk polycondensation, in the absence of toxic solvents and catalysts. The UPs' structures were confirmed by FTIR and ^{1}H NMR spectroscopies. The thermal properties were also evaluated and revealed that the T_g of the BioUPs showed to be dependent on the composition, with the higher values observed for BioUP_1 and BioUP_6 (22.3 and 24.9 ºC, respectively).

Regarding the BioUPRs, prepared using Sty as reactive solvent, high gel content values were obtained and their surface hydrophobicity is very similar to that of the commercial resin. DMTA analysis presented two transitions (γ and α) for all resins. Although the BioUPRs have presented interesting thermomechanical characteristics, BioUPR_7 is the resins that present closer properties to the commercial UPR.

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CHAPTER 4 - **Unsaturated Polyester Resins based on Vegetable Oils**

Parts of this chapter have been published:

C. S. M. F. Costa, A. C. Fonseca, J. Moniz, M. Godinho, A. C. Serra, J. F. J. Coelho. "Soybean and coconut oil based unsaturated polyester resins: Thermomechanical characterization." *Industrial Crops and Products* **2016**, *85*, 403-411.

4.1 Abstract

Novel unsaturated polyesters (UPs) were successfully developed based on soybean and coconut oils by polycondensation reactions. Unsaturated polyester resins (UPRs) were also obtained by crosslinking the UPs with a reactive monomer. The chemical structure of the different UPs was confirmed by ATR-FTIR and ^{1}H NMR and the thermal and mechanical properties of the UPs and UPRs were extensively evaluated. Thermogravimetric analysis (TGA) revealed that biobased UPs are thermally stable until temperatures of 250 °C. The glass transition temperature (T_g) values obtained for these new UPs varied between −11 °C and 2 °C, being the UP composed by biobased soybean oil and propylene glycol the resin with the highest T_g. As expected, after crosslinking, the UPRs showed to be thermally more stable than the UPs. The dynamic mechanical thermal analysis (DMTA) revealed that the storage modulus (E') and the T_g could be easily tailored by varying the monomers in the formulation. Characterized by high E', loss modulus (E'') and damping values, the formulation with soybean oil (SO), maleic anhydride (MA), phthalic anhydride (PhA) and propylene glycol (PG) presented the better thermomechanical properties.

4.2 Introduction

In last decades, vegetable oils have been seen as one of the most viable alternative to petrochemical-based materials, presenting abundant availability, reactive functionalities and competitive cost[1-3]. A variety of oils like palm, linseed and castor oil have already been used for the synthesis of biobased UPs and UPRs[4-8]. SO, particularly, is a vegetable oil with interest in the polymers industry because of its abundant availability, reactive functionalities and low cost[9,10]. This renewable material is constituted by triacylglycerols with a mixture of fatty acids, being 51 % of linoleic acid and has about 4.5 double bonds per molecule. SO has been used in the manufacturing of plastics, adhesives, for coating applications and also to prepare oil-based UPs[9-11]. Miyagawa *et al.*[12] developed UPRs making use of a mixture of a fossil-based UP diluted in styrene (Sty) with epoxidized methyl soyate (EMS), which is a mixture of epoxidized fatty methyl esters. The authors evaluated the effect of increasing amount of EMS on the thermomechanical properties of the resulting materials. The results showed a decrease in the E' and in the heat deflection temperature as the amount of EMS increased in the formulation. In turn, the Izod impact strength value did not change for higher amounts of EMS. Unmodified SO was used by Li *et al.*[11] to obtain biobased UPRs. A monoglyceride mixture was firstly obtained by transesterification between glycerol and SO and, in the second step, this mixture was reacted with PG, MA and PhA. The mechanical properties of the UPs were later evaluated in a second contribution[13]. According to the authors, using Sty as the diluent and with a content of SO monoglyceride between 15 and 20 %, resins with good impact strength, tensile strength and flexibility were obtained. Also, cured resins presents a lower curing shrinkage (4 %) compared with commercial UPR.

Besides SO, coconut oil (CO) is also an abundant natural source with a relatively low cost, being largely used in cosmetic and pharmaceutical industries and much less explored in the UPRs synthesis[14]. Since, CO is mainly composed by saturated fatty acids (>91 %), it is not explored in the synthesis of crosslinked resins[15]. However, the presence of non-crosslinked carbon chains would be favorable to prepare materials with relatively high impact strength.

In this chapter different UPs based on SO and CO with high "green" content were prepared by bulk polycondensation and characterized chemically and thermally. The polyesters were further crosslinked with Sty and the thermomechanical properties of the UPRs were studied in order to evaluated the impact of the incorporation of renewable monomers in the properties of the obtained materials.

4.3 Experimental Section

4.3.1 Materials

SO, CO, ethylene glycol (EG, 99.8 %) and PG (99 %), Sty (>99 %), tetrahydrofuran (THF, >95 %) and *p*-xylene (99 %) were purchased from Sigma-Aldrich. MA (>99 %), PhA (99 %) and 1,3-propanediol (PDO, >98 %) were purchased from TCI Europe. Succinic acid (SuAc, 99 %) and potassium hydroxide solution (1 N, in ethanol) were purchased from Acros Organic. Cobalt Octoate (CoO) was purchased from AGAMI, phenolphthalein was obtained from Riedel-de-Häen and MEKP from Algarplás. Hydroquinone (HQ, >99 %) was purchased from Analar and deuterated THF (THF-d_8, 99.5 %) was purchased from Eurisotop. All the reactants were used as received, unless otherwise stated.

4.3.2 Synthesis of the Vegetable Oil-based UPs

The SO and CO-based unsaturated polyesters (SO_UP and CO_UP) were prepared by bulk polycondensation. The monomers were charged into the four-necked glass reactor, equipped with a mechanical stirrer, a nitrogen inlet and a condenser connected to a round-bottom flask. The polycondensations were carried out at 205 ºC. The end of reaction was set when the acid value (AV) reached a constant value of 30 mg KOH.g^{-1} (according to ISO 2114 – 00) and the kinematic viscosity of resultant polyesters was also determined.

4.3.3 Preparation of the UPRs

The synthesized SO_UPs and CO_UPs were dissolved in 32 wt.% Sty. The initiator MEKP (2 wt.%) and accelerator CoO (1 wt.%) were added under continuous stirring until a homogeneous mixture was obtained[16]. The formulations were cured in a Teflon mold (16 x 7 x 0.5 mm) at room temperature for 12 hours and post-cured at 80 ºC for 3 hours, for the obtainment of SO_UPRs and CO_UPRs[17,18].

4.3.4 Characterization Techniques

Chemical Structure Identification

ATR-FTIR analysis of UPs was carried out with a Jasco FT-IR-4200 spectrometer, from Jasco Inc. equipped with a Golden Gate Single Reflection Diamond ATR. Data collection was performed with 4 cm^{-1} spectral resolution and 64 accumulations.

^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer, from Bruker using a 5 mm TIX triple resonance detection probe, in THF-d_8, at room temperature. Tetramethylsilane (TMS) was used as the internal reference.

Thermal Properties

The thermal stability of samples was evaluated by TGA, using a TA Instruments Q500 thermogravimetric analyzer (thermobalance sensitivity: 0.1 μ g). The equipment was calibrated within a temperature interval ranging from 25 ºC to 1000 ºC, at a heating rate of 10 ºC.min^{-1}, running tin and lead as melting standards. The samples were analyzed using open alumina crucibles, in the temperature range 25 ºC to 600 ºC and at a heating rate of 10 ºC.min^{-1}, under dry nitrogen purge flow of 100 mL.min^{-1}.

The viscoelastic properties of the UPs and UPRs were measured by DMTA with a Tritec 2000 DMA, from Triton Technology, Ltd. SO_UPs and CO_UPs were analyzed in the single cantilever bending geometry using stainless steel material pockets. The properties of SO_UPRs and CO_UPRs were analyzed in the dual cantilever bending geometry. All DMTA measurements were carried out in a -150 °C to 200 °C temperature range, at frequencies of 1 and 10 Hz, using a heating rate of 5 ºC.min^{-1}. The T_g of the UPs and UPRs was determined from the maximum of tan δ, at 1 Hz.

Kinematic Viscosity

The kinematic viscosity of synthesized UPs was determined by Gardner- Holdt Bubble Viscometer. The sample is placed into a standard viscosity tube and is thermostated at 25 ºC. The viscosity of the sample is determined by comparison to the standard bubble viscometer tubes (or Gardner-Holdt tubes) with standard viscosity marked alphabetically, in which an air bubble rises with the same speed as it does in the tube of the sample being tested. The standard tube with the same viscosity as the sample has a letter that can be converted to the kinematic viscosity, in Stokes (St)[19]. The viscosity of all polyesters was determined in a solution of 2:1 by weight of the UP in 2-ethoxyethanol (adapted from [20]).

Gel Content

The degree of curing of UPRs was determined by the gel content test (according to ASTM D2765-16). The gel content was determined by Soxhlet extraction using THF as solvent. The samples were weighed and placed in the Soxhlet's extractor for 8 hours. After that, the samples were dried until constant weight. Gel content was calculated according to the Equation 1:

$$Gel\ Content = \frac{w_f}{w_o} \times 100 \qquad \text{(Equation 1)}$$

where w_0 and w_f represent, respectively, the weight before and after extraction.

4.4 Results and Discussion

4.4.1 Synthesis of Vegetable Oil-based UPs and Their Chemical Structure Identification

Different UPs were prepared by polycondensation between one vegetable oil and different saturated and monomers accordingly Table 4.1. To develop polyesters with high "green" content, different commercially available biobased feedstocks were selected for the condensation reaction. SO and CO were the selected vegetable oils, since they possess significantly different unsaturation degrees of substitution, which contribute to different thermomechanical properties of the final properties.

Table 4.1- Weight percentages of the different compounds in the feed formulations.

Formulation	MA (wt.%)	PhA (wt.%)	SuAc (wt.%)	EG (wt.%)	PG (wt.%)	PDO (wt.%)	SO (wt.%)	CO (wt.%)
SO_UP1	25%	19%		12%	15%		19%	
SO_UP 2	25%	19%			27%		19%	
SO_UP 3	25%	19%				27%	19%	
SO_UP 4	25%		19%	12%	15%		19%	
CO_UP 1	25%	19%		12%	15%			19%
CO_UP 2	25%	19%			27%			19%
CO_UP 3	25%	19%				27%		19%
CO_UP 4	25%		19%	12%	15%			19%

As can be seen in Table 4.1, the amount of vegetable oil (SO or CO) was fixed to 19 wt.% and also the amount of MA to 25 wt.%. Hence the total amount of double bond available to reticulation is the same for all the formulations. This fact tends do "homogenize" the reticulation degree for all the formulations. Different observed properties are mainly due to the presence of the other monomers. UP2, when compared with UP1, has no EG and a higher content of PG, which is a monomer known to confer hardness to the materials[21]. UP3 has also no EG but PDO and was used to understand about the influence of the length of the diols in the properties of the UPRs. In formulation UP4, PhA was replaced by SuA, to study the effect of this replacement in the final thermomechanical properties of the UPRs. The same pattern of substitution was followed for CO_UP1 to CO_UP4 but in this case the difference is the vegetable oil and, consequently, the unsaturation level. The different monomers used in the polycondensation reactions are schematized in Figure 4. 1.

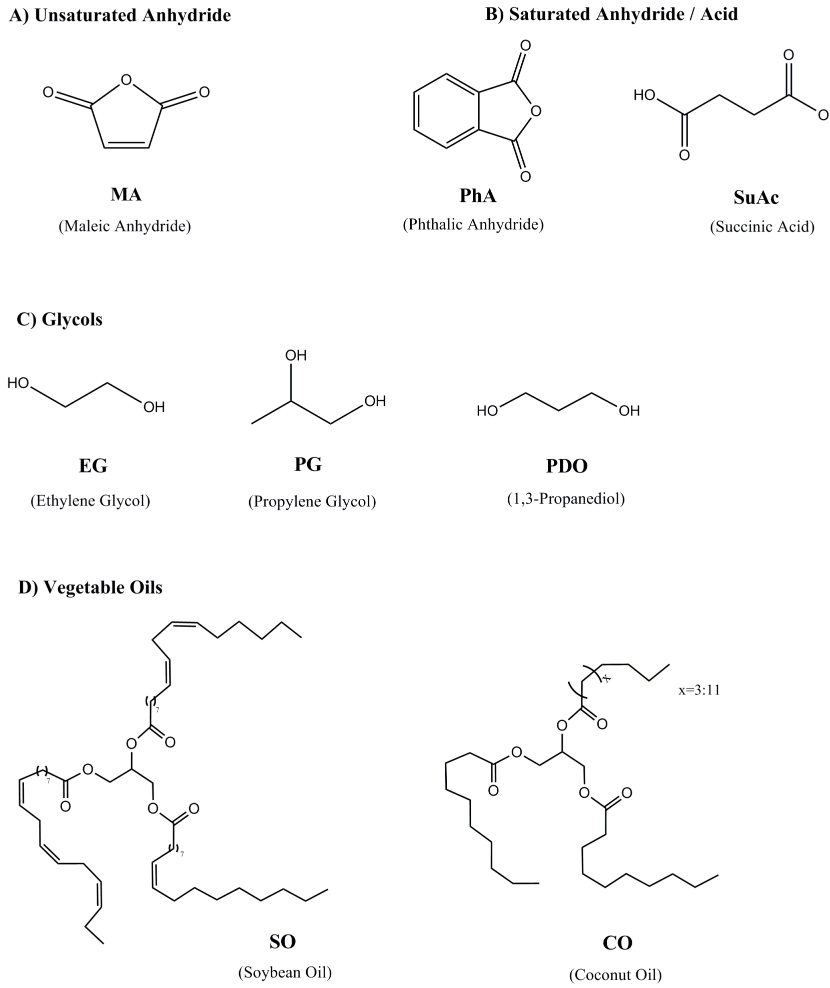


Figure 4. 1- Schematic chemical structures of the different monomers selected for the polycondensation reactions.

The chemical structure of the synthesized SO_UPs and CO_UPs were analyzed by ATR-FTIR. The presented spectra in Figure 4.2 shows bands corresponding to the stretching vibration of the carbonyl group of the ester linkage (a), (1750-1725 cm^{-1}), characteristic of polyesters and also present in the triglyceride structure[22]. The absorption band in the region 1280-1240 cm^{-1} (b) is related to the C-O-C and C-O stretching of ester group[23]. The band appearing at ca. 1650 cm^{-1} (c) can be ascribed to the stretching vibration of the double bonds[24]. The presence of absorption peaks at *ca.* 2980, 2930 and 2860 cm^{-1} (e) can be attributed to the vibrational modes from the CH stretching[23]. For the formulations with phthalic anhydride (SO_UP1-SO_UP3 and CO_UP1-CO_UP3), it is also possible to observe the characteristic bands of the aromatic ring at 1615-1580 cm^{-1} and 1510-1450 cm^{-1} (d)[22] that, as expected, are absent in SO_UP4 and CO_UP4. As expected the spectra presents the same substitution pattern due to the similar structures.

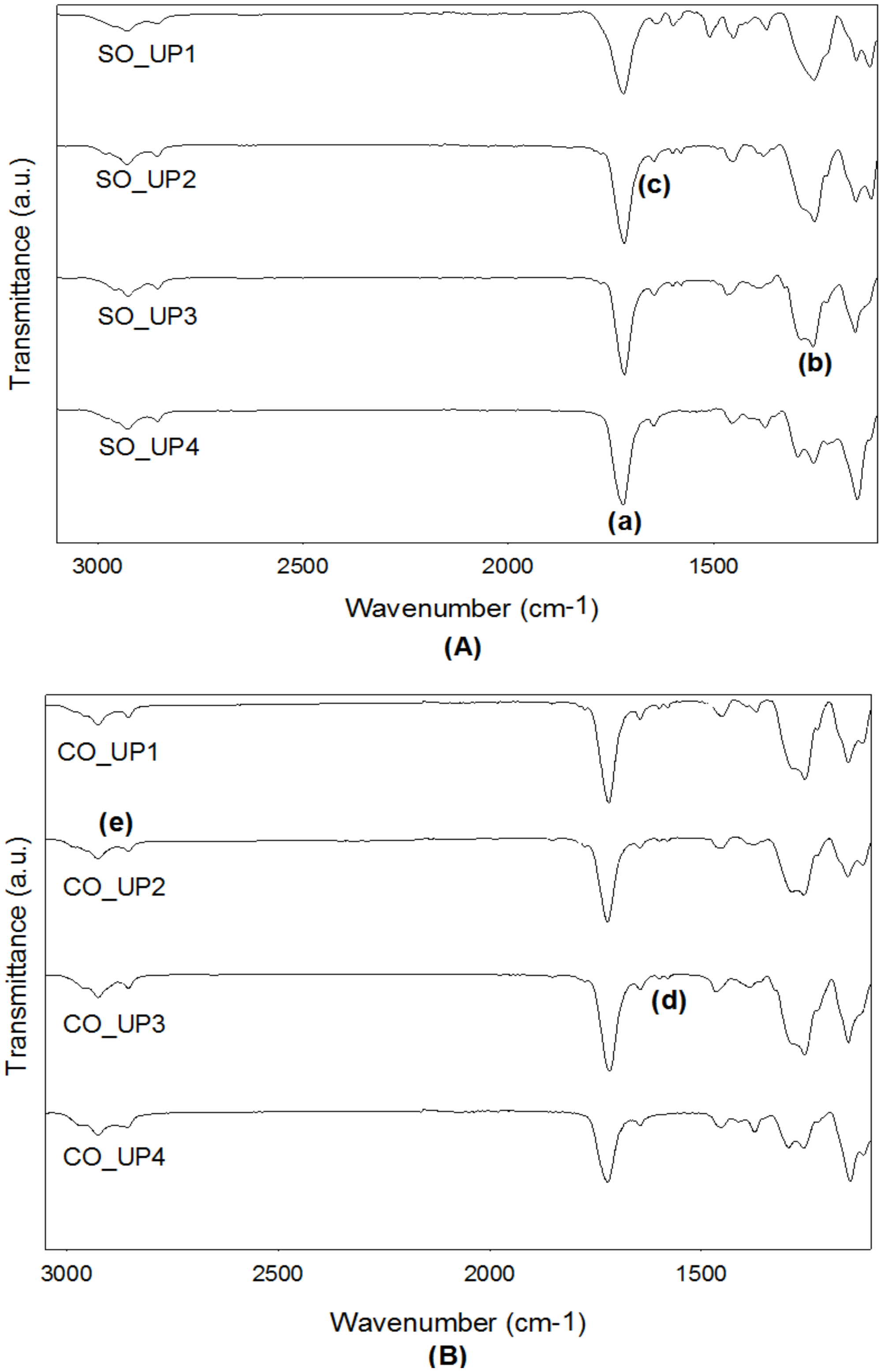


Figure 4.2- ATR-FTIR spectra of SO_UP (A) and CO_UP (B).

Further insights onto the chemical structure of the UPs were given by ^{1}H NMR (Figure 4.3 and Figure 4.4).

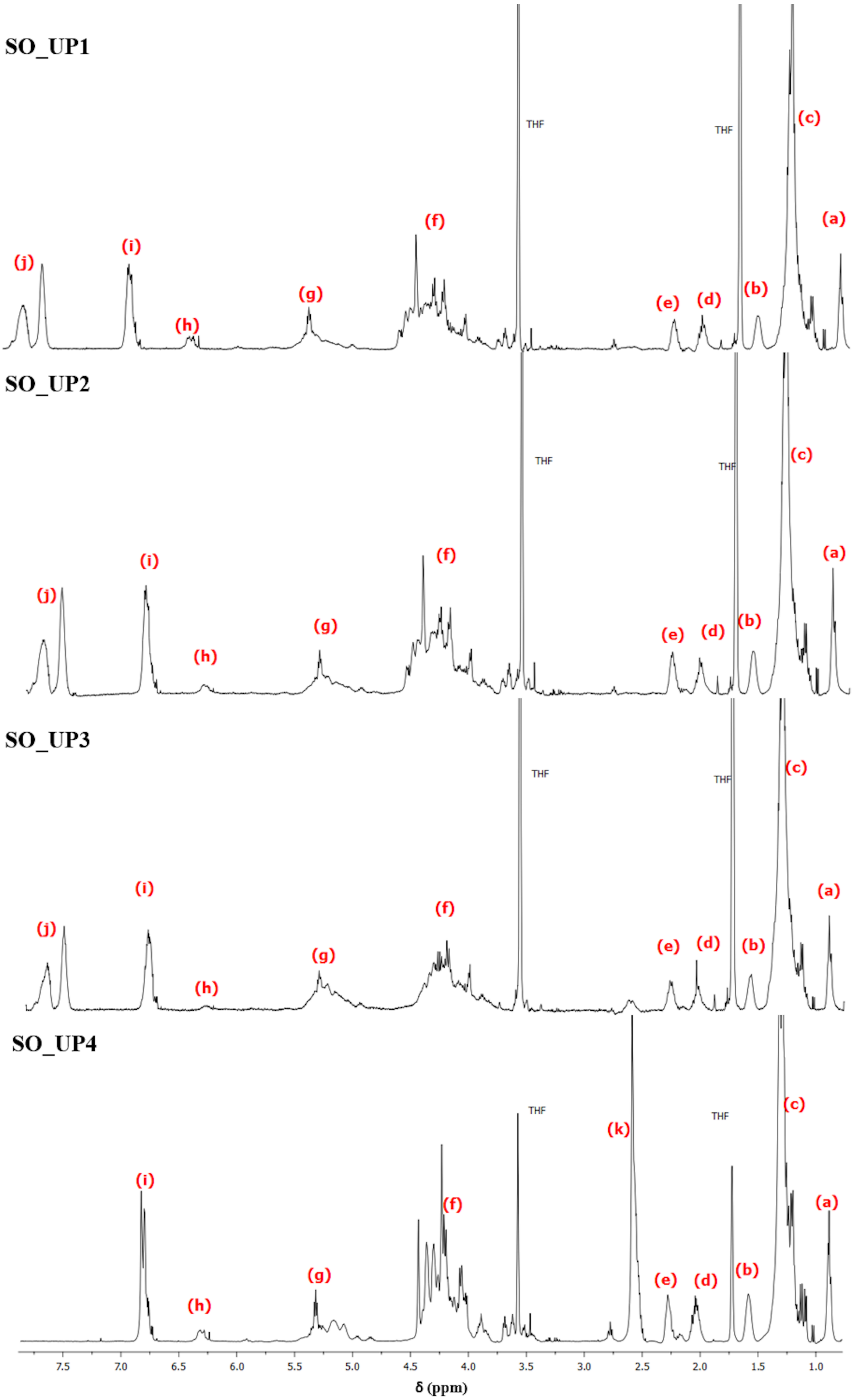


Figure 4.3- ^{1}H NMR spectra of SO_UP.

Figure 4.3 and Figure 4.4 show the ^{1}H NMR spectra of SO_UPs and CO_UPs, respectively. In both spectra it is possible to observe the signals corresponding to both oils. The peaks around 0.9 ppm (a) correspond to the terminal methyl groups of the fatty acids chains whereas the peaks at 1.6 ppm (b) are ascribed to the -C**H₂** protons attached to this terminal group[24-26]. At 1.25-130 ppm (c) it is possible to identify the peaks belonging to the internal -C**H₂** protons of the carbon chains[25,27] as well as the -C**H₃** protons of PG. The peak around 2 ppm (d) can be related to the -C**H₂** attached to the double bond while the peak at 2.3 ppm (e) corresponds to the -C**H₂** connected to the different ester groups[27]. The peaks of the protons of glycerol core and to the -C**H₂** protons of glycols are seen at 4-4.8 ppm (f)[25,28,29]. At 5.3 ppm (g) it is possible to see the protons of the double bonds present in the oils structure[25,27]. At 6.3 ppm (h) and 6.8 ppm (i) it is possible to identify peaks assigned to the maleate and fumarate vinyl protons, respectively[30].

The formulations containing PhA (SO_UP1-SO_UP3, CO_UP1-CO_UP3) present resonances at 7.52-7.73 ppm (j), due to the protons of the aromatic ring. The formulations containing SuAc (SO_UP4 and CO_UP4) show a characteristic peak at around 2.59 ppm (k), belonging to the internal -C**H₂** protons[28]. From these assignments it is possible to calculate the approximate composition of the resins comparing with the feed composition.

The approximate composition of the obtained UPs after the polycondensation was also determined from the ^{1}H NMR analysis of the different zones of NMR spectra, making use of the relationship between the integrals of the different protons. Table 4.2 presents the amounts of the different monomers used in the synthesis of the UPs, as well as their AV values and final viscosity values.

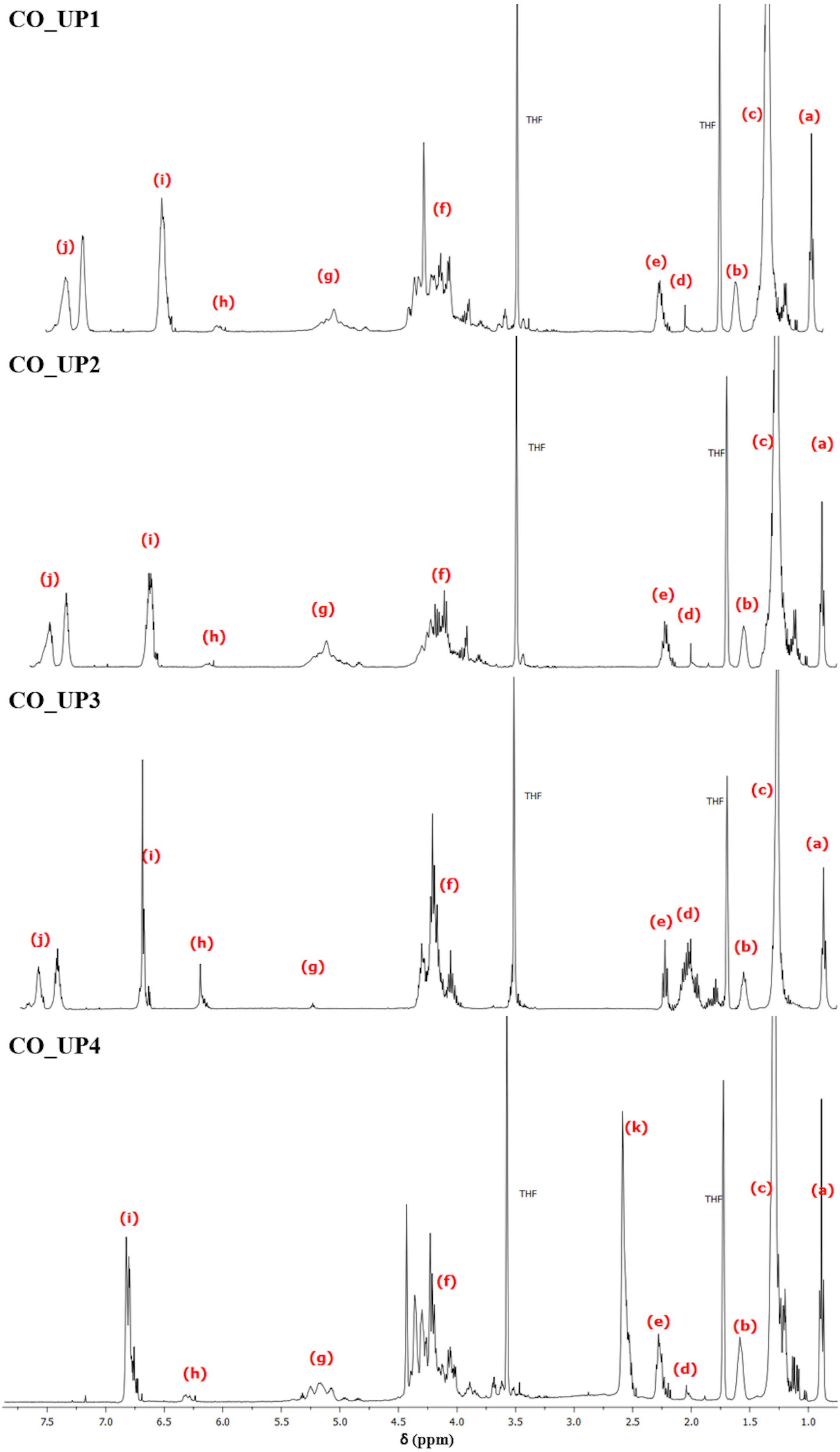


Figure 4.4- ^{1}H NMR spectra of CO_UP.

Table 4.2- Weight percentages viscosity and AV of the different monomers in the final formulations, of the different UPs.

Formulation	Molar Ratio$_{Feed}$ (%)	Molar Ratio$_{NMR}$ (%)	Viscosity (St)	AV (mg KOH.g^{-1})
SO_UP1	32 MA /16 PhA /25 PG /24 EG /3 SO	25 MA /19 PhA /53 PG+EG /4 SO	1.65	30
SO_UP 2	34 MA /17 PhA /46 PG /3 SO	23 MA /18 PhA /55 PG /4 SO	2.50	27
SO_UP 3	34 MA /17 PhA /46 PDO /3 SO	29 MA /23 PhA /42 PDO/6 SO	1.00	29
SO_UP 4	24 MA /38 SuAc /18 PG /18 EG /2 SO	23 MA /25 SuAc /49 PG+EG /4 SO	1.40	30
CO_UP 1	31 MA/16 PhA /24 PG /24 EG /5 CO	31 MA /18 PhA /47 PG+EG /4 CO	0.70	31
CO_UP 2	33 MA /17 PhA /45 PG /5 CO	33 MA /18 PhA /44 PG /5 CO	0.50	30
CO_UP 3	33 MA /17 PhA /45 PDO /5 CO	28 MA /16 PhA /50 PDO /6 CO	0.58	31
CO_UP 4	23 MA /38 SuAc /18 PG /18 EG /3 CO	28 MA /23 SuAc /45 PG+EG /4 CO	0.60	31

As can be observed in Table 4.2, there are some differences between the molar amount of monomers in the feed and the calculated amount of each monomer in the final structure of UPs. In what concerns the anhydrides, when compared to the molar ratio of monomers in the feed, a lower loss of the PhA relatively to MA in the UPs structure was observed which could be due to the higher boiling point (295 ºC and 202 ºC respectively).

The viscosity of the UPs is a very important characteristic related to commercial applications, since it has important influence in the preparation of the UPRs. It was determined by using a Gardner- Holdt Bubble Viscometer (Table 4.2). Regarding the obtained viscosities it is not easy to find precise correlations. UPs based on coconut oil always presented lower values when compared to the equivalent SO_UPs. The results also revealed that a variety of viscosity might be obtained simple by varying the monomers in the formulation.

4.4.2 Thermal Properties of the UPs

The thermal stability of the UPs was evaluated by thermogravimetric analysis (TGA), in a 25-600 ºC range, in a nitrogen atmosphere. Figure 4.5 presents the thermogravimetric curves for the different UPs.

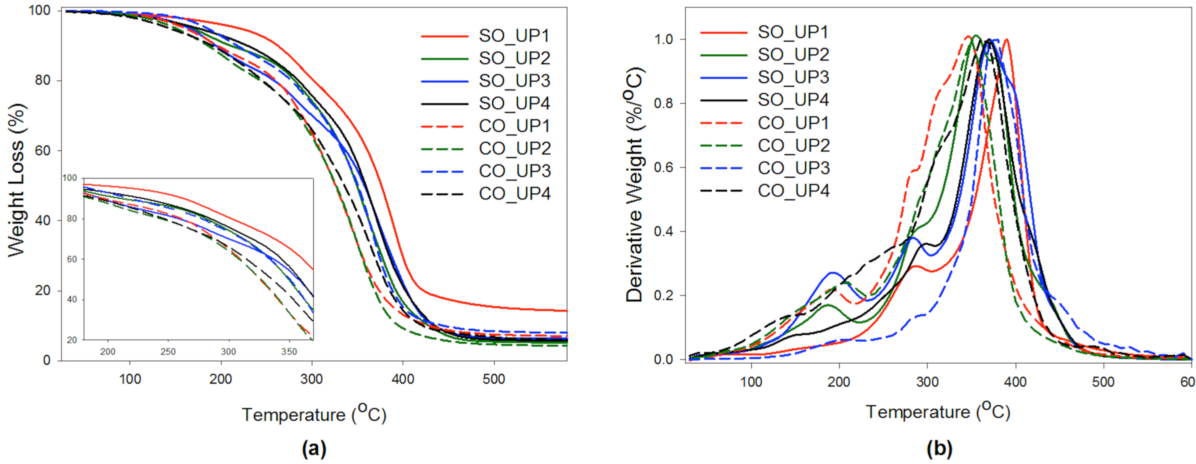


Figure 4.5- Thermogravimetric curves of SO_UP and CO_UP: (a) TG and (b) DTG.

The UPs present two main stages of weight loss, the first in the 100-250 ºC range, and the second occurs between 250-450 ºC. The first might be ascribed to the degradation of oligomeric segments of very low molecular weight (M_n), whereas the second stage comprises both the degradation of the ester linkages and the oil [28,31,32]. The $T_{5\%}$, $T_{10\%}$ values obtained from the thermogravimetric curves were used as criteria for thermal stability and are presented in Table 4.3.

Table 4.3- Characteristic temperatures of the UPs taken from the TGA. $T_{5\%}$: temperature corresponding to 5 % of mass loss; $T_{10\%}$: temperature corresponding to 10 % of mass loss.

	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
SO_UP1	221	262
SO_UP2	168	210
SO_UP3	165	194
SO_UP4	175	228
CO_UP1	146	186
CO_UP2	150	185
CO_UP3	184	217
CO_UP4	143	190

Comparing the values of the $T_{5\%}$ and $T_{10\%}$ of SO_UPs with the CO_UPs, it is possible to observe that the SO-based UPs are thermally more stable that their CO-based counterparts, with the exception of CO_UP3. A significant decrease in the thermal stability of the SO_UPs is observed when the PhA is replaced by SuAc (SO_UP1 *vs* SO_UP4). In the case of CO_UPs this is not verified, indicating that in these UPs the replacement of PhA and SuAc does not have a detrimental effect on the thermal stability. For formulations with SO, it is observed that the replacement of PG by PDO led to a decreased thermal stability. However, for CO-based UPs, this is not verified. CO_UP3 shows the highest thermal stability.

The thermal transitions of the UPs below the degradation temperature were studied by DMTA. The results are presented in Table 4.4.

Table 4.4- T_g of the UPs.

UPs	T_g (°C)
SO_UP1	-0.6
SO_UP2	1.9
SO_UP3	-10.6
SO_UP4	-9.9
CO_UP1	-1.2
CO_UP2	-5.8
CO_UP3	-1.2
CO_UP4	-8.0

It is possible to see that SO_UP2 has the highest value of T_g, which agrees with the observed highest value of viscosity (see Table 4.2), which is indicative of a higher M_n when compared to the remaining UPs. As expected, due to an increase in chain mobility, a decrease in the T_g value was observed when an aromatic monomer (PhA) was replaced by SuA. It is known that the presence of unsaturation contributes to an increase of the polymeric chain stiffness. Taking this fact into account, one would expect the SO containing UPs to have higher T_g than the corresponding CO containing UPs. This is verified in the case of the SO_UP1 and SO_UP2 *vs* CO_UP1 and CO_UP2 but not in the remaining UPs.

4.4.3 Development and Characterization of Vegetable Oil-Based UPRs

UPRs have a wide-range of industrial applications, and with the replacement of the fossil-based UPs by their 'greener' counterparts, new markets will be opened. To obtain the UPRs, the synthesized UPs were dissolved in Sty, the most used reactive solvent, and the mixture was then thermally cured in the presence of an initiator and accelerator[33,34].

The gel content was determined and was used as a measure of the crosslinking density of the UPRs. Table 4.5 presents the values of the gel content for the UPRs prepared in this work.

Table 4.5- Gel content of the SO_UPRs and CO_UPRs.

Formulation	Gel Content (%)
SO_UPR1	97.5
SO_UPR2	100
SO_UPR3	95.3
SO_UPR4	98.5
CO_UPR1	89.0
CO_UPR2	83.0
CO_UPR3	92.3
CO_UPR4	93.5

The results presented in Table 4.5 suggest that the higher unsaturation degree of SO when compared with CO provides a higher number of crosslinking points, leading to UPRs with higher gel contents[35]. It is also possible to observe that the lowest gel content values were obtained for the formulations with EG and PG (SO_UPR1 and CO_UPR1).

The thermal stability of the obtained biobased UPRs was also evaluated by TGA, in a nitrogen atmosphere. Figure 4.6 presents the thermogravimetric curves for the biobased UPRs.

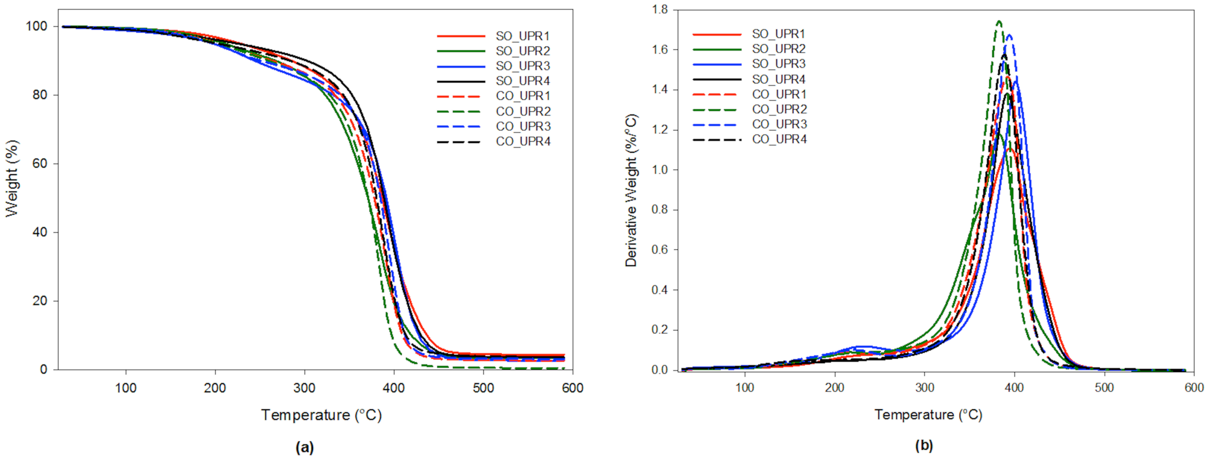


Figure 4.6- Thermogravimetric curves of SO_UPR and CO_UPR: (a) TG and (b) DTG.

The profiles presented in Figure 4.6 suggest that the studied UPRs present a main stage of weight loss (300-450 ºC), with a shoulder (150-250 ºC). The presence of the shoulder might be ascribed to the presence of segments that can be side-bonded to the network, starting to degrade earlier.

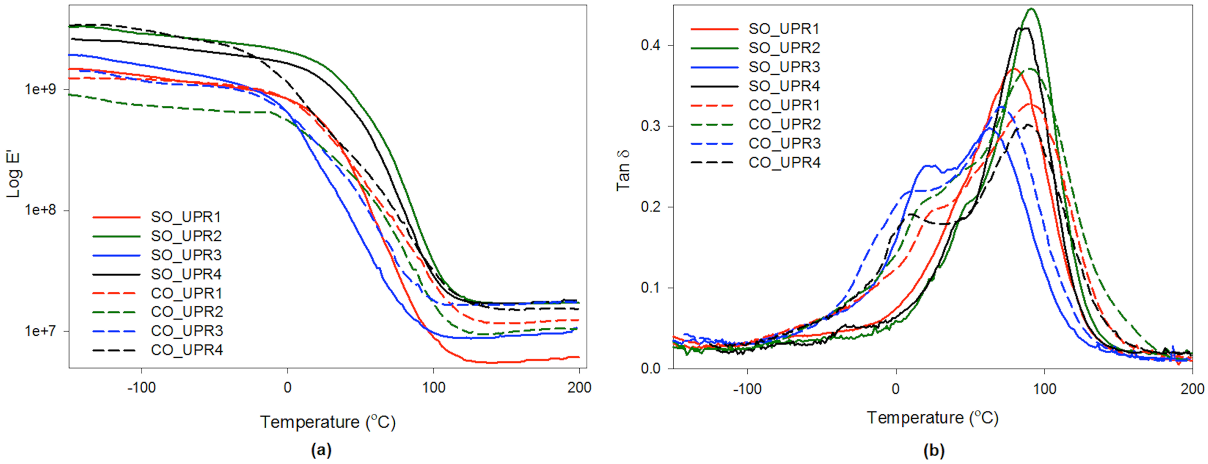
The $T_{5\%}$, $T_{10\%}$ values obtained from the thermogravimetric curves of UPRs were also used as criteria for thermal stability and are presented are presented in Table 4.6.

Table 4.6- Characteristic temperatures of the UPRs taken from the TGA. $T_{5\%}$: temperature corresponding to 5 % of mass loss; $T_{10\%}$: temperature corresponding to 10 % of mass loss.

	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
SO_UPR1	228	285
SO_UPR2	210	267
SO_UPR3	198	244
SO_UPR4	225	303
CO_UPR1	204	264
CO_UPR2	203	259
CO_UPR3	197	251
CO_UPR4	202	284

As can be seen from Table 4.6, all the UPRs present higher values of $T_{5\%}$ and $T_{10\%}$ when compared with the UPs (see Table 4.3), indicating a superior thermal stability. Regarding the effect of the kind of vegetable oil used, it is possible to observe that, in general, the SO_UPRs are thermally more stable than the CO_UPRs. In what concerns the monomers used, resins without PhA showed a small increase of thermal stability. The presented results also suggest that the presence of PDO in resins contributes to the decrease of the thermal stability of the UPRs.

The thermomechanical properties of the UPRs were evaluated by DMTA. This technique is extremely versatile allowing the measurement of the stiffness and damping of the materials in terms of modulus (E' and E'') and tan δ. The E' represents the elastic response of the material, the E'' the viscous response and the tan δ measures the capacity of the sample to dissipate energy, being the ratio between E'' and E' [36]. Figure 4.7 presents the DMTA curves (E' and tan δ) of the UPRs.



(a)

(b)

Figure 4.7- DMTA traces of UPRs based on SO and CO in terms of E' (a) and tan δ (b).

Figure 4.7 (a) shows that all the UPRs have similar E' profiles, being possible to distinguish three different regions: the glassy region, the glass transition region and the rubbery plateau. In the first region, the UPRs behave as stiff and glassy materials. In the glass transition region, a sharp decrease in the elastic modulus occurs (about three orders of magnitude); the temperature at which such decrease occurs is directly related to the composition of the material. Interestingly to note is that in the SO containing UPRs this decrease is sharper than in the CO containing UPRs. This result means that in the SO_UPRs, the polymeric chains start to move nearly at the same time. In the rubbery plateau the material becomes flexible. In Figure 4.7 (b) are shown the tan δ traces. It is possible to see that the tan δ trace has different amplitudes, which indicates that the UPRs have different capacities to dissipate energy. The peak observed in the tan δ trace corresponds to T_g. The UPRs present different T_g values, and a shoulder is observed in all resins (values presented in brackets in Table 4.7). This fact might be ascribed to the presence of two different phases that start to move at different temperatures. Table 4.7 shows the thermomechanical parameters of the UPRs prepared in this work.

Table 4.7- Mechanical and thermal properties of vegetable oil-based UPR.

Formulation	E' (MPa) -50ºC	E' (MPa) 25ºC	E' (MPa) 150ºC	T_g (ºC)	$T_{shoulder}$ (ºC)	tan δ_{max}
SO_UPR1	1093	512	5.6	79	46	0.37
SO_UPR2	2504	1553	17	91	51	0.45
SO_UPR3	1237	210	7	59	26	0.30
SO_UPR4	2025	1165	17	83	46	0.42
CO_UPR1	1120	453	17	91	31	0.33
CO_UPR2	671	321	9.8	90	17	0.36
CO_UPR3	1060	304	17	71	12	0.32
CO_UPR4	2428	493	15	88	14	0.30

The results presented in Figure 4.7 and Table 4.7 also suggest that changes in the formulations had impact not only on the stiffness of the UPRs but also on their damping properties. The results show that SO_UPR2 is the UPR with the best elastic properties and also shows the higher value of T_g, which might be related with its gel content value (100 %). SO_UPR2 is also the resin with the higher value of tan δ_{max}, indicating a higher capacity to dissipate energy when compared with the remaining UPRs. It should be pointed out that the damping values for SO_UPRs are in the same line of those reported by Miyagawa *et al.*[12], for UPRs from functionalized SO.

The obtained results also show that the replacement of PhA by SuAc did not change significantly the values of T_g. One should expect the PhA containing UPRs (SO_UPR1 and CO_UPR1) to have higher T_g than those having SuAc in the structure (SO_UPR4 and CO_UPR4), due to the expected contribution of the aromatic ring to chain rigidity. However, in this case this is not totally verified and SO_UPR4 (with SuAc) presents high T_g than CO_UPR1. In terms of E', CO_UPR2 and SO_UPR2 are, respectively, the highest and the lowest values, at low temperatures. This result might be ascribed to the values of gel content of both UPRs: SO_UPR2 presents the highest value (100 %), whereas CO_UPR2 presents the lowest value (83 %). However, for temperatures above 100 ºC, SO_UPR1 presents the lowest

E’ value, being the less elastic resin. As also can be seen in Table 4.7, SO_UPR3 and CO_UPR3 show the lowest T_g values, and this result might be related to the presence of PDO in the structure of the UPRs, that being a C3 diol contributes to higher chain mobility. [28,37]

One should expected CO_UPR to have lower values of T_g when compared with SO_UPR due to the lower crosslink density (see Table 4.5, for the gel content values). However, in some cases this is not verified. For instance, SO_UPR1 with a gel content of 100 % has a lower T_g value than CO_UPR1 with a gel content of 89 %. At this point, due to the scarcity of information in literature about this type of resins, a plausible explanation for such fact cannot be given. The tan δ peak is broader for the UPRs containing CO, fact that can be ascribed to the higher heterogeneity of the CO composition when compared with SO[37].

4.5 Conclusions

Vegetable oil-based UPs were synthesized from ‘green’ monomers PG, PDO and SuA. The polymer structures were confirmed by ATR-FTIR and ^{1}H NMR. The UPs showed a good thermal stability and, in general, the SO_UPs presented better thermal stability than the CO_UPs. As expected, it was also observed that for the SO_UPs the replacement of the aromatic monomer (PhA) by an aliphatic one (SuA) led to a decrease in the thermal stability. Regarding the T_g values, it was also found that the change of PhA for SuAc led to a decrease in the T_g for both SO_UPs and CO_UPs. Surprisingly, some of the CO_UPs presented higher T_g than the SO based counterparts. Regarding UPRs, as expected, due to their crosslinked network these structures revealed higher thermal stability than the corresponding UPs. The results provided by the DMTA also showed that the UPR based on SO, MA, PhA, PG (SO_UPR2) have the higher values of E’ and T_g, and also the higher capacity to dissipate energy (tan δ). The results also showed that UPRs made from the UPs containing PDO in the structure (SO_UPR3 and CO_UPR3) presented the lowest values of T_g.

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CHAPTER 5 – Replacement of Styrene in Unsaturated Polyester Resins: New Greener Alternatives

5.1 Abstract

The main goal of this work was the development of viable biobased unsaturated monomers (UMs) able to replace styrene (Sty), partially or totally, in a commercial and in a low viscous biobased unsaturated polyester resin (UPR) formulation. Vanillin (Van) and sobrerol (Sob) were successfully modified with methacrylic anhydride (MeAn) and new UMs, with low volatility were obtained. Due to the very high viscosity of formulations with methacrylated vanillin (MetVan), this UM was also used in a mixture with Sty (50/50 w/w). The gel content of the formulations containing the biobased UMs were lower than those containing Sty. In terms of thermal stability, the main stage of weight loss occurs nearly at the same temperature for all the studied formulations. In what concerns the thermomechanical properties, the data provided by the dynamic mechanical thermal analysis (DMTA) showed that the UPR in which a mixture of Sty/MetVan was used as UM present properties very close to the Sty-based UPR.

5.2 Introduction

UPRs, one of the most widely used thermoset polymers in industry, are obtained from the free radical polymerization of unsaturated polyesters (UPs) in the presence of an UM, also known as reactive solvent. The UM, that accounts for 30 to 40 % in weight in the formulation, has not only the role of reducing the viscosity of the UP and also to function as a crosslinking agent[1,2]. Sty is by far the most common UM used in industry of UPRs, mainly because of its availability, processing viscosity, low cost and high ability to react with UPs[1-3]. Additionally, the UPRs in which Sty is used as the UM usually present excellent physical and mechanical properties such as high tensile and flexural strength[4-7]. However, Sty has some disadvantages that cannot be disregarded. The most important concerns its high volatility during the processing of UPRs[2,6], originating high levels of volatile organic compounds (VOCs). On this matter, Sty is classified as a hazardous air pollutant (HAP)[8]. In 2011, this UM was also classified as "human carcinogen" by the USA's Department of Health and Services[9,10]. In this sense, over last years, different alternatives have been sought to partially or totally replace this monomer in the UPRs' formulation. The Sty substitute should present low volatility, good compatibility with the UP, and should also permit to obtain an UP/UM mixture with suitable viscosity (0.05- 6 Pa.s)[8]. Furthermore, due to the growing concerns regarding the environmental issues and fossil-based feedstocks depletion, it would be highly desirable to replace Sty by a UM obtained from biobased resources.

In the last years, different biobased compounds functionalized with methacrylate groups have been studied as potential Sty substitutes in polyester based thermosets, both UPRs and vinyl ester (VE) resins. Cousinet and *et al.*[10] used four biobased methacrylate derivatives (*viz.*, methyl methacrylate, butanediol dimethacrylate, isobornyl methacrylate and lauryl methacrylate) to replace Sty in a commercial UPR formulation and studied their volatility, their compatibility with the UP and the final properties of the crosslinked networks. From all studied monomers, only butanediol dimethacrylate showed simultaneously low volatility and the ability to completely dissolve the UP. The final UPR presented high stiffness, but poor resilience. To improve the mechanical properties of the UPRs the authors used, as UMs, mixtures of butanediol dimethacrylate with the remaining biobased monomers. The UPR in which a mixture of methyl methacrylate/butanediol dimethacrylate was used showed the most promising thermomechanical properties. In a different approach, the same research group studied the vinyl levulinate (VL) as Sty substitute in a commercial UPR[2]. The monomer showed to have a lower volatility when compared with Sty, being also odorless. The mixture of VL with the UP presented a viscosity suitable for the curing reaction. However, the thermomechanical properties of the VL-based UPR were inferior to those of Sty-based UPR. Later, Wu and Li reported the use of pure AESO to replace Sty in two different commercial UPRs (one synthesized with isophthalic acid, propylene glycol and maleic anhydride[9] and the other only with the two latter monomers[8]), for fiber-reinforced composites. Different weight ratios of AESO-UP were studied and the results showed that the formulations with 60 wt.% of AESO had the adequate viscosity to be used in the preparation of composites (with kenaf fiber[9] or glass fiber[8]). In both works, it was shown that the formulation with 60 wt.% of AESO led to composites with similar mechanical properties to those in which Sty was used as the UM. Unfortunately, the authors do not present any comparison between the neat UPRs (without fibers). Very recently, Dai *et al.*[11] prepared new UPs from 2,5-furandicarboxylic acid (FDCA), itaconic acid (ItaAc), and 1,3-propanediol (PDO) and studied their crosslinking reaction with guaiacol methacrylate (GM). Although being a very interesting approach that allowed the preparation of a fully biobased UPR, the authors did not performed any comparative study using Sty as UM. In this sense, it is not possible to accurately evaluate the ability of GM to be used as a Sty substitute.

Taking into account the literature related with the replacement of Sty in UPRs, one can say that a reliable Sty substitute was not yet found, being this one of the major challenges in the UPRs' industry. In this chapter, two different methacrylated-based monomers from renewable resources, Van and Sob, were prepared and studied as partial and/or total substitutes of Sty in

UPR formulations. Both Van and Sob came from biobased feedstocks and present rigid structures (Van present an aromatic ring, Sob present a cyclic ring), which in principle would contribute to afford UPRs with enhanced thermomechanical properties. Vanillin-based monomers have been used as Sty substitutes, but only in the field of VE resins. Regarding the sobrerol-based monomers, those have never been used at all neither in the field of VE resins nor in the field of UPRs. The Sty replacement was studied in a commercial resin and in a low viscosity biobased UPR (Bio_UP3 developed in the Chapter 3 of this thesis). The UPRs were characterized in terms of their gel content, thermal stability and thermomechanical properties and the impact of the Sty replacement in their properties was studied and discussed.

5.3 Experimental Section

5.3.1 Materials

Methacrylic anhydride (MeAn, 94 %) and Sty (>99 %) were purchased from Sigma-Aldrich. α-Pinene Oxide (>95 %) and 4-dimethylaminopyridine (DMAP, >99 %) were obtained by TCI Europe and cobalt Octoate (CoO) was purchased from AGAMI. Van (99 %), tetrahydrofuran (THF, >99.5 %) petroleum ether (>90 %) and anhydrous sodium sulfate (Na_2SO_4, >99 %) were supplied from Acros Organic. Methyl ethyl ketone peroxide (MEKP) was purchased from Algarplás. Deuterated THF (THF-d_8) and deuterated chloroform ($CDCl_3$) were purchased from Eurisotop. Ethyl acetate (>99.5 %) and hydroquinone (HQ, >99 %) were obtained from Analar and sodium bicarbonate ($NaHCO_3$, >99.5 %) was purchased from Panreac. All the reactants were used as received, unless otherwise stated.

5.3.2 Reaction of Vanillin with Methacrylic Anhydride

Into a 100 mL flask, Van (0.13 mol) was mixed with DMAP (0.003 mol; 2 mol% of anhydride) and the reaction vessel was sealed. The mixture was stirred and purged with nitrogen gas during 1 hour, at room temperature. Then, MeAn (1.20 mole equivalents based on Van) was added to the flask. The mixture was purged and stirred for more 15 minutes, at room temperature, and then heated to 50 ºC for 30 hours[12]. After this time, the final solution was cooled to room temperature and dissolved in ethyl acetate. The product was washed with distilled water and the organic phase was dried over anhydrous Na_2SO_4 and removed on a rotary evaporator under reduced pressure, to yield the methacrylated Van (MetVan).

5.3.3 Synthesis of Sobrerol

Into a 500 mL flask, 200 mL of water were bubbled with CO_2, at 37 ºC, until pH = 5. Then, α-pinene oxide (100 g, 0.66 mol) was added to the flask and the temperature was raised to 70 ºC during 24 hours, with continuous CO_2 bubbling[13,14]. Then, the mixture was cooled to 10 ºC. Sob was then purified through continuous cycles of washing with petroleum ether and centrifugation (4000 rpm for 2 minute cycles) until a crystalline white powder was obtained.

5.3.4 Modification of Sobrerol with Methacrylic Anhydride

In a round bottom flask, Sob (0.06 mol) and DMAP (1.17 mmol) were dissolved in THF (50 mL). MeAn (0.06 mol) was added to the flask and the mixture was stirred for 15 minutes, at room temperature. The temperature was then raised to 50 °C and kept for 24 hours. After the removal of THF, the obtained product was dissolved into ethyl acetate and washed with a $NaHCO_3$ aqueous solution (0.5 M). The organic phase was dried over anhydrous Na_2SO_4 and removed on a rotary evaporator under reduced pressure, to yield the methacrylate Sob (MetSob).

5.3.5 Crosslinking of the UPs with MetVan and MetSob

The different UPs were dissolved in 32 wt.% of the different UMs, at 100 ºC, according to Table 5.1.

Table 5.1- Formulations for the UPRs to be studied.

UPR	UP	UM
Resipur_Sty	Resipur	Sty
Resipur_Sty/MetVan		Sty/MetVan (50/50 w/w)
Resipur_MetVan		MetVan
Resipur_MetSob		MetSob
BioUPR3_Sty	BioUPR_3	Sty
BioUPR3_Sty/MetVan		Sty/MetVan (50/50 w/w)
BioUPR3_MetVan		MetVan
BioUPR3_MetSob		MetSob

After the dissolution of the UP, at room temperature, the initiator MEKP (2 wt.%) and accelerator CoO (1 wt.%) were added under continuous stirring until a homogeneous mixture was obtained[15]. It should be pointed out that, due to the high viscosity of the mixture, the initiator and accelerator were added to Resipur_MetVan at 50 ºC. The formulations were then cured in a Teflon mold (16 x 7 x 0.5 mm) at room temperature for 24 hours and post-cured at 80 ºC for 3 hours[16,17].

5.3.6 Characterization Techniques

Chemical Structure Identification

ATR-FTIR analysis of the monomers was carried out with a Cary 630 FTIR spectrometer. Data collection was performed with 4 cm^{-1} spectral resolution and 64 accumulations, in 650 and 4000 cm^{-1} wavenumber range.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer, from Bruker using a 5 mm TIX triple resonance detection probe, in THF-d_8 and $CDCl_3$, at room temperature. Tetramethylsilane (TMS) was used as the internal reference.

Thermal Properties

The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA), using a TA Instruments Q500 thermogravimetric analyzer (thermobalance sensitivity: 0.1 μg). The equipment was calibrated within a temperature interval ranging from 25 ºC to 1000 ºC, at a heating rate of 10 $ºC.min^{-1}$, running tin and lead as melting standards. The samples were analyzed using open alumina crucibles, in the temperature range 25 ºC to 600 ºC and at a heating rate of 10 $ºC.min^{-1}$, under dry nitrogen purge flow of 100 $mL.min^{-1}$.

The viscoelastic properties of the UPRs were measured by DMTA with a Tritec 2000 DMA, from Triton Technology, Ltd. The properties of resins were analyzed in the dual cantilever bending geometry. The samples BioUPR3_MetVAn and BioUPR3_MetSob were analyzed in the single cantilever bending geometry using stainless steel material pockets. All DMTA measurements were carried out in a -150 °C to 200 °C temperature range, at frequencies of 1 and 10 Hz, using a heating rate of 2 $ºC.min^{-1}$. The T_g of the UPRs was determined from the maximum of tan δ, at 1 Hz.

Viscosity

The viscosity of the monomers and the UP_UM formulations was determined by a Haake Mars III rotational rheometer with a Peltier temperature control. The rotation method was carried out with a plate/cone C35/1º (of titanium) and the viscosity was obtained after 40 steps, with an equilibrium step of 15 s between each step, for 25 and 80 ºC.

Gel Content

The degree of curing of UPRs was evaluated by the gel content. This characteristic was evaluated by Soxhlet extraction using THF as solvent (according to ASTM D2765 - 16). The samples were weighed and placed in the Soxhlet's extractor for 8 hours. After that, the samples were dried until constant weight. The gel content was calculated according to the Equation 1:

$$Gel\ Content = \frac{w_f}{w_o} \times 100 \qquad \text{(Equation 1)}$$

where w_0 and w_f represent, respectively, the weight before and after extraction.

Volatility

The volatility of Sty, MetVan and MetSob was measured by TGA, using a TA Instruments Q500 thermogravimetric analyzer (thermobalance sensitivity: 0.1 μg). The equipment was calibrated within a temperature interval ranging from 25 ºC to 1000 ºC, at a heating rate of 10 ºC.min^{-1}, running tin and lead as melting standards. The samples were analyzed using open alumina crucibles, for 9 hours, using an isothermal of 25 ºC, under dry nitrogen purge flow of 100 mL.min^{-1}.[2]

5.4 Results and Discussion

5.4.1 Synthesis of Biobased Unsaturated Monomers And Their Chemical Structure Identification

In this work, the main objective was the development of biobased UMs able to replace Sty in the UPRs' formulation. For such purpose, Van and Sob were modified with MeAn (Figure 5.1), yielding methacrylated vanillin (MetVan) and methacrylated sobrerol (MetSob). These monomers were evaluated in terms of potential to partially or totally replace Sty in a commercial UP and in a low viscosity biobased UP developed in the Chapter 3 of this thesis (Bio_UP3). The stringent selection of monomers was based not only on their source, but also on the expected properties that they could impart to the UPR.

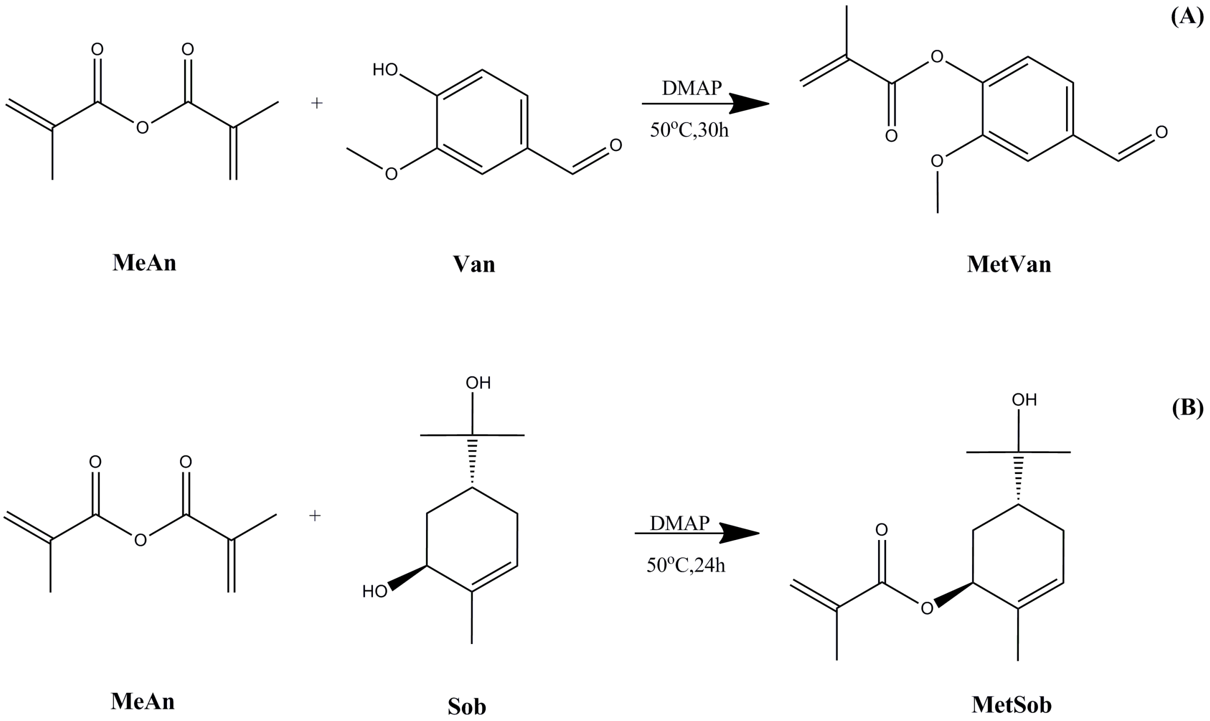

Figure 5.1- Modification of biobased monomers with methacrylate functionality on MetVan (A) and MetSob (B).

Van is a lignin derivative that has emerged as viable alternative to petrochemical-based materials, presenting high abundance and competitive cost. Van is also one of the few phenolic biobased monomers already produced on an industrial scale[18-20]. Furthermore, this aromatic compound presents two reactive functionalities that can be chemically modified, yielding new monomers with high potential for a wide range of applications. MetVan was already reported in literature[12,21,22], but it has never been used as a Sty substitute in the field of UPRs. MetVan is solid at room temperature (T_m~ 43 ºC), which could justify its non-use in the field of the UPRs. Nevertheless, the monomer is known to have high reactivity. Thus, in this work it was decided to employ MetVan as a partial Sty substitute in UPs of high viscosity and a total Sty substitute in UPs of low viscosity (22.3 Pa.s).

In addition to lignin, terpenic compounds have also attracted increasing attention as important renewable raw materials sources[23,24]. Sob, a monoterpenic compound derivative obtained from the hydration of α-pinene oxide, has been widely studied for cosmetic and namely for pharmaceutical applications as mucolytic agent and expectorant due to its biological activities [14,25]. Additionally, the synthesis route to obtain of Sob contributes to CO_2 fixation. Sob, due to the presence of a cyclic ring in its structure, could give promising derivatives for Sty substitution in UPRs. Thus, is this work it was decided to prepare MetSob and use it to totally replace Sty, both in a commercial and in a biobased UP. To the best of our knowledge, the preparation of MetSob and its use as a monomer has never been reported, being an innovative aspect of this work.

The structural features of pure Van and MetVan were characterized by infrared spectroscopy (Figure 5.2).

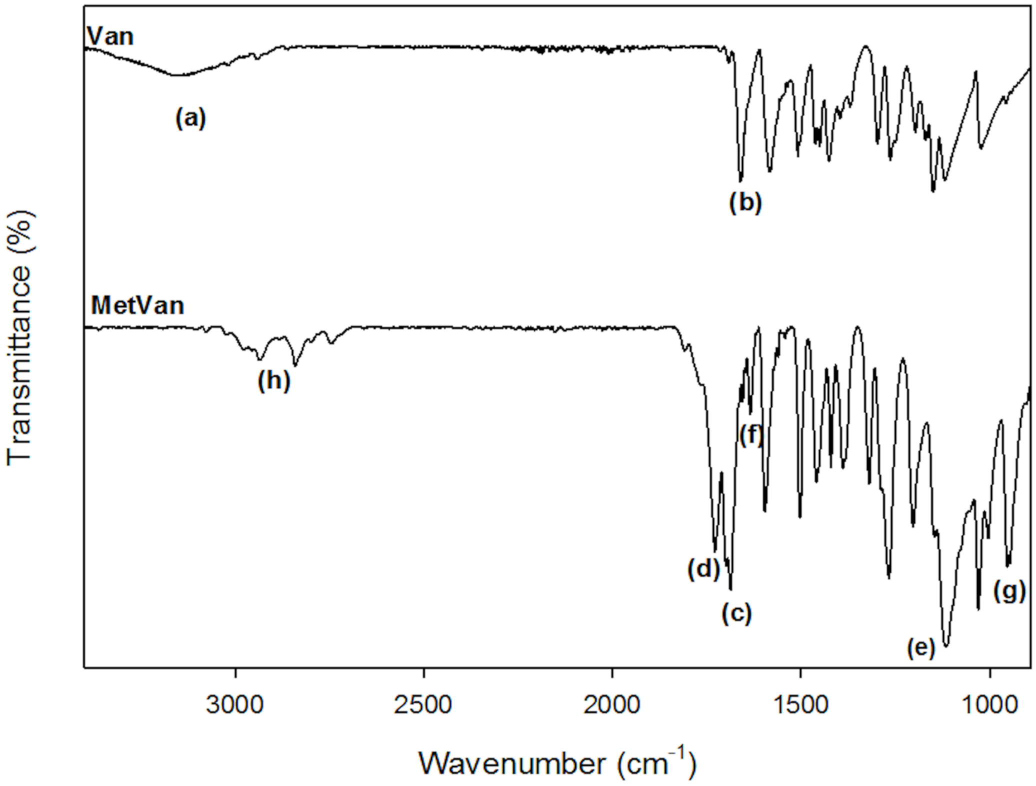

Figure 5.2- ATR-FTIR spectra of Van and MetVan.

The FTIR spectra presented in Figure 5.2 shows bands corresponding to the hydroxyl functionality in Van structure, in the region 3600-3200 cm^{-1} (a)[26]. In MetVan, as expected, this band disappears. The band ascribed to the vibration of the carbonyl group of the aldehyde linkage shifted to *ca.* 1664 cm^{-1} (b) in Van from *ca.* 1694 cm^{-1} (c) in MetVan[22,27]. A set of new bands also appears in the MetVan spectrum, namely at *ca.* 1737 cm^{-1} (d) corresponding to the stretching vibration of the carbonyl group of the ester linkage and the band in the region 1300-1100 cm^{-1} (e) is ascribed to the C-O stretching of the same linkage. The band at *ca.* 1638 cm^{-1} (f) is due to the vibrational modes of the terminal vinyl group whereas, at *ca.* 947 cm^{-1} (g), appears the band of its bending vibration[12,27]. The appearance of this set of bands suggests the success of the reaction. In both spectra it is also possible to observe the absorption peaks in the region 2976-2820 cm^{-1} (h) attributed to the vibrational modes from stretching vibrational modes of methoxy group[26].

Van and MetVan were also analysed by ^{1}H NMR and ^{13}C NMR spectroscopies, presented in Figure 5.3 and Figure 5.4, respectively. For ^{1}H NMR spectra, the integration area of the peaks is indicated in brackets in all spectra.

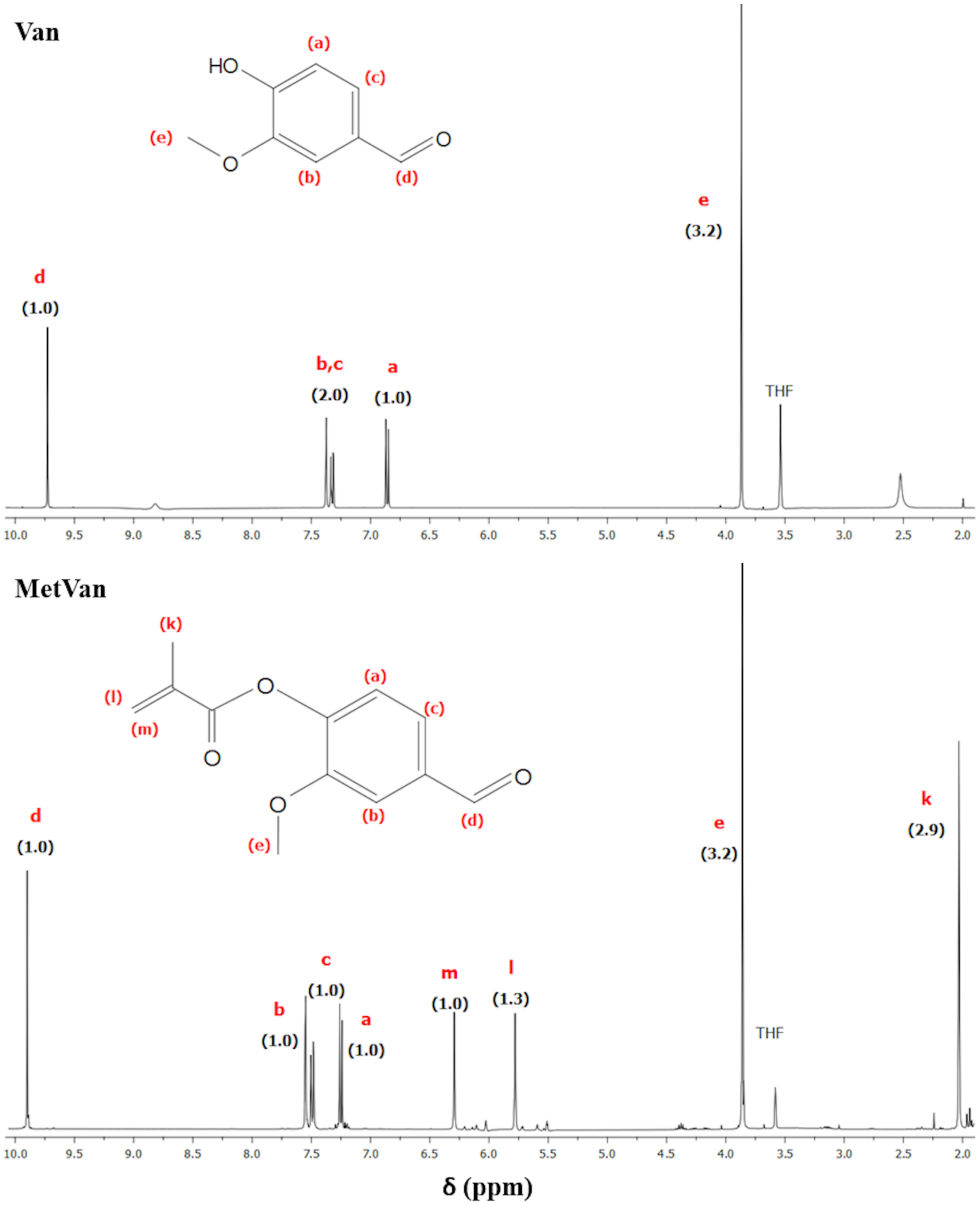

Figure 5.3- ^{1}H NMR spectra of Van and MetVan.

As can be seen in Figure 5.3, both Van and MetVan present the characteristic resonances attributed to the -**CH** of the aldehyde group (d), at δ ~ 9.92 ppm, and the pendant -$\mathbf{CH_3}$ attached to the ether group at ~ 3.86 ppm[22]. In the ^{1}H NMR spectrum of MetVan, it is possible to identify at 2.02 (k), 5.79 (l) and 6.30 ppm (m) the resonances of the protons ascribed to the methacrylate functionality in the MetVan structure[12,22,28]. Additionally, the shift in the resonance of the -C**H** proton (a) of the aromatic ring closest to the –OH group, from 6.91 ppm (Van) to 7.27 ppm (MetVan), indicates the success of the modification. It should be also pointed out that the calculated integral values are in accordance with the anticipated chemical structure, indicating the success of the reaction.

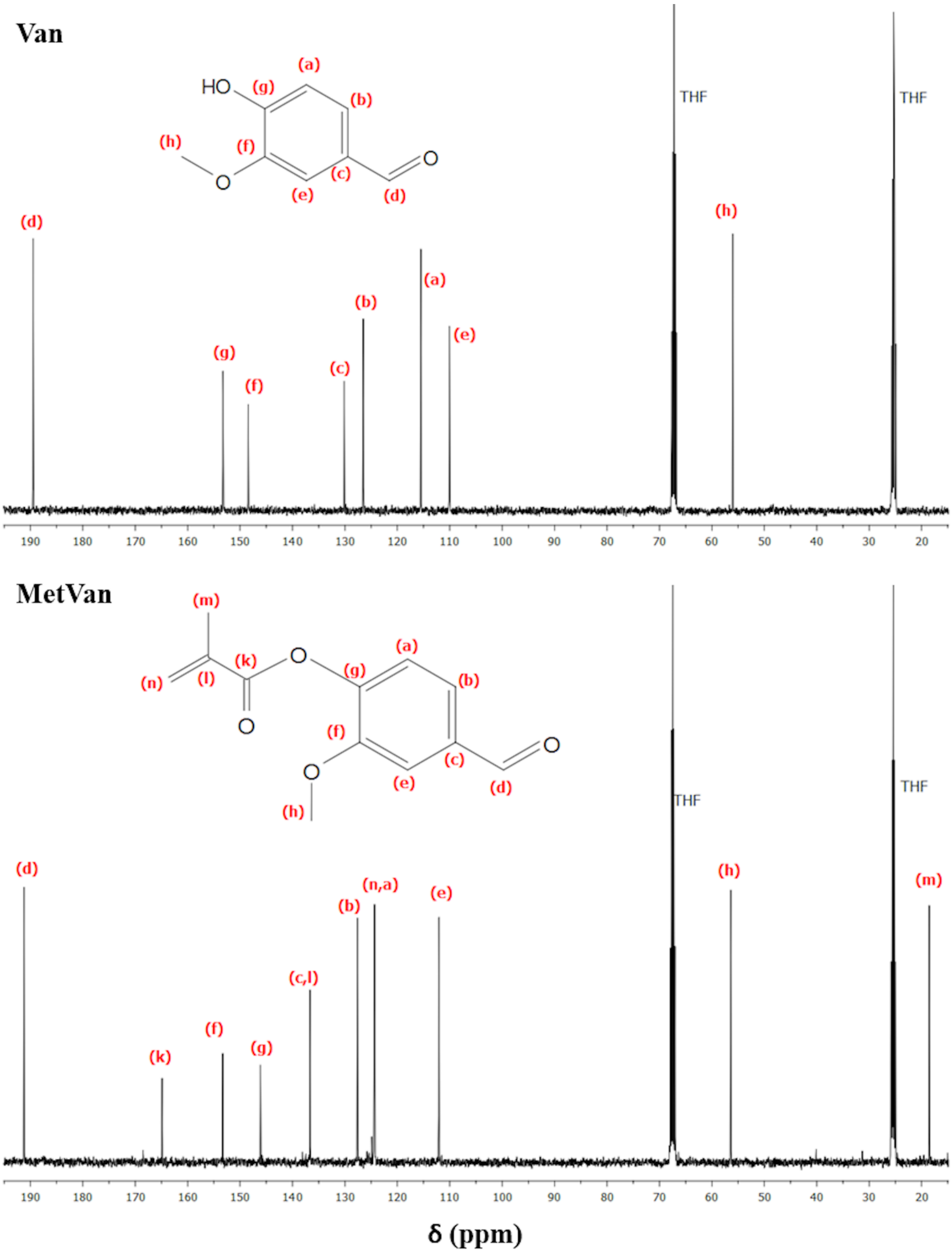

Figure 5.4- ^{13}C NMR spectra of Van and MetVan.

The ^{13}C NMR spectra of the monomers are consistent with the main ^{1}H NMR features and also with literature data on similar methacrylated monomers[27]. As can be seen in Figure 5.4, the main differences between Van and MetVan spectra can be found in the resonances characteristics of methacrylated group in MetVan. A new resonance in MetVan is present at δ ~ 164.9 ppm (k), and is ascribed to the -**C**=O carbon of the ester group and at δ ~ 18.68 ppm can be identified the pendant -**C**H_3 (m). The resonances at 136.40 (l) and 127.61 ppm (n) can be attributed to the -**C**=**C**H_2 of the methacrylate functionality. Furthermore, the -**C**H of the aromatic ring (g) also presented different resonances when attached to the hydroxyl group (154.15 ppm, in Van) or in the presence of the methacrylate functionality (146.23 ppm, in MetVan).

Similarly, the structural features of pure Sob and MetSob were also characterized by ATR-FTIR and ^{1}H NMR and ^{13}C NMR spectroscopies. Figure 5.5 presents the FTIR spectra of Sob and MetSob.

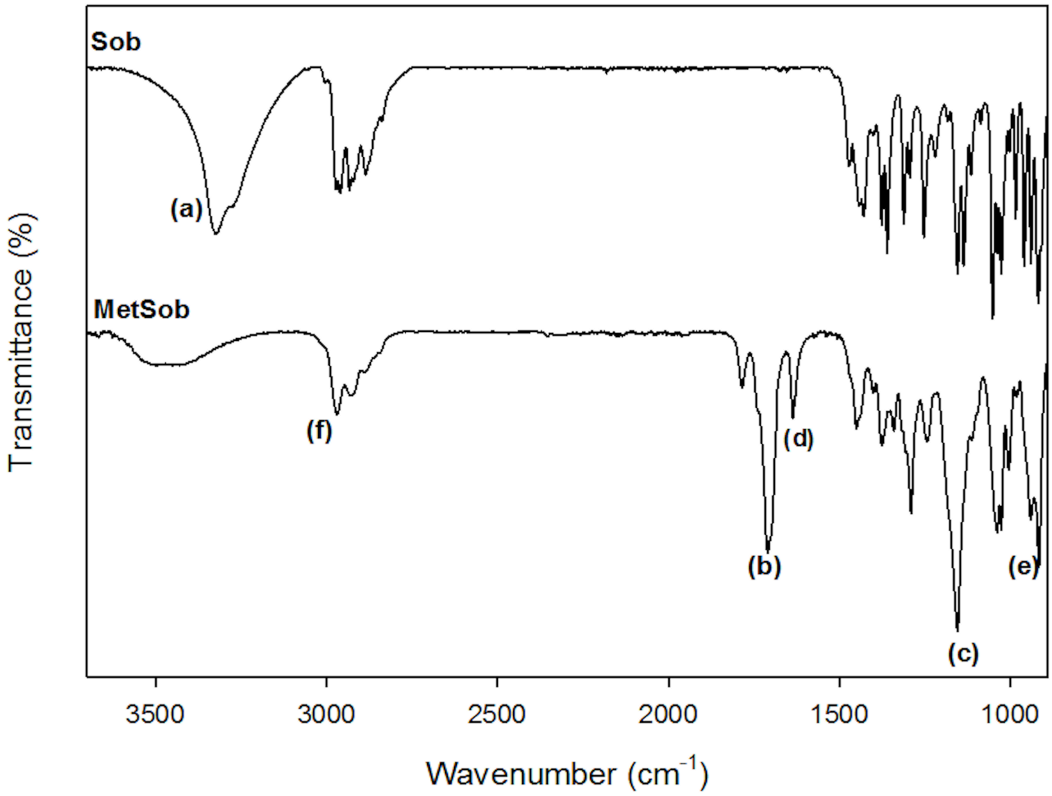

Figure 5.5- ATR-FTIR spectra of Sob and MetSob.

As expected, the spectrum of Sob shows bands in the region 3600-3200 cm^{-1} (a), corresponding to the -OH groups present in its structure[25]. When compared with the Sob, the spectrum of MetSob presents a significant decrease in this region. For the MetSob spectrum, it is also possible to observe an absorption peak at *ca.* 1715 cm^{-1} (b) that can be ascribed to the -C=O stretching vibration of the ester linkage, whereas at *ca.* 1153 cm^{-1} (c) is present the -C-

O stretching of the same group[26,29], indicating the formation of an ester linkage. The absorption peaks at *ca.* 1639 cm^{-1} (d) and 941 cm^{-1} (e) are related to the stretching vibration and bending vibration of the terminal vinyl groups, respectively[12,27]. The bands in the region 2976-2820 cm^{-1} (f) are ascribed to the -CH vibrational stretching modes[30].

Figure 5.6 and Figure 5.7, present the ^{1}H NMR and ^{13}C NMR spectra, respectively, of Sob and MetSob.

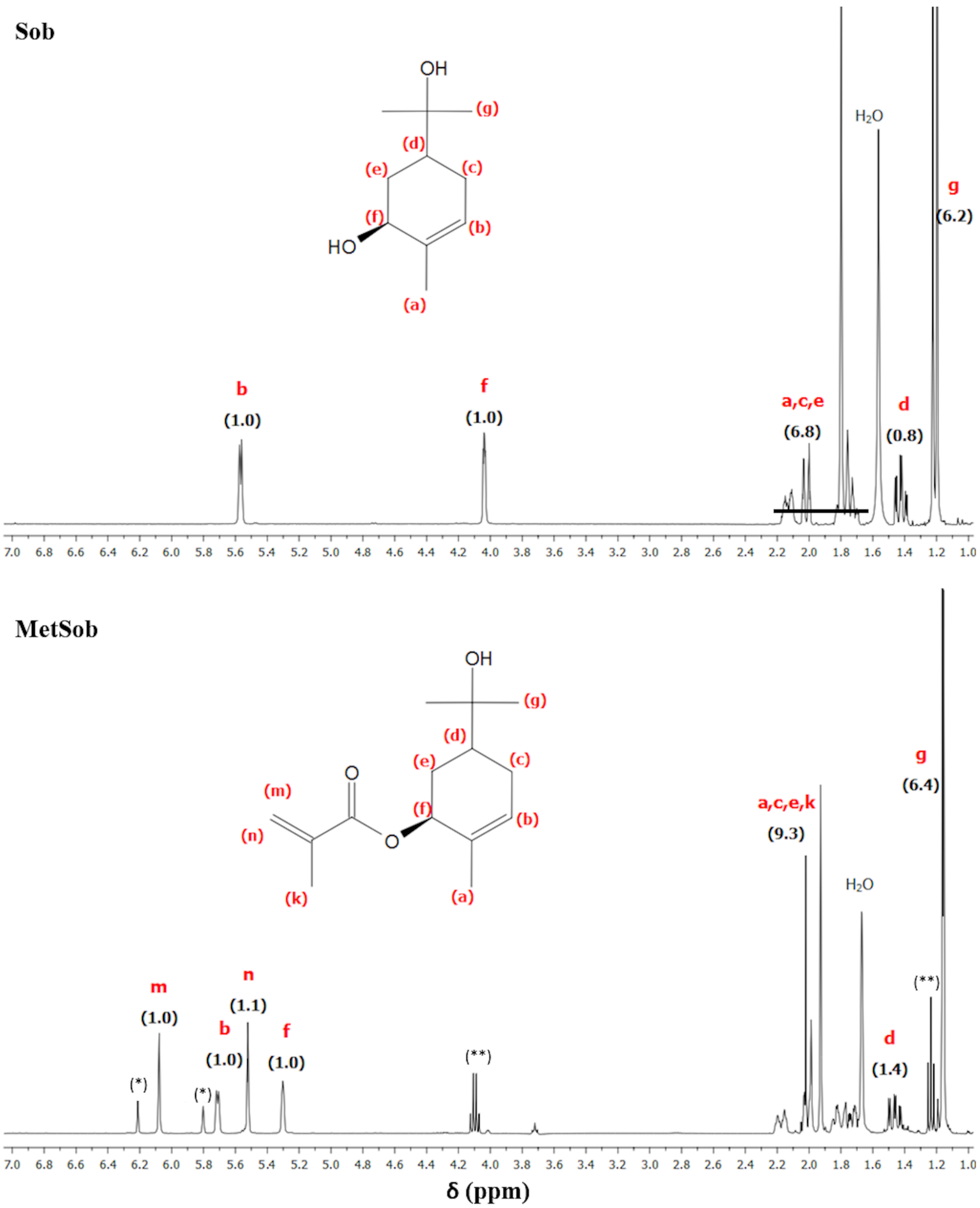

Figure 5.6- ^{1}H NMR spectra of Sob and MetSob; (*) corresponds to the presence of residual MeAn and (**) to residual ethyl acetate.

According to the Figure 5.6, the modification of Sob with MeAn was successfully achieved. When comparing the spectra of both monomers, it is clear that the signal of -C**H** linked to the hydroxyl group in Sob, at 4.04 ppm, presents a significant deviation in MetSob, appearing at 5.30 ppm (f). The resonances of the vinyl group of methacrylate functionality are also clearly visible at 6.08 ppm (m) and 5.52 ppm (n)[28]. The resonances corresponding to the -C**H$_3$** (g) protons of Sob, at 1.17 ppm, did not changed in the MetSob ^{1}H NMR spectrum, indicating that the –OH group attached to the –C**H**$_3$ is not reactive under the reaction conditions used. At *ca.* ~ 5.80 and ~ 6.21 ppm (*), two signals are detected and can be ascribed to the presence of MeAn. The chemical composition of both Sob and MetSob was also studied by ^{13}C NMR (Figure 5.7).

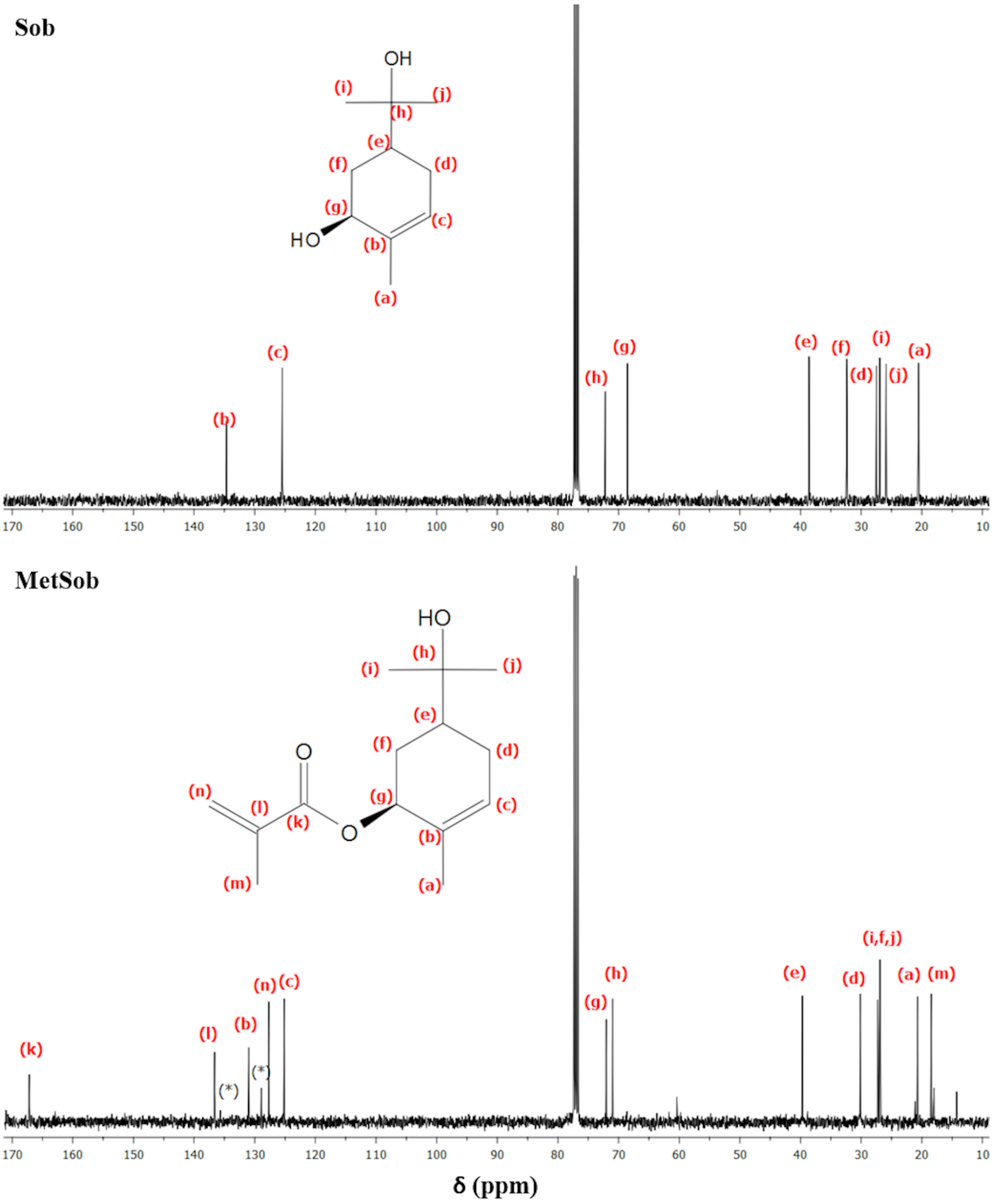

Figure 5.7- ^{13}C NMR spectra of Sob and MetSob.

The ^{13}C NMR data concerning the Sob and MetSob is in accordance with the anticipated chemical structure and the ^{1}H NMR analysis. The main differences between the spectrum of Sob and MetSob is the presence of methacrylate group in the latter, confirmed by the resonances at *ca.* 167.46 ppm (k), 136.07 ppm (l), 128.04 ppm (n) and 18.64 ppm (m). Moreover, due to the presence of this new group, the -C**H** protons represented by (f) and (g) in the monomers also present a deviation from 27.14 to 32 ppm and from 68.75 to 72.08 ppm, respectively. Thus, for both methacrylated-based UM under study, the spectroscopic results confirmed the success of the corresponding modification reactions.

The volatility of the UM is a key issue in the UPRs' field. The evaporation or emission of the UM can lead to important environmental and health concerns. In this sense, the volatility of the UMs developed in this work was evaluated[10]. Figure 5.8 presents the percentage of weight loss as a function of time for Sty, MetVan and MetSob, determined by TGA analysis under nitrogen atmosphere, at 25 ºC for 9 hours.

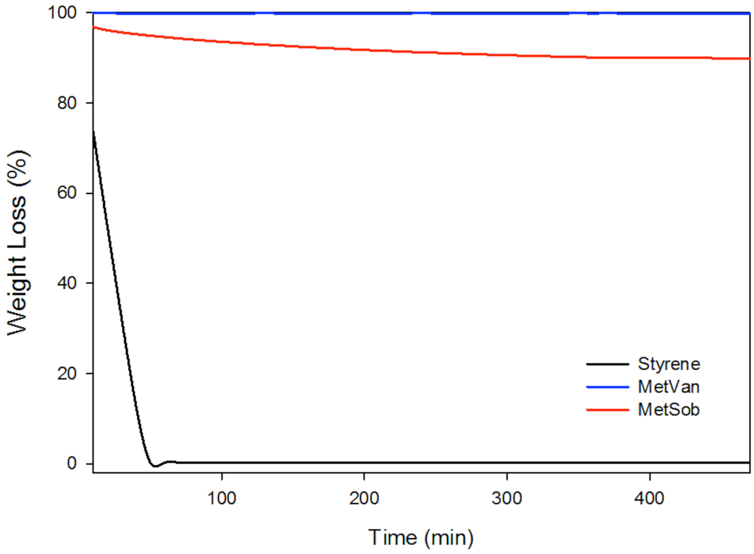

Figure 5.8- Volatility analysis for Sty and methacrylated-based UM under study.

As expected, Sty presents a high volatility at room temperature and, only after 50 minutes, all the monomer evaporated. In turn, the UMs prepared in this work, show substantially lower volatility when compared with Sty. MetVan does not show any mass loss during the analysis period and MetSob shows a mass loss of about 10 %. In the case of MetSob, this mass loss has contribution of the volatilization of the MeAn present in the sample (see ^{1}H NMR and ^{13}C NMR discussion). Nevertheless, MetSob has a significantly lower volatility when compared with Sty, which can be ascribed to its high molecular weight (*ca.* 238 g.mol^{-1}) in comparison with Sty (*ca.* 104 g.mol^{-1}) and also to the establishment of intermolecular H-bonds between the carbonyl group of the ester linkage with the free hydroxyl group (-C=O···OH). In the case of MetVan, since it has no groups able to establish intermolecular H-bonds, the difference in volatility to Sty might be explained by its high molecular weight (*ca.* 220 g.mol^{-1}).

5.4.2 Development and Characterization of MetVan and MetSob-based UPRs

In the development of new UMs for Sty replacement in UPR formulations, it is essential to ensure good compatibility between the UP and the UM and guarantee a suitable viscosity of the final mixture in order to avoid problems in the processing step.

In this chapter, MetVan and MetSob were used as UMs to prepare UPRs based on a commercial resin (Resipur®) and a biobased UP with low viscosity (Bio_UP3), developed in the Chapter 3. Since MetVan has a T_m~43 ºC, for both resins, this UM was firstly used in a 50/50 (w/w) mixture with Sty. In a second approach, it was used to totally replace Sty in both UPs formulations. MetSob, in turn, is liquid at room temperature and, therefore, only the total replacement of Sty was studied. Table 5.2 summarizes the viscosities of the formulations (UP+UM) at different temperatures.

Table 5.2- Newtonian Viscosity for the UP+UM formulations under study.

Formulation	Newtonian Viscosity [Pa.s]	
	25 ºC	80 ºC
Resipur_Sty	0.614	0.057
Resipur_Sty/MetVan	5.664	0.114
Resipur_MetVan	58.14	0.303
Resipur_MetSob	10.90	0.115
BioUPR3_Sty	0.257	0.056
BioUPR3_Sty/MetVan	1.002	0.104
BioUPR3_MetVan	10.22	0.234
BioUPR3_MetSob	4.597	0.204

As can be seen in Table 5.2, the viscosity of the formulations containing the UMs is significantly higher than that observed for the formulations containing Sty. The formulations in which MetVan was used as UM present the highest viscosity. Since this monomer is solid at room temperature, it does not promote the diluent effect that is expected for an UM, giving mixtures with high viscosity. When Sty is added to the mixture, a decrease in the viscosity is observed, result that can be attributed to the solvancy power of Sty. In what concerns MetSob, it is possible to observe that this UM also gives mixtures with a viscosity higher than those with Sty due to the presence of hydroxyl groups that can establish H-bonds with the carbonyl groups of the ester linkages in the UP can contribute to the high viscosities of the mixtures. It should be noted that, despite the high viscosities, at 25 ºC the formulation with Sty/MetVan and MetSob as UM still remain in an available range for some applications, such as preparation of composites by the hand lay-up method[8,9].

Upon increasing temperature, from 25 ºC to 80 ºC, a significant reduction in the viscosities of the mixtures is observed. In the case of MetVan, at 80 ºC, it is liquid and acts as a *true* solvent of the UPs. In the case of MetSob, an increase in temperature can led to the disruption of the H-bonds, leading to a decrease in the viscosity.

Table 5.3 presents the results for the gel content for the resins under study.

Table 5.3- Gel content of the UPR specimens.

Sample	Gel Content
Resipur_Sty	99.9
Resipur_Sty/MetVan	93.0
Resipur_MetVan	83.8
Resipur_MetSob	86.2
BioUPR3_Sty	98.9
BioUPR3_Sty/MetVan	81.3
BioUPR3_MetVan	61.9
BioUPR3_MetSob	70.0

As can be seen in Table 5.3, the partial or total replacement of Sty by the biobased UMs led to UPRs with lower gel content values. This result might be ascribed to the lower reactivity of the methacrylate derivatives when compared with Sty[12,27]. UPRs' formulations containing Sty also have a significantly lower viscosity in comparison with those containing the biobased UMs, which helps the crosslinking reactions (see Table 5.2). Thus, in the former group of formulations, the UP and the UM have higher freedom of movements which enable a much more effective crosslinking reaction, leading to higher gel contents. The UPRs formulations containing MetSob also have higher gel contents than those containing MetVan and the reason for such result can also be ascribed to the lower viscosity of the former group of formulations.

All the UPRs developed with the BioUP3 present lower gel contents than the UPRs prepared with the commercial UP formulation, although the viscosity of the former group of formulations is lower. This result is quite unexpected, since in principle lower viscosity would be translated in higher gel content, as explained before. Thus, this result can be tentatively assigned to affinity issues of the BioUP3 with the novel biobased UMs.

The thermal stability of the UPRs under study was also evaluated by TGA, in a 25-600 ºC temperature range, under nitrogen atmosphere. Figure 5.9 presents the weight loss profile of each UPR under study. The relevant temperatures obtained from the thermoanalytical curves are summarized in Table B. 1.

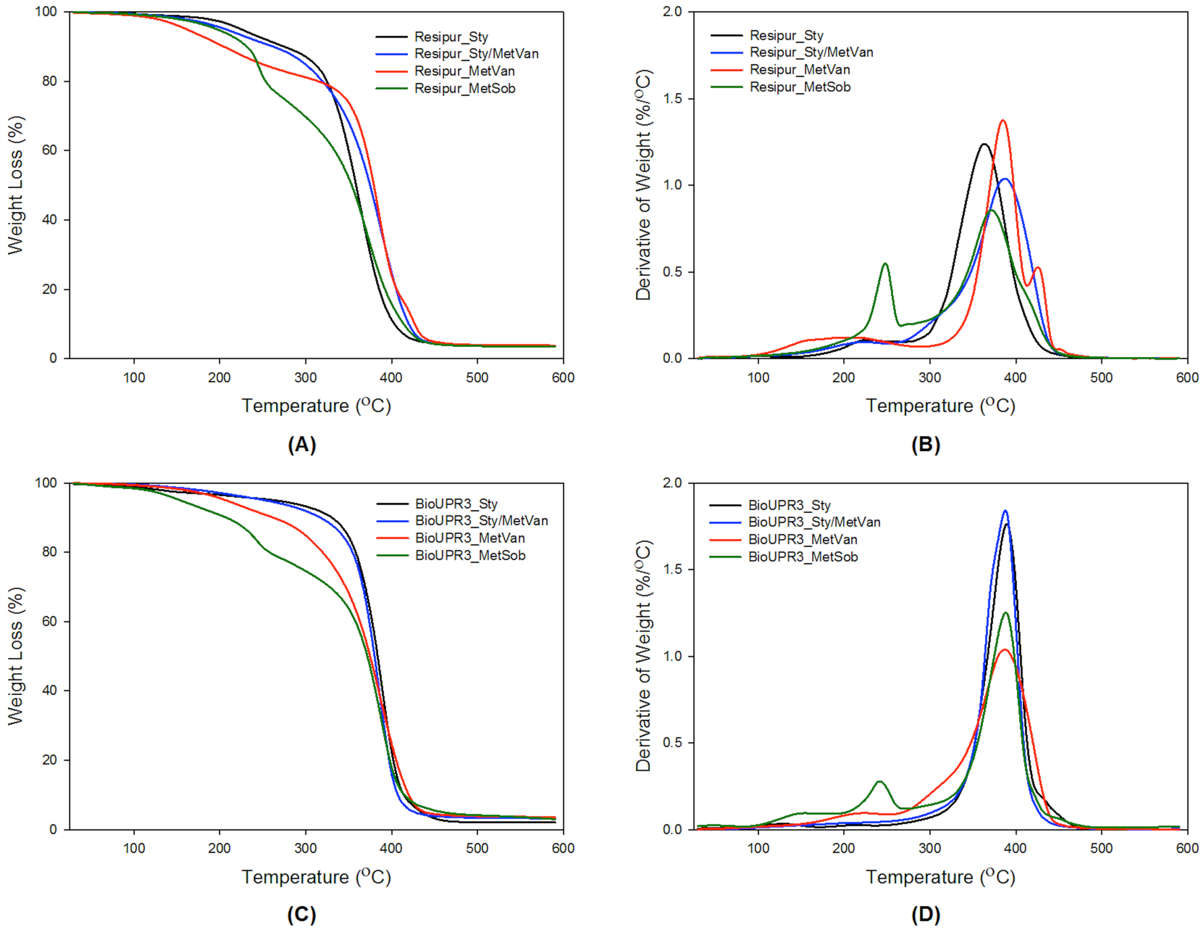

Figure 5.9- Thermogravimetric curves of the UPRs from Resipur ((A) and (B)) and BioUPR3 ((C) and (D)).

As can be seen in (Figure 5.9 (A) and (B)), all the developed UPRs present a main stage of weight loss (*ca.* 300-420 ºC) that can be ascribed to the degradation of the 3D network[31]. In the case of Resipur®-based formulations, an additional weight loss stage can be observed (*ca.* 200-250 ºC for Resipur_Sty and Resipur_Sty/MetVan, *ca.* 150-200 ºC for Resipur_MetVan and 190-220 ºC for Resipur_MetSob). In the case of BioUPR3-based formulations (Figure 5.9 (C) and (D)), this additional weight loss is only seen in BioUPR3_MetVan and BioUPR3_MetSob. For the UPRs with Sty and MetVan, the initial weight loss can be ascribed to the volatilization of residual moisture and also to the degradation of small oligomeric species that are side bonded to the 3D network and can start to degrade earlier[32]. However, for the formulations with MetSob, this first weight loss stage is more pronounced which could be ascribed to the degradation of some amount of MetSob homopolymer presented in the UPR.

The thermomechanical properties of the UPRs were assessed by DMTA, at two frequencies (1, 10 Hz), in a temperature range of -150 ºC to 150 ºC. The T_g of the UPRs was determined from the maximum of the tan δ curve, at 1 Hz. The DMTA traces of the different samples are shown in Figure 5.10 and their relevant features are summarized in Table 5.4.

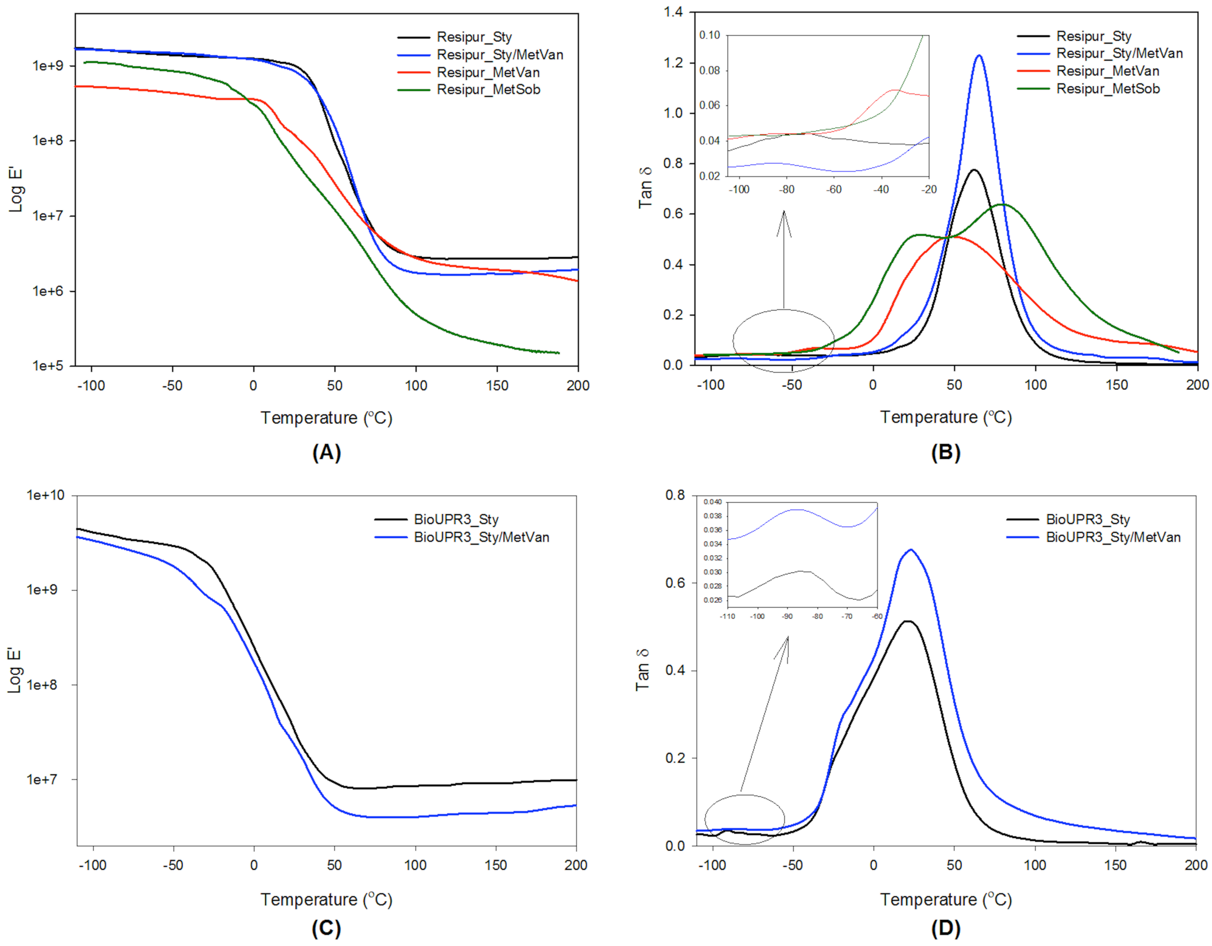

Figure 5.10- DMTA traces of the UPRs in terms of E' ((A) and (C)) and tan δ ((B) and (D)).

Figure 5.10 (A) presents the E' traces of the UPRs from Resipur. It is possible to observe that the partial replacement of Sty by MetVan in the UPRs' formulation did not jeopardize the thermomechanical properties of the UPR. In the UPR in which Sty was totally replaced by MetVan or MetSob, the E' value at room temperature decreased significantly and this result can be related with the lower gel content of the samples. Figure 5.10 (B) shows the tan δ traces of these resins. With the exception of Resipur_MetSob, all the UPRs presented a tan δ curve with a main peak, sensitive to frequency, being therefore ascribed to an α transition. This transition corresponds to the T_g of the resins and is related with the motions of the UPR's main domain. In addition, for Resipur_Sty and Resipur_Sty/MetVan an additional peak at negative temperatures (*ca.* -80 ºC) is present and might be attributed to the γ transition, due to the motions of the aromatic group in poly(Sty) or oligo(Sty) moieties[4,33]. In the case of Resipur_MetVan and Resipur_MetSob, the peak corresponding to the α transition is broader than that observed for Resipur_Sty and Resipur_Sty/MetVan. This result can be related to some heterogeneity of the UPRs, due to an inefficient curing step in virtue of the high viscosity of the mixture (see Table 5.2). A similar behavior was observed by Stanzione *et al.*[21] in VE resins crosslinked with methacrylate derivatives of guaiacol and eugenol.

In Figure 5.10 (C) and (D) are presented the thermomechanical traces of the UPRs from BioUPR3. Both BioUPR3_Sty and BioUPR3_Sty/MetVan present similar E' values. BioUPR3_MetVan and BioUPR3_MetSob were analyzed in stainless steel material pockets and their E' profile cannot be evaluated. Regarding the tan δ curve of BioUPR3_Sty and BioUPR3_Sty/MetVan, two peaks are also identified and correspond to the, γ and α transitions. For both UPRs, the main tan δ peak presents an additional shoulder, indicating the presence of two different phases within the 3D network that start the molecular motion at different temperatures.

Table 5.4 summarizes the main values obtained from DMTA data.

Table 5.4- Thermomechanical parameters of the studied UPRs.

Formulation	$E'_{25°C}$ (MPa)	T_γ (ºC)	$T_{shoulder}$ (ºC)	T_g (ºC)	tan δ_{max}
Resipur_Sty	100×10^1	-75.4	----	62.9	0.97
Resipur_Sty/MetVan	872	-84.8	----	66.2	1.23
Resipur_MetVan	2.78	----	----	48.8	0.51
Resipur_MetSob	56.2	----	----	26.1/ 79.3	0.53/ 0.65
BioUPR3_Sty	32.7	-84.3	-24.6	21.8	0.51
BioUPR3_Sty/MetVan	24.1	-85.9	-19.0	23.18	0.68
BioUPR3_MetVan	----	----	----	-25.2	0.35
BioUPR3_MetSob	----	----	----	-28.3	0.19

Looking at the results presented in Table 5.4, it is possible to observe that, at 25 ºC, for both UPs formulations the partial replacement of Sty by MetVan does not influence significantly the elastic properties of the materials. On the other hand, for Resipur, a significant decrease in E' is observed when Sty it totally replaced by the new UMs. As mentioned before this result might be related with the low gel content of the samples. The moieties that compose the soluble fraction can act as plasticizers, reducing the E' value. In what concerns the T_g values, it is observed that the partial replacement of Sty by MetVan did not translate in a significant alteration of the T_g. In turn, the total substitution of Sty by MetVan or MetSob led to noticeable changes in the T_g value. A decrease of *ca.* 14 ºC from Resipur_Sty to Resipur_MetVan is observed, and this result might be justified by the presence of a more voluminous lateral group in the case of MetVan (aromatic group with a pendent methoxy group)[21,27], which increases the free volume between the polymer chains in the network. In the case of Resipur_MetSob, two distint T_g can be identified. The higher T_g might correspond to crosslinked domains having a high concentration of Sob moieties (voluminous groups that restricts the movements of the polymer chains and existence of free –OH groups that can establish H-bonds with the ester groups), whereas the lower T_g can be tentatively assigned to domains composed mainly by crosslinked UP moieties.

In what concerns the Bio_UPR3, it is possible to see that the T_g from the BioUPR3_Sty does not differ significantly from the BioUPR3_Sty/MetVan. However, the use of MetVan and MetSob as the UM led to a substantial decrease of the T_g. In this case, it seems that the fact of the resins have a high content of soluble fraction (that may act as plasticizer) overlaps the existence of the bulky side groups that would contribute to a restriction of the movements.

5.5 Conclusions

The aim of this chapter was to study the ability to partially or totally replace Sty by new biobased UMs, in UPRs formulations. The novel biobased UMs were successfully prepared from the reaction of Van or Sob with MeAn, yielding MetVan and MetSob. Both UMs showed a significantly lower volatility when compared with Sty. Nevertheless, the viscosities of the biobased UMs/UPs mixtures, at 25 ºC, were considerably higher than those obtained for the Sty/UPs mixtures. This result can be related with structural particularities of the developed UMs.

The UPRs obtained from the reaction of the UPs with the biobased UMs showed between 20-30 % of soluble fraction with the crosslinked network. This fact can be ascribed to the high viscosity of the mixtures that impair an effective crosslinking reaction to take place. Regarding the thermomechanical properties, the total replacement of Sty by the biobased UMs led to UPRs with inferior properties. Nonetheless, in the formulations in which Sty was partially replaced by MetVan no substantial differences in the thermomechanical properties were observed.

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CHAPTER 6 – Preparation of Novel Unsaturated Polyester Resins from Citric And Tartaric Acids with 2-Hydroxyethyl Methacrylate

6.1 Abstract

A new family of unsaturated polyester (UPs) from citric acid (CiAc) or tartaric acid (TaAc) was successfully synthesized in this work by bulk polycondensation. The use of ATR-FTIR and ^{1}H NMR spectroscopies confirmed the chemical structure of the unsaturated polyesters (UP) and showed that no crosslinked structures were obtained. The UPs also showed molecular weights and polydispersity values in the typical range for these type of materials. The totally biobased UPs were next crosslinked with 2-hydroxyethyl methacrylate (HEMA), used as an alternative to styrene, and new UPRs were obtained. These novel resins showed to have similar hydrophilic nature and thermomechanical properties. The new UPRs also presented a thermal stability, swelling behavior and *in vitro* hydrolytic degradation tests very dependent on the used saturated acid. The overall results showed that these novel UPRs proved to be good candidates for biomedical fields.

6.2 Introduction

In recent years, the replacement of fossil materials by monomers from renewable resources has been increasingly explored and significant developments have been achieved[1-9]. Citric acid (CiAc) is a widely available and inexpensive tricarboxylic acid, which is a common metabolite of plants and animals. With an annual production of *ca*. 9 million tons, CiAc has been industrially produced by a fermentation process with *Aspergillus niger* strains, using molasses, rapeseed oil, corncobs and brewery wastes as substrates[10,11]. This acid is suitable for numerous applications, such as a preservative, pH regulator, antioxidant, flavor enhancer, plasticizer and stabilizer[10-12]. In addition to CiAc, tartaric acid (TaAc) is also an abundant and low-cost dicarboxylic acid, with two pendant hydroxyl groups. This natural molecule is present in a variety of fruits and in the grape juice fermentation. Being an important by-product of the wine industry, this acid is currently obtained by fermentation processes and is mainly used in food (as preservative, antioxidant and taste enhancer) and pharmaceutical industries[13-16]. Taking into account the interesting characteristics of these two carboxylic acids, their use in the preparation of polymers, namely polyesters, for biomedical applications (e.g., scaffolds for tissue engineering and drug delivery systems) have been widely explored[17-21]. As an illustrative example, Chandorkar *et al.*[22] developed polyesters from CiAc, SeAc, rinoleic acid (RAc) and *D*-mannitol (*D*-MA), that presented interesting mechanical properties (such as elastic modulus and tensile strength) and very promising *in vitro* degradation and cytocompatibility results. These materials demonstrated a huge potential for scaffolds fabrication and also for drug delivery systems. TaAc-based polyesters have also been reported in literature, finding applications mainly for drug delivery systems[13,23]. Some interesting studies in this field include the works of Dhamaniya *et al.* who used TaAc and its derivatives on the development of polyesters using different approaches: polyesters with pendant hydroxyl and lateral isopropylidene groups[24]; hydroxyl copolyesters from dimethyl 2,3-*O*-isopropylidene[25] and the synthesis of a variety of chain-coupled polyesters from TaAc[26]. The reported materials in the aforementioned works proved to be suitable for biomedical engineering.

The use of CiAc and TaAc in the field of polymer science field also has been exclusively done in the preparation of saturated polyesters. However, it is well known that the preparation of unsaturated polyesters (UPs) and unsaturated polyester resins (UPRs) from biobased monomers has been attracted considerable attention from the scientific community[27-29]. Particularly, in the last years, biobased UPs/UPRs have been explored in the preparation of materials for biomedical applications (e.g., scaffolds for tissue engineering)[30,31]. This fact is related with the myriad of structures and properties that can be achieved with these materials. UPRs can be processed by additive manufacturing techniques, enabling the preparation of tailor made 3D structures with very well defined structure and porosity. These properties are especially important and relevant in the context of tissue engineering, since they could have an effective impact on cell adhesion, differentiation and proliferation of cells [32].

In this chapter, a new class of biobased UPs were obtained for the first time by the bulk polycondensation of propylene glycol (PG), fumaric acid (FuAc) and CiAc or TaAc. It should be pointed out that all of these monomers are used in applications related with the cosmetic, food or pharmaceutical industry[10-15,33,34]. Moreover, the UPs were further crosslinked with 2-hydroxyethyl methacrylate (HEMA), a reactive solvent that has been amply used for preparation of polymeric materials for biomedical applications. The crosslinked networks were further characterized in terms of their gel content, thermomechanical properties, swelling capacity and *in vitro* hydrolytic degradation behavior.

6.3 Experimental Section

6.3.1 Materials

FuAc (99%), PG (99%), CiAc (>99%), phosphate buffered saline (PBS) tablets and tetrahydrofuran (THF, >95%) were purchased from Sigma-Aldrich. Potassium hydroxide solution (1 N, in ethanol) and HEMA (97%) were purchased from Acros Organic. Sodium azide (NaN_3, 99%) and TaAc (99%) were purchased from Panreac. Cobalt Octoate (CoO) was purchased from AGAMI, benzoyl peroxide (BPO, 97%) was purchased from Fluka, phenolphthalein was obtained from Riedel-de-Häen and hydroquinone (HQ, >99%) was purchased from Analar. Deuterated THF (THF-d_8, 99.5%) was purchased from Eurisotop. All the reactants were used as received, unless otherwise stated.

6.3.2 Synthesis of the UPs

The biobased UPs were synthesized by uncatalysed bulk polycondensation reaction between the unsaturated acid, the saturated dicarboxylic acid and the glycol. The monomers and the radical inhibitor HQ (0.1% of the total weight) were charged in a four head reactor equipped with a mechanical stirrer, a nitrogen inlet, and a condenser connected to a round-bottom flask. The polycondensation reactions were carried out according to the temperatures presented in Table 6.1. The end of the polycondensation reactions was set when the acid value (AV) reached a constant value (determined according to ISO 2114 – 00).

Table 6.1- Amount of reactants and temperatures used in the synthesis of the UPs.

Entry	n(PG) (mol)	n(FuAc) (mol)	n(CiAc) (mol)	n(TaAc) (mol)	t (h)		
					150ºC	160ºC	190ºC
1	52	15	33	----	----	2.5	----
2	52	14	34	----	3.5	----	----
3	53	14	33	----	5.0	----	----
4	55	14	33	----	5.5	----	----
5	55	13	34	----	8.0	----	----
6	55	13	----	34	8.0	*	----
7	55	13	----	34	8.0	----	6.0

* The AV value did not decrease.

6.3.3 Preparation of the UPRs

The UPs were dissolved in 32 wt.% HEMA. The initiator BPO (3 wt.%) and accelerator CoO (1 wt.%) were added under continuous stirring until a homogeneous mixture was obtained[35]. The formulations were cured in a Teflon mold (16 x 7 x 0.5 mm) at room temperature for 24 hours and post-cured at 80ºC for 3 hours, for the obtainment of UPRs[36,37].

6.3.4 Characterization Techniques

Chemical Structure Identification

ATR-FTIR analysis of UPs was carried out with a Cary 630 FTIR spectrometer. Data collection was performed with 4 cm^{-1} spectral resolution and 64 accumulations, in 650 and 4000 cm^{-1} wavenumber range.

^1H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer using a 5 mm TIX triple resonance detection probe, in THF-d_8, at room temperature. Tetramethylsilane (TMS) was used as the internal reference.

Molecular Weight Distribution

The molecular weight (M_n) and the polydispersity ($Đ$) of the biobased UPs were determined using high performance size exclusion chromatography HPSEC; Viscotek with a refractive index (RI) detectors. The column set consisted of one Viscotek Tguard column (8 µm), one Viscotek T2000 column (6 µm), one Viscotek T3000 column (6 µm) and one Viscotek

LT4000L column (7 µm), from Malvern (Malvern, UK). HPLC pump was set with a flow rate of 1 mLmin^{-1}. The system was also equipped with an online degasser. The tests were carried out at 30 ºC using an Elder CH-150 heater. The samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2 µm pore, before the injection (100 µL). Tetrahydrofuran (THF) was used as the eluent. Conventional calibration was done with narrow polystyrene standards (M_n (g.mol^{-1}) = 1980; 4290; 10050; 30300; 52220 and 96000).

Thermal Properties

The thermal stability of samples was evaluated by TGA, using a TA Instruments Q500 thermogravimetric analyzer (thermobalance sensitivity: 0.1 μ g). The equipment was calibrated within a temperature interval ranging from 25 ºC to 1000 ºC, at a heating rate of 10 ºC.min^{-1}, running tin and lead as melting standards. The samples were analyzed using open alumina crucible, in the temperature range 25 ºC to 600 ºC and at a heating rate of 10 ºC.min^{-1}, under dry nitrogen purge flow of 100 mL.min^{-1}.

The differential scanning calorimetry (DSC) studies were performed in a TA Instruments Q100 model, equipped with a RCS90 cooling unit. The heat flow and the heat capacity were calibrated 5 ºC.min^{-1} using indium and sapphire standards, respectively. The samples were analyzed in aluminum pans with an ordinary aluminum lid loosely placed. A heating rate of 5 ºC.min^{-1} and a dry nitrogen purge flow of 50 mL.min^{-1} were used in all measurements. The samples were heated at 5 ºC.min^{-1} from -80 ºC to 200 ºC, after performing a cycle in which the samples were heated from room temperature to 120 ºC and cooled down to -80 ºC to erase their thermal history.

The viscoelastic properties of the UPs and UPRs were measured by DMTA with a Tritec 2000 DMA. CiAc and TaAc-based UPs were analyzed in the single cantilever bending geometry using stainless steel material pockets. The measurements were carried out in a -150 °C to 200 °C temperature range, at frequencies of 1 and 10 Hz, using a heating rate of 5 ºC.min^{-1}. The properties of UPRs were analyzed with a Netzsch DMA 242D in the dual cantilever bending geometry. The analyses were carried out in a -150 °C to 200 °C temperature range, at frequencies of 1, 2, 5 and 10 Hz, using a heating rate of 2 ºC.min^{-1}.

The molecular weight between crosslinking (M_c) and the crosslink density (n) were calculated from DMTA data, according to the Equation 1[22,38]:

$$M_c = \frac{3\rho RT_{[T_g+50K]}}{E'_{[T_g+50K]}} = \frac{\rho}{n} \quad \text{(Equation 1)}$$

where ρ is the density of the crosslinked sample and R represents the universal gas constant (8.314 J/mol). The E' is the storage modulus determined in an equilibrium zone, specifically for a temperature at T_g + 50K.

Kinematic Viscosity

The kinematic viscosity of synthesized UPs was determined by Gardner- Holdt Bubble Viscometer. The sample is placed into a standard viscosity tube and is thermostated at 25 ºC. The viscosity of the sample is determined by comparison to the standard bubble viscometer tubes (or Gardner-Holdt tubes) with standard viscosity marked alphabetically, in which an air bubble rises with the same speed as it does in the tube of the sample being tested. The standard tube with the same viscosity as the sample has a letter that can be converted to the kinematic viscosity, in Stokes (St).[39] The viscosity of all polyesters was determined in a 50% solution by weight of the UP in 2-ethoxyethanol (adapted from [40]).

Gel Content

The degree of curing of UPRs was determined by the gel content test (according to ASTM D2765 - 16). The gel content was determined by Soxhlet extraction using THF as solvent. The samples were weighed and placed in the Soxhlet's extractor for 8 hours. After that, the samples were dried until constant weight. Gel content was calculated according to the Equation 2:

$$Gel\ Content = \frac{w_f}{w_o} \times 100 \qquad \text{(Equation 2)}$$

where w_0 and w_f represent, respectively, the weight before and after extraction.

Water Contact Angles

The water contact angles (WCA) were measured on the surface of biobased UPRs. The analyses were carried out in a Contact Angle System OCA, equipped with Dataphysics SCA20 software. For the measurements, a 10 µL drop of distilled water was dispensed, at a rate of 0.5 $mL.s^{-1}$, and the final WCA was determined as the average of four different drops deposition measurements.

Swelling Capacity

Dried UPRs, with a known weight, were immersed in 40 mL of water, at 37 ºC, until a swelling equilibrium be achieved. At regular intervals, the samples were taken out of the solution, its surface carefully cleaned with filter paper, and weighted. The procedure was repeated until a constant weight was reached. The swelling capacity was determined according to the Equation 3[31]:

$$Swelling\ Capacity\ (\%) = \frac{w_s - w_d}{w_d} \times 100 \qquad \text{(Equation 3)}$$

where w_s and w_d represent, respectively, the weight of dry samples before immersion and the weight of swollen samples. Two measurements were carried out for each UPR.

In Vitro Hydrolytic Degradation

These tests were carried out in PBS solution (pH=7.4, 0.01M), at 37 ºC, during 60 days. Dried UPRs, with a known weight, were immersed in the PBS solution and incubated at 37 ºC. At predetermined periods of times, the samples were removed from the solution and washed with distilled water. The samples were then dried under vacuum until constant weight. The degree of degradation was determined according to the Equation 4[31]:

$$Weight\ Loss\ (\%) = \frac{w_0 - w_t}{w_o} \times 100 \qquad \text{(Equation 4)}$$

where w_0 and w_t represent, respectively, the weight of UPRs before immersion and the weight of the samples after incubation for t days. Two measurements were carried out for each UPR.

6.4 Results and Discussion

6.4.1 Synthesis of UPs and their Chemical Structure Identification

In this work, new biobased UPs were synthesized by bulk polycondensation between a glycol, an unsaturated acid and one of two saturated acids accordingly to Figure 6.1. The reactions were carried out in the absence of any catalysts or toxic solvents, very important features for further application of these materials in the biomedical area[22].

To develop UPs with high biobased content, four biobased monomers were carefully selected for the polycondensation reactions. PG is recognized as the most common glycol used in the industrial synthesis of UPs and, currently, is already available from natural sources[5,41,42] and it is considered as a ‘Generally Recognized as Safe’ (GRAS) substance by the Food and Drug Administration (FDA) of the United States of America[34]. FuAc is a biobased source of double bonds, able to replace the most commonly used unsaturated anhydride, maleic anhydride, being also used in the food industry[33]. In turn, CiAc and TaAc are saturated acids presented in human metabolic cycles and in fruits, being non-toxic and inexpensive natural resources[18,20,24,26]. The polyfunctional structure of these monomers can also contribute to different properties of the materials, making them interesting raw materials for the development of a new class of biobased UPs.

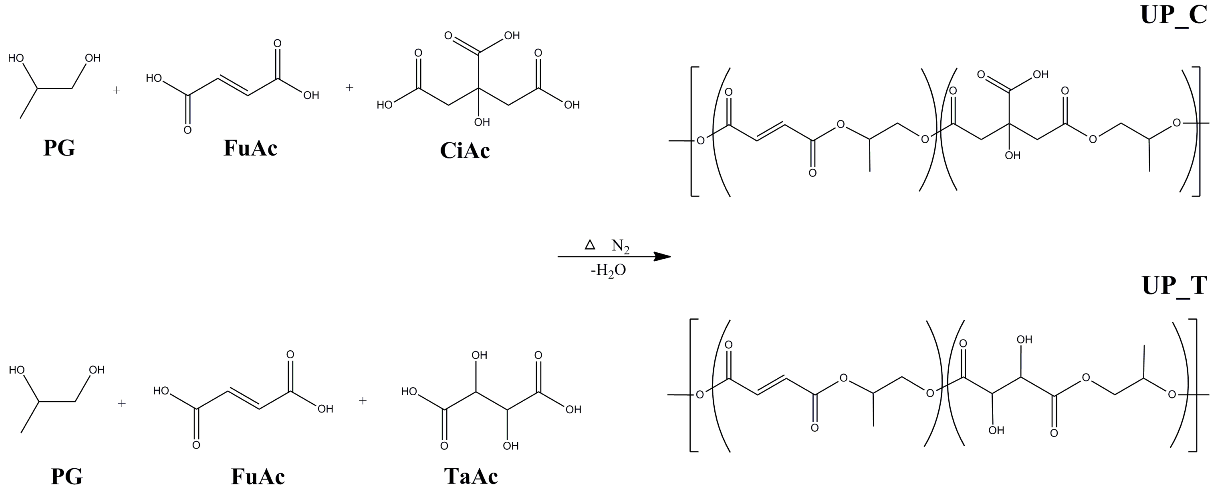

Figure 6.1- Synthesis of UPs based on citric acid (UP_C) and tartaric acid (UP_T).

Different formulations and different temperature of reaction were tested in the polycondensation reactions (see Table 6.1). The first set of experiments was conducted with CiAc (Entry 1 to Entry 5), that is known to be a very challenging monomer to be used in polycondensation reactions, since it is prone to suffer side reactions (dehydration and decarboxylation) at temperatures above 180 ºC[43]. Taking this into account, all the experiments with CiAc were conducted at temperature of 150 ºC or 160 ºC[17]. Different amounts of monomers were screened, but the only formulation that did not form a gel was that from Entry 5 (see Table 6.1). In order to confirm this particular result, the experiment of Entry 5 was repeated twice and similar results were obtained. In the case of TaAc (Entry 6 and 7), it was decided to perform the experience with the same amount of monomers that gave the best results for CiAc. Since no gelification occurred in this case, no further experiments were conducted with TaAc. It should be pointed out that, comparing the experiments conducted with TaAc, a higher temperature was applied in Entry 7 in order to achieve higher conversions and, consequently, a lower AV value. Henceforth, the formulations of CiAc (Entry 5) and TaAc (Entry 7) will be designated as UP_C and UP_T, respectively.

ATR-FTIR and ^{1}H NMR spectroscopies were used to evaluate the chemical structure of the synthesized UPs. Figure 6.2 presents the ATR-FTIR spectra of UP_C and UP_T. In the presented spectra it is possible to identify for both UPs the stretching vibration of the carbonyl group of the ester linkage (a)[44-46], (1750-1720 cm^{-1}), and a band in the region 1300-1100 cm^{-1} (b), related to the C-O stretching of the same group[21,24,47]. The band at *ca.* 1650 cm^{-1} (c) can be ascribed to the stretching vibration of C=C bond of FuAc[28,43]. The bands at *ca.* 2980, 2940 and 2880 cm^{-1} (d) are due to the vibrational modes of the CH stretching[20,46]. It is also possible to identify a band at 3460 cm^{-1} for the polyesters under study, corresponding to the stretching vibration of the –OH group[45,46,48].

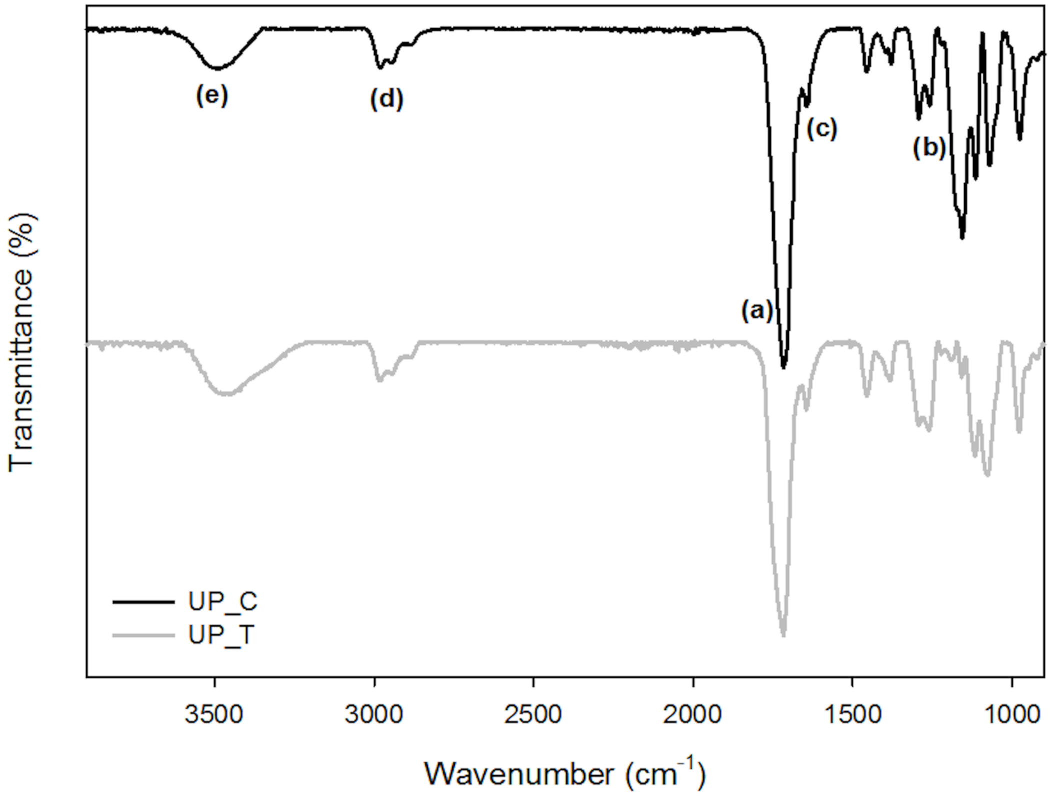

Figure 6.2- ATR-FTIR spectra of UP_C and UP_T, respectively.

The ^{1}H NMR spectra of the UPs are presented in Figure 6.3. In both UPs, it is possible to identify the peaks belonging to the -CH_3 protons of propylene glycol (PG), at 1.25-1.40 ppm (d)[28]. The peaks of the -CH_2 protons from this diol are also seen at 4.0-4.4 ppm (b) and the -**CH** proton is observed at around 5.20 ppm (c)[28,49]. Moreover, other resonances that correspond to this glycol (peaks b', c' and d') show the presence of PG terminal group, confirming the presence of chain ends for both UPs. The peaks between 6.5 and 7.0 ppm (a) correspond to the protons of the double bonds of FuAc moieties[50]. As expected, the spectra exhibit distinct peaks for saturated dicarboxylic acids. In the spectrum of UP_C, it is possible to see the -CH_2 protons of the CiAc at 2.6-2.9 ppm (e)[18,22,48]. In this spectrum, the protons of the unsubstituted -O**H** of CiAc at 3.4-3.6 ppm (f)[18,22,45,48] can also be observed. For UP_T, it is also present the signals of unsubstituted -O**H** of TaAc in the same region[48]. Furthermore, the peaks of the -C**H** protons belonging to this saturated acid are identified at 4.4-4.8 ppm (e)[48]. It is worth to be mentioned that it is possible to identify the resonances corresponding to the –OH groups at 3.4-3.6 ppm (f) for both UP_C and UP_T[29] (see Figure 6.3), indicating that the UPs have a linear structure.

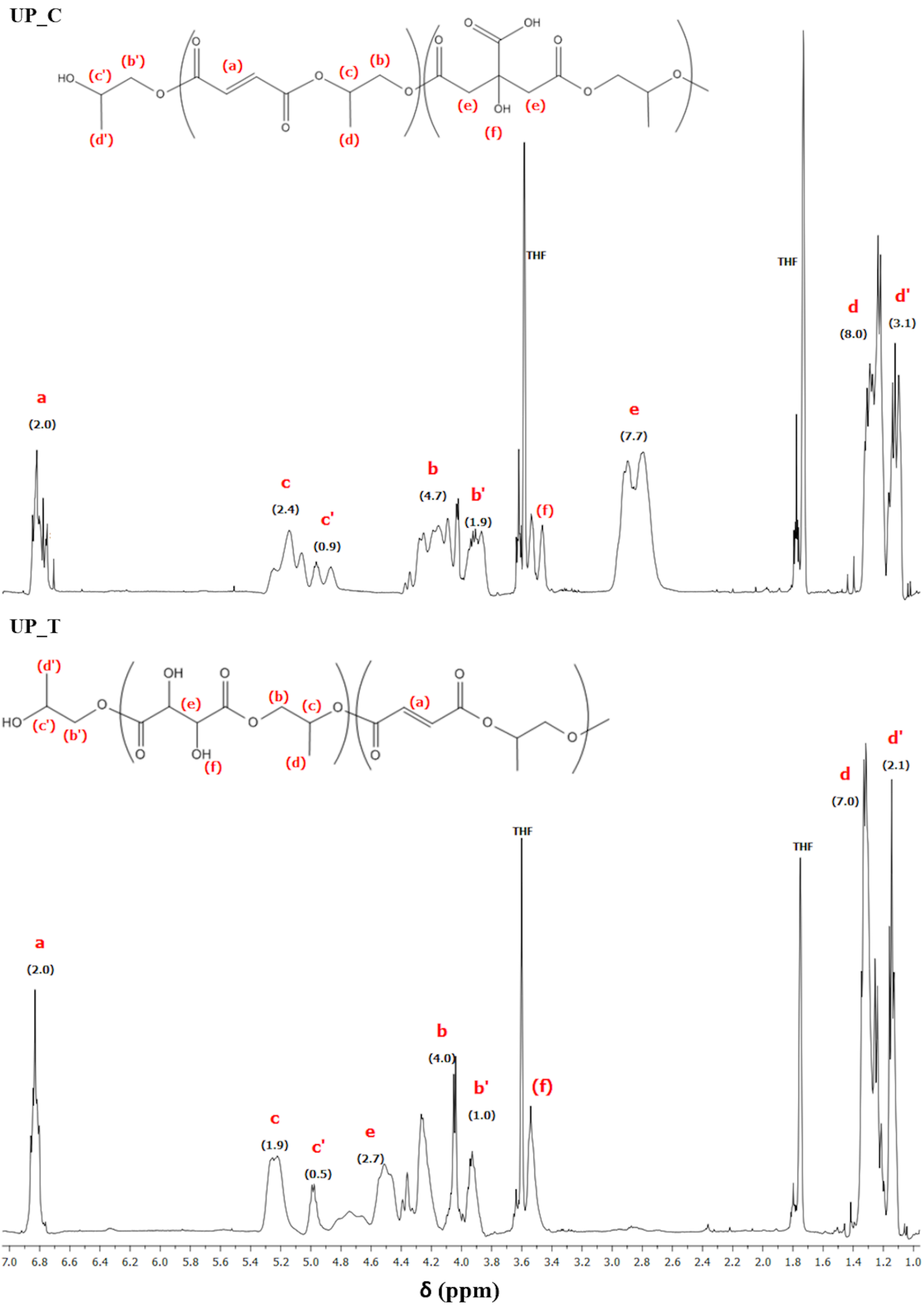

Figure 6.3- ^{1}H NMR spectra of UP_C and UP_T. The integration area of the peaks is indicated in brackets.

The relative molar amount of the incorporated monomers in the UPs structure was evaluated taking into account the integral values of the peaks corresponding to the different monomers in the structure. The results are shown in Table 6. 2.

Table 6. 2- Comparison between the feed amounts of the different monomers and their relative percentages in the final structure of the UPs, determined by ^{1}H NMR.

Formulation	Composition	Initial Molar Ratio (%)	Final Molar Ratio (%)
UP_C	CiAc/FuAc/PG	34/13/55	29/15/56
UP_T	TaAc/FuAc/PG		25/19/56

The values obtained for the amount of monomers incorporated in the polymeric chains (Table 6. 2) suggest that the initial amount fed was quantitatively incorporated. This result is particularly interesting and shows that with the proper reaction conditions, not only gelification was avoided, but also a quantitative incorporation of CiAc and TaAc was achieved. Unfortunately, it is not possible to compare the results of incorporation obtained in this work with data from literature, because the available reports do not present this specific analysis.

Table 6.3 summarizes the reaction times, AV, M_n, *Đ* and the Gardner viscosity values of the UPs.

Table 6.3- Molecular weight and polydispersity of the synthesized UPs.

Formulation	AV (mg KOH.g^{-1})	M_n (g.mol^{-1})	*Đ*	Viscosity (St)
UP_C	49	1945	1.31	8.84
UP_T	38	1290	1.64	5.25

Typically, the UPs used in the preparation of commercial UPRs have AV ranging from 25 to 50 mg KOH.g^{-1},[51] which is in the interval of values determined for the biobased UPs prepared in this work. The M_n and *Đ* values obtained for the UPs are in the range typically obtained for UPs that are used, for instance, in additive manufacturing techniques[32,52,53]. The value of *Đ* <2 suggest that the UPs have a linear structure, as also suggested from the ^{1}H NMR analysis (Figure 6.3).

6.4.2 Thermal Properties of UPs

The thermal stability of the UPs was evaluated by TGA, in a 25-600 °C range, under nitrogen atmosphere. Figure 6.4 presents the thermogravimetric curves for the UPs under study.

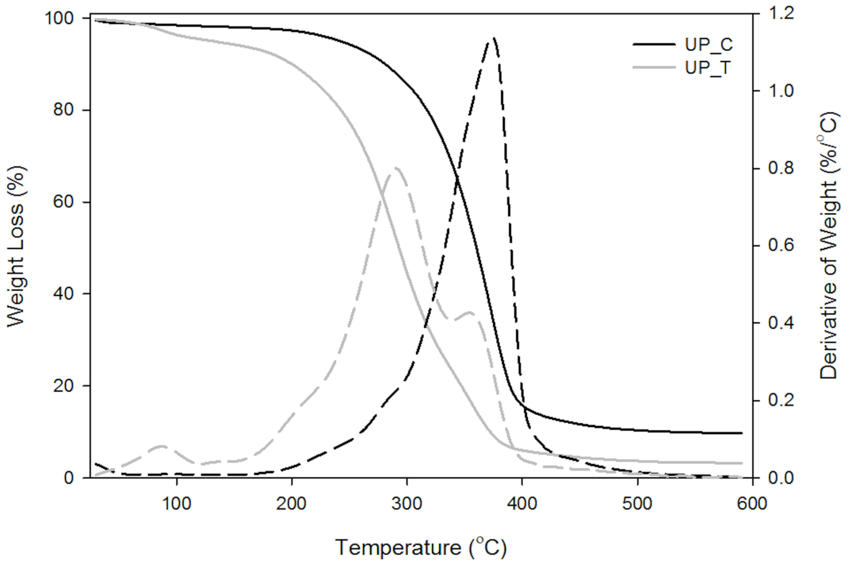

Figure 6.4- Thermogravimetric curves of UP_C and UC_T (___ TG and _ _ _ DTG).

As can be observed, the UPs have different weight loss profiles, as can be easily observed in the DTG curves. UP_C presents a weight loss with a single stage (300-400 ºC), with a small shoulder for temperatures between 200-300 ºC. UP_T, in turn, evidence a small degradation stage at temperatures between 30 ºC and 100 ºC (~ 4%), that might correspond to the evaporation of residual moisture, and two weight loss stages (between 260-310 ºC and 350-360 ºC). The difference between the weight loss profile of samples might be related with their M_n and $Đ$ values (Table 6.3). UP_T starts to degrade earlier as it is composed of oligomer chains of lower molecular weight. Nevertheless, this dissimilarity in thermal stability can also be related with structural differences (presence of CiAc *vs* TaAc) between the UPs cannot be totally ruled out. Unfortunately, it was not possible to found out in the related literature any explanation regarding this issue.

UPs' thermal events below degradation temperature were evaluated in more detail by DSC and DMTA. Figure 6. 5 represents the heat flow curves of both UPs.

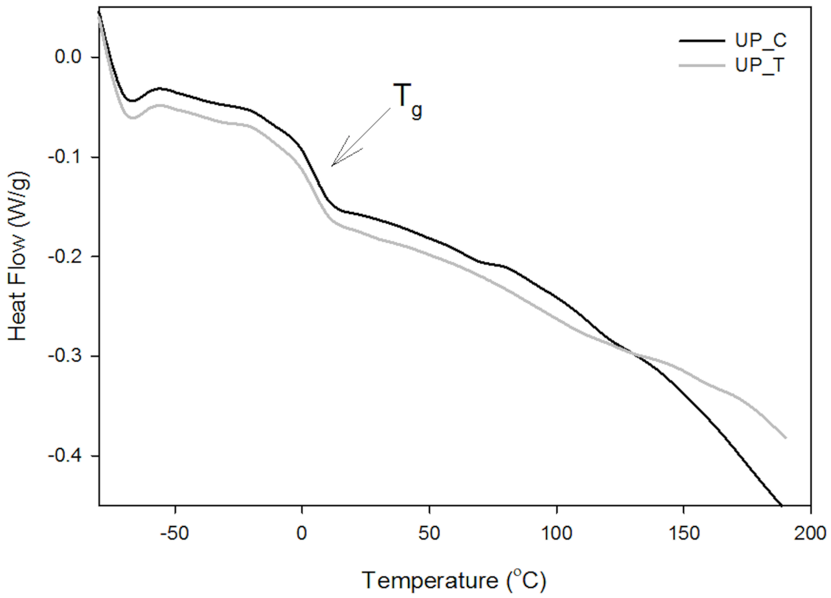

Figure 6. 5- Heat flow curves (from the second heating cycle) of the UPs under study.

The heat flow curves (see Figure 6. 5) of both UPs only present a thermal transition in the studied range of temperatures that is attributed to the T_g. According to these results, as expected, both UPs have amorphous nature, with no crystallization or melting events. Sarkar *et al.*[20] and Thomas *et al.*[21] observed the same pattern in polyesters derived from CiAc.

Table 6.4 presents the values of T_g obtained from DSC and DMTA.

Table 6.4- T_g of the biobased UPs obtained from DSC and DMTA.

Formulation	T_g (°C)	
	DSC	DMTA
UP_C	9.75	21.23
UP_T	5.61	11.40

Regarding the results summarized in Table 6.4, some differences in the T_g values can be observed, which can be explained by the composition of the UPs. In both techniques, UP_C showed the highest T_g value. This fact is related to the presence of strong intermolecular interactions from CiAc that reduce the molecular segmental movements and, consequently, increase the T_g of the polymer. Hazarika and Karak[45] observed the same pattern for their CiAc-based polyesters.

6.4.3 Development and Characterization of UPRs

The successfully synthesized UPs present in their backbone double bonds that can be used for radical crosslinking in the presence of a reactive solvent, HEMA. In fact, some authors have recently report the use of this monomer, as alternative to styrene, for the preparation of UPRs to be used in biomedical applications due to its low toxicity and high hydrophilicity, favorable to cell culture[31,55].

Table 6.5 presents the gel content and WCA values for the obtained UPRs.

Table 6.5- Gel content and WCA of the resins.

	Gel Content (%)	WCA (°)
UPR_C	84.1	63.00±0.85
UPR_T	65.3	56.55±0.64

The values of gel content of the two UPRs are significantly different, with the UPR_T exhibiting the lowest value. Both UPRs are obtained from the crosslinking reaction of the respective UPs with HEMA. In turn, UP_T has a lower gel content probably due to a high content of chains with low M_n.

In what concerns the WCA, it is possible to see that both UPRs have WCA values clearly below 90º, meaning that they have a hydrophilic nature. This result is not only due to the presence of the CiAc and TaAc, but also due to the presence of HEMA. It should be also pointed out that the hydrophilic nature of the UPRs is desirable, for instance, in applications related with the biomedical field, since hydrophilic materials allow a better interaction with cells, protein deposition, biological response of the materials, having also an important impact on the materials' degradation rate[20,21,24,47,55].

- *Thermomechanical Properties Of The UPRs*

The thermomechanical properties of the UPR_C and UPR_T were studied by DMTA, at two frequencies (1, 10 Hz), in a temperature range from -150 to 200 ºC. The T_g of the UPRs was determined from the maximum of the tan δ curve, at 1 Hz. The DMTA traces of the UPRs, at 1 Hz, are presented in Figure 6.6.

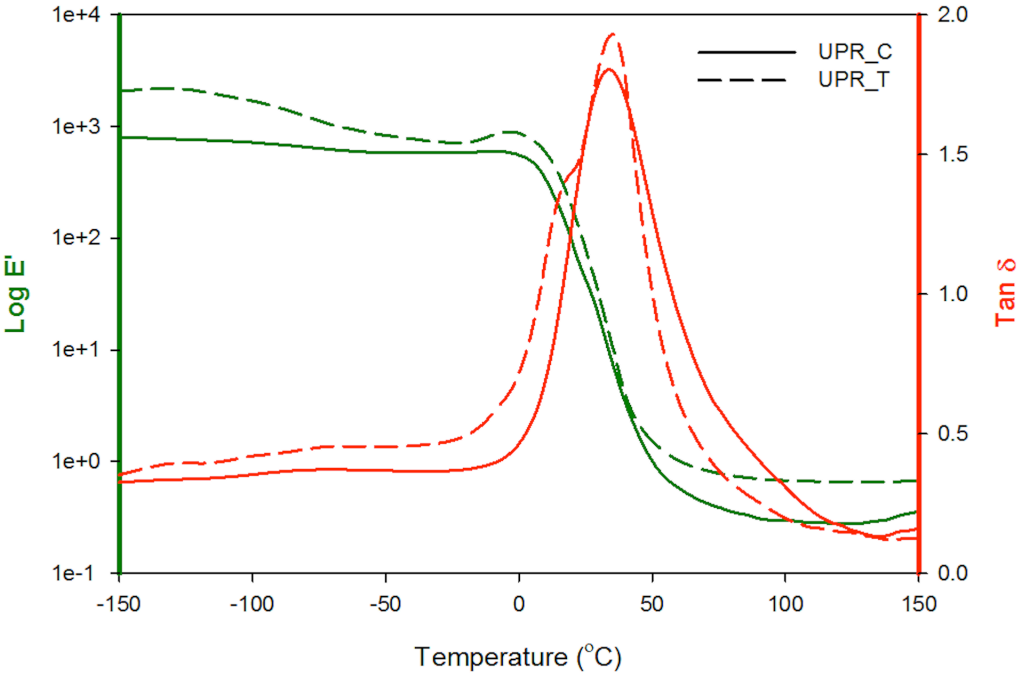

Figure 6.6- DMTA traces of the CiAc and TaAc-based UPRs in terms of E' and tan δ.

According to Figure 6.6, it is possible to observe that despite the differences in the gel content of the samples, the thermomechanical properties of both samples are similar. In the glassy region the UPR_C is slightly less rigid than the UPR_T. This trend is also observed for high temperatures, in the rubbery plateau. As expected, in the glass transition region, a sharp decrease in the E' is observed for both resins. Moreover, in the same temperature range, a peak in tan δ curve is expected. According to the tan δ traces, it is possible to identify at high temperatures the α transition, corresponding to the T_g of the resins, which is related to the vibration of the UPRs' main domains. Both resins present a very similar T_g values (34.2 ºC and 35.0 ºC for UPR_C and UPR_T, respectively) but an additional shoulder can also be observed for UPR_T. This result indicates that within the crosslinked network there are two different phases that initiate their segment motion at different temperatures. Regarding the values of E' at 37 ºC (average biological temperature), UP_C and UP_T have values of 5 MPa and 2 MPa, respectively. These values are in the same line of those reported by Nuvoli *et al.*[56], for crosslinked poly(diol citrate)s. For crosslinked polymers based on TaAc, no information regarding the typical E' value was found in the literature.

The DMTA can also be used to infer about the crosslinking density of a given sample using the theory of rubber elasticity[57]. From the DMTA data it is possible to determine the M_c, that corresponds to the molecular weight between entanglements or cross-link sites, and the *n,* corresponding to the crosslinking density (Table 6.6).

Table 6.6- M_c and crosslinking density of the resins.

	M_c (kg/mol)	n (mol/m^3)
UPR_C	13.41±2.3	76.92±3.5
UPR_T	17.71±2.0	41.73±0.2

According to the results presented, it is observed that UPR_T has lower *n* and a higher M_c value than those observed for UPR_C, indicating that this UPR_T has a looser crosslinked network. This result might be due to the presence of segments of very low molecular weight (UP_T has a higher *Đ* than UP_C), that prevent the close packaging of the chains, impairing an effective crosslinking (both chemical and physical) to take place. This feature is particularly relevant for the degradation profile of the samples. In principle, samples with lower *n* values will allow an easy penetration of the degradation medium in the crosslinked network, contributing to a higher degradability of the materials.

- *Swelling Capacity of the UPRs*

The swelling capacity of the resins was evaluated in water, at 37 ºC, until the swelling equilibrium was reached (Figure 6.7).

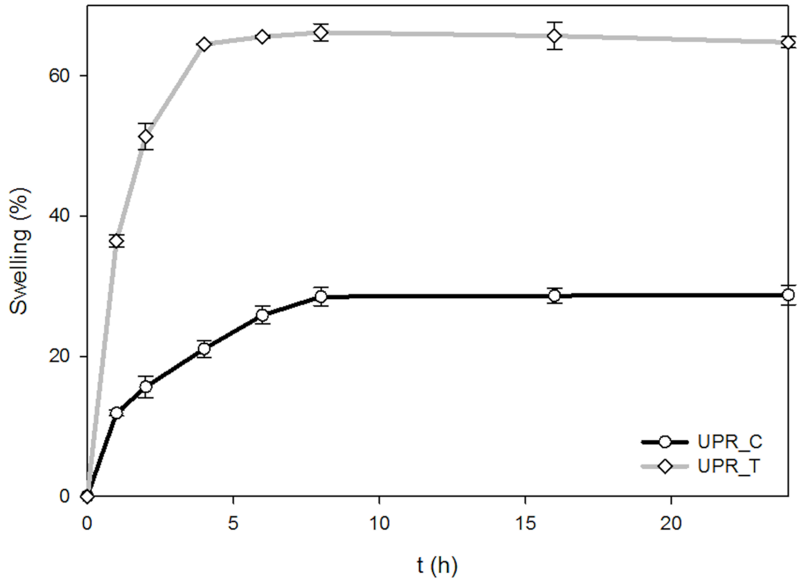

Figure 6.7- Swelling behavior of the UPRs.

As can be seen in Figure 6.7, the resins reached their swelling equilibrium approximately 7 hours after immersion. These results were expected due to the presence of pendant hydrophilic functionalities in the structure of CiAc and TaAc (carboxylic and hydroxyl groups)[18,22]. Comparing the swelling capacity of the UPRs, UPR_T presents a maximum swelling degree of 60 %, whereas for UPR_C, the value obtained was 30 %. In addition, this resin also reaches its swelling equilibrium earlier. This behavior can be ascribed to lower crosslinking density of UP_T when compared with UP_C (see Table 6.6). UPRs with low crosslinking density present looser crosslinked networks and, consequently, the water has less difficulty to penetrate in the network.

- *In Vitro Degradation Of The UPRs*

The *in vitro* hydrolytic degradation behavior of the UPRs was studied in PBS, 37 ºC, pH= 7.4, for 60 days. The degradation of each sample was evaluated by weight loss measurements over the immersion time. Figure 6.8 shows the weight loss profile of the UPRs.

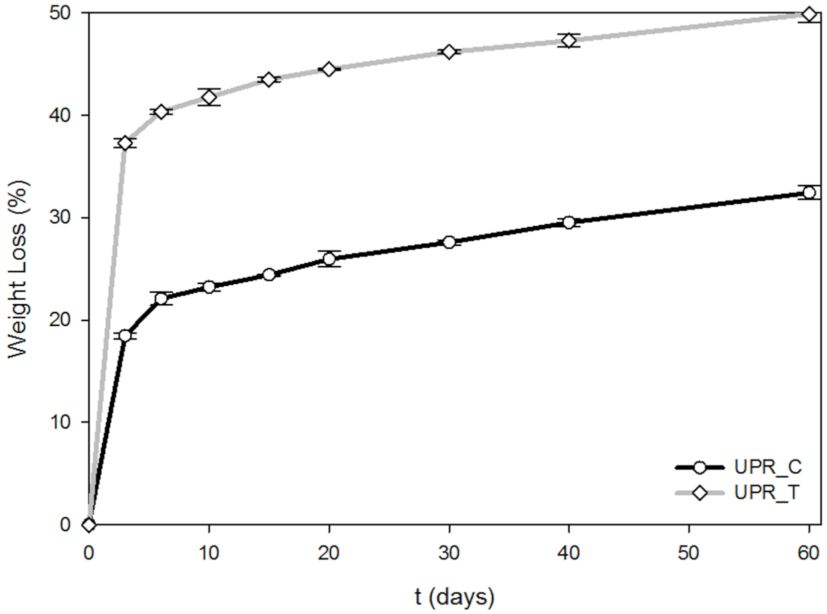

Figure 6.8- Weight loss profile of UPR_C and UPR_T.

Globally, a continuous increase of the weight loss with time is observed for both resins. From Figure 6.8, it is possible to observe that both samples present a significant weight loss just after 3 days of immersion: *ca.* 38 % for UPR_T and *ca.* 20 % for UPR_C. This value of weight loss is very similar to the amount of soluble fraction present in the resins (16 % for UPR_C and 35 % for UPR_T, see Table 6.5 of gel content). Thus, this initial weight loss might be attributed to the migration of the species that are not part of the crosslinked network. Despite the initial release of such moieties, it is not expected the occurrence of an acute cytotoxic effect, since all the monomers employed in the synthesis are safe to be used in applications for human contact (*e.g.*, food preservatives, cosmetics, devices for biomedical applications). After this initial weight loss, both UPRs lose weight in a steady way. After the

60 days of immersion in the medium, the total weight loss was 50 % and 30 % for UPR_T and UPR_C, respectively. UPR_T has the lowest *n* and highest M_c values (Table 6.6) allowing the degradation medium to penetrate more easily in the crosslinked network, and hydrolyze the ester bonds. This fact justifies the higher value of weight loss observed for this UPR.

6.5 Conclusions

In this chapter, the synthesis of novel fully biobased UPs with CiAc and TaAc was successfully accomplished. After being synthesized by bulk polycondensation, without any catalyst, the new UPs were directly crosslinked with HEMA through thermally-induced radical polymerization. A detailed study of the UPs' structures was carried out by FTIR and ^{1}H NMR spectroscopies. The UPs revealed to have an amorphous nature and T_g values that are dependent on their composition.

Regarding the UPRs, the WCA analysis showed that the resins presented a hydrophilic nature, which is a mandatory requirement for a good interaction with cells. Some differences were observed in the gel content values, being the lowest value obtained for UPR_T. This UPR also showed a higher swelling degree and higher weight loss value when compared with UPR_C. These results are explained by the lowest crosslinking density of UPR_T when compared with UPR_C. Both UPR_C and UPR_T presented very similar thermomechanical properties.

Taking into account the nature of the monomers and the overall properties of the developed UPRs, one can anticipate its application, for instance, in additive manufacturing techniques to prepare scaffolds for biomedical applications.

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CHAPTER 7 – Final Remarks

7.1 Conclusions

In the last decades, growing attention has been paid to environmental and sustainability advantages involving the preferential use of monomers from renewable resources. One of the major challenges in polymer science remains in the synthesis of materials making use of building blocks from renewable resources, whose properties are at least similar or even better than those presented by fossil-based materials. UPRs, due to their interesting properties, have been one of the families of polymers in which the use of biobased monomers have been highly explored. However, in the works presented in the related literature, the developed UPRs still do not have the suitable characteristics to replace their fossil-based counterparts.

In this work, a set of UPRs, making use of renewable building blocks, were prepared and some of them presented very interesting characteristics aiming to replace some of their fossil-based counterparts.

Novel partially biobased UPs were prepared by azeotropic polycondensation, following the industrial procedures, and were subsequently crosslinked with Sty (Chapter 2). The properties (e.g., gel content, thermal stability, shrinkage and thermomechanical behavior) presented by the UPRs were very similar to those of the commercial resin, indicating that the partial replacement of fossil-based by biobased monomers did not jeopardize the overall performance of the materials. One of the UPRs developed in Chapter 2 was produced at the industrial scale, being already a commercial product.

Taking into account the interesting results obtained in Chapter 2, in the Chapter 3 fully biobased UPs for further crosslinking with Sty were developed. The UPs were prepared by bulk polycondensation, a more environmentally friendly reaction process when compared with the azeotropic polycondensation. Different biobased monomers were selected in order to obtain BioUPRs with characteristics as similar as possible to those of a commercial resin (Resipur®). The properties of the fully biobased UPs were evaluated and revealed that their thermal stability and T_g values could be easily tailored by varying the monomers in the formulation. In turn, the obtained UPRs were characterized by gel content values, surface hydrophobicity and thermal stability that were very similar to that of Resipur®. In addition, one of the new UPRs presented very close stiffness and damping profiles to the commercial resin and showed to be a potential candidate for scale-up and industrial application. Thus, it was proved that, with the judicious combination of different biobased monomers, it is possible the development of an UPR able to compete with a petroleum-based UPR.

In a different approach (Chapter 4), soybean and coconut oils were combined with some of the biobased monomers used in the aforementioned Chapters for the development of a new class of vegetable oil-based UPRs with high “green” content. Both thermal stability and thermomechanical properties of the UPRs proved to be highly dependent on the chemical composition of the formulations.

The results obtained in Chapter 2, Chapter 3 and Chapter 4 showed the possibility to combine different biobased monomers to tailor the properties of the UPs that, after crosslinking reactions, led to UPRs able to compete with the commercial resins. However, the use of Sty as the UM to obtain UPRs also poses some environmental concerns, related with its volatilization during the curing process. Thus, it is of prime importance the development of new UPRs making use of UPs based on renewable building blocks, and UMs with a significant lower volatility than Sty, that also bear the ‘green stamp’.

In this line, in Chapter 5, two biobased materials (vanillin and sobrerol) were chemically modified with methacrylate moieties and were used to replace Sty in a commercial UPR and in a biobased formulation developed in Chapter 3, characterized by the lowest viscosity of all UPs. Both UMs presented low volatility but, when dissolved with the UPs, formulations with high viscosities were obtained. Since the modified vanillin (MetVan) was solid at room temperature, this UM was also used in a mixture with Sty. After crosslinking, the new UPRs presented lower gel content than those prepared only with Sty. However, the thermal stability of the samples was not greatly affected by the replacement of Sty by the biobased UMs. It is worth to note that promising thermomechanical properties were achieved when Sty was partially replaced with MetVan.

Finally, in a different vein, fully biobased UPs from CiAc and TaAc were synthesized, by bulk polycondensation, and afterwards crosslinked with HEMA. In what concerns the gel content values, the lowest value was observed for the UPR with TaAc (UPR_T). Both UPRs presented hydrophilic surfaces. In addition, UPR_T was also characterized by higher values of swelling capacity and *in vitro* hydrolytic degradation, which could be related to their low crosslinking density. The data from the DMTA showed that the elastic modulus is in the same range of those reported for the modulus of tendon or cartilage. Thus, the UPRs could be used for instance in the development of scaffolds for tissue engineering.

In summary, this PhD work allowed the development of new biobased UPs and UPRs with the "green stamp" and with high performance properties. It was also demonstrated that these properties could be manipulated by changing the composition of the polyester to find the perfect balance between the structure and the thermomechanical properties of the materials.

7.2 Future Work

The results presented in this PhD thesis contributed significantly to the state of the art related with the development of UPRs from renewable building blocks. Nevertheless, several work possibilities remain to be explored and the following research topics are considered to be of particular relevance:

- To continue the optimization of polycondensation reactions through the use of more "greener" polymerization methods; the use of enzymes can be an interesting approach. In this field, the Lipase B from *Candida Antarctica* (CALB) appears as the most promising candidate and different formulations can be tested to afford UPs with different molecular weights and tunable characteristics.

- To continue the development of a new biobased monomer able to replace Sty. It will be interesting the selection of new monomers (e.g., tyrosol, menthol, resorcinol) and different modification approaches to find a new UM that combines low volatility, low viscosity, high reactivity and the ability to led to UPRs able to compete with the commercial ones.

- The preparation of UPs bearing pendant vinyl groups in their structure, able to self-crosslink in the absence of Sty. The vinyl groups could be introduced in the polycondensation step or, alternatively, they could be introduced by a post-polycondensation modification.

- The development of photoresponsive UPs based on cinnamic acid derivatives. In principle, these UPs will lead to crosslinked structures without the need of an UM.

Annexes

Annex A

Supporting information for:

Chapter 3- Going Greener: Synthesis of Fully Biobased Unsaturated Polyesters for Styrene Crosslinked Resins with Enhanced Thermomechanical Properties.

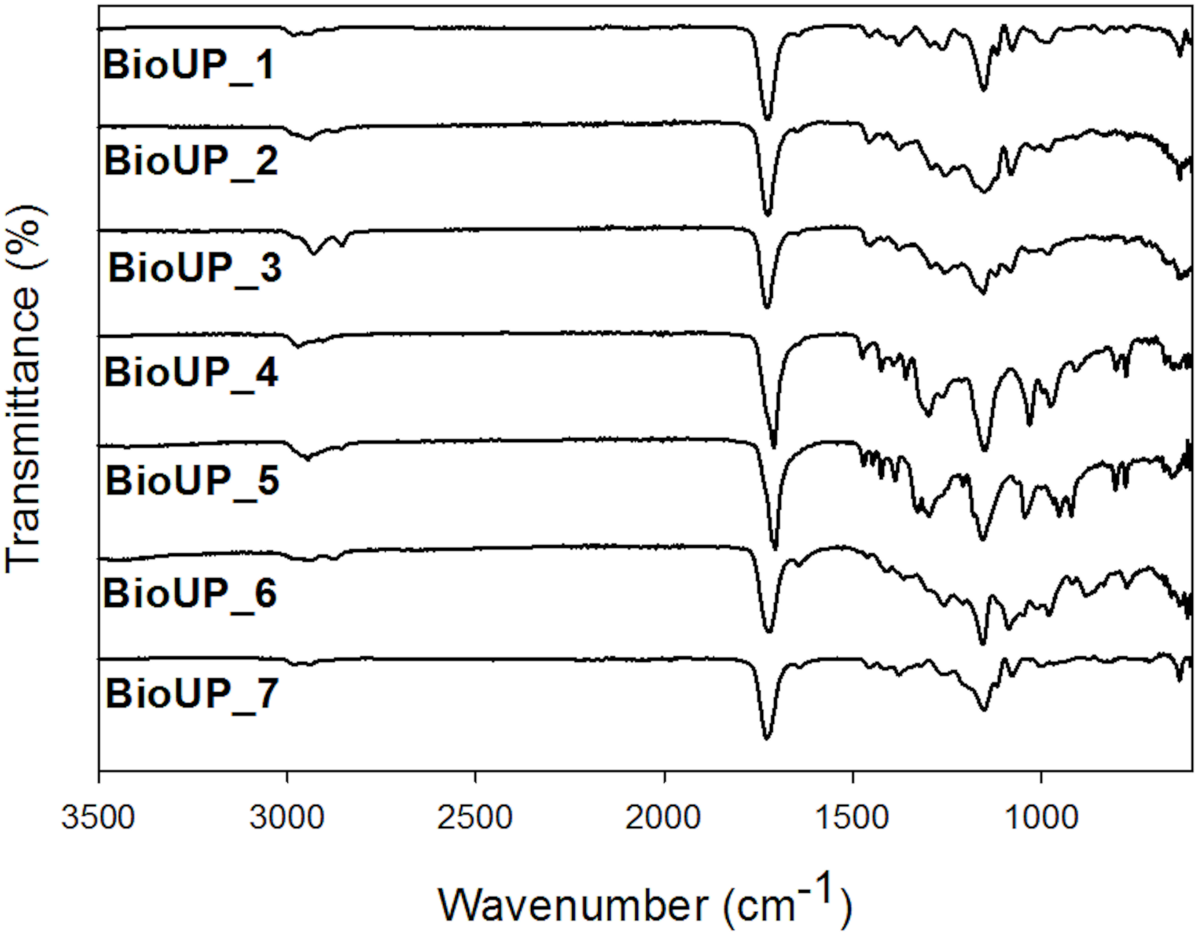

Figure A.1- ATR-FTIR spectra of biobased UPs.

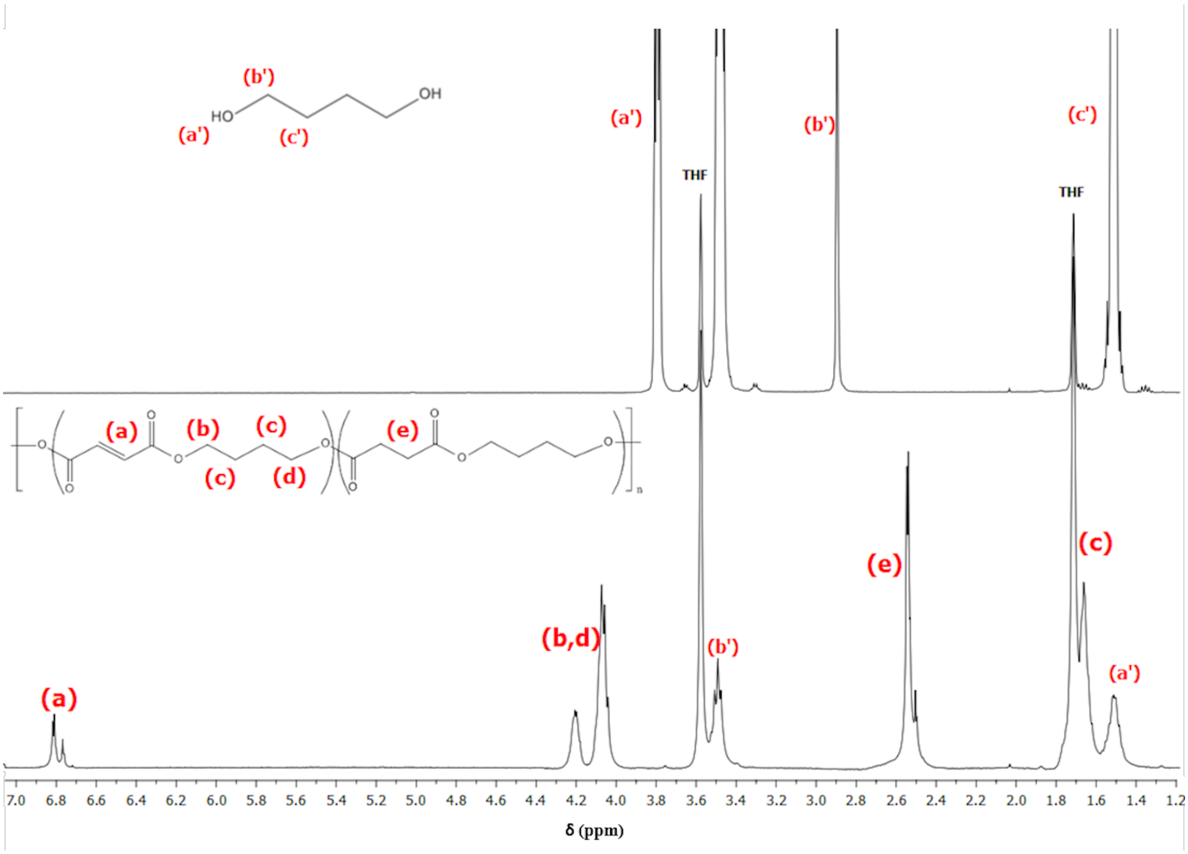

Figure A.2- ^{1}H NMR spectra of 1,4-butanediol and BioUP_5.

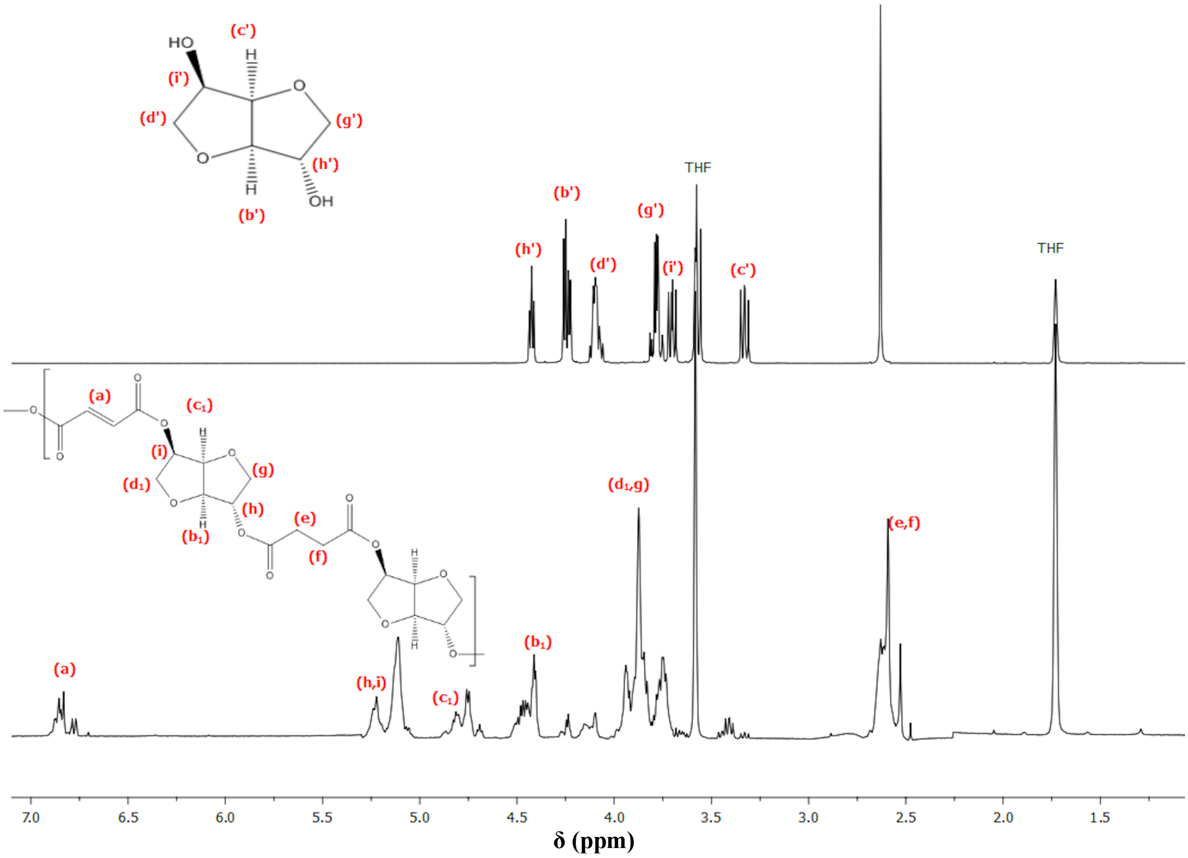

Figure A.3- ^{1}H NMR spectra of isosorbide and BioUP_6.

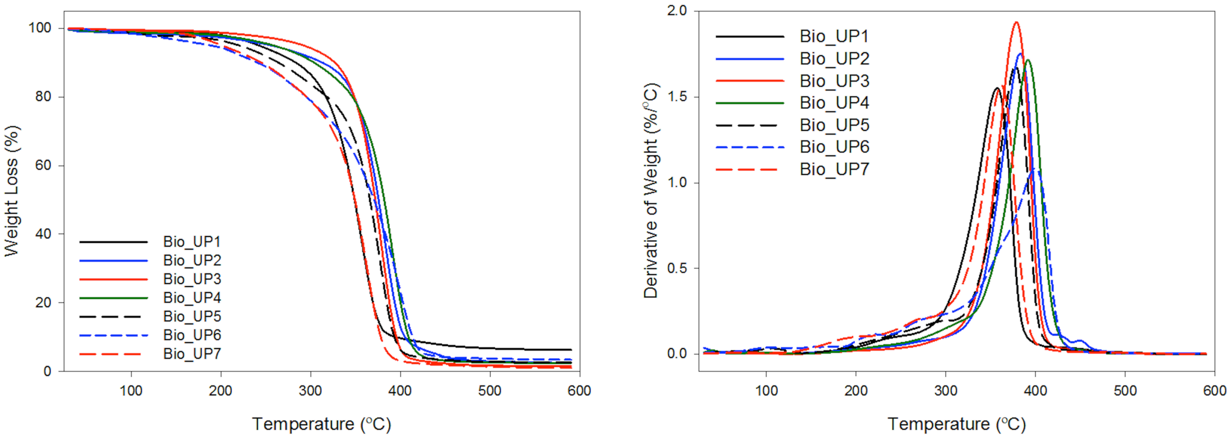

Figure A.4- Thermogravimetric curves of the biobased UPs.

Annex B

Supporting information for:

Chapter 5- Vanillin and Sobrerol: New Developments for Styrene Replacement in Unsaturated Polyester Resins

Table B. 1- Characteristic temperatures of the UPRs taken from the TGA. $T_{5\%}$: temperature corresponding to 5 % of mass loss; $T_{10\%}$: temperature corresponding to 10 % of mass loss; T_p: peak temperature (DTG curve).

	$T_{5\%}$ (˚C)	$T_{10\%}$ (˚C)	T_p (˚C)
Resipur_Sty	226	275	365
Resipur_Sty/MetVan	207	262	387
Resipur_MetVan	162	205	385
Resipur_MetSob	197	231	371
BioUPR3_Sty	279	331	390
BioUPR3_Sty/MetVAn	253	317	387
BioUPR3_MetVAn	196	239	388
BioUPR3_MetSob	153	209	388