

Going greener: Synthesis of fully biobased unsaturated polyesters for styrene crosslinked resins with enhanced thermomechanical properties

C. S. M. F. Costa^{1,2}, A. C. Fonseca^{2*}, J. Moniz¹, M. Godinho¹, J. F. J. Coelho², A. C. Serra²

¹Resiquímica - Resinas Químicas, S.A., Rua Francisco Lyon de Castro 28, 2725-397 Mem Martins, Portugal

²CEMMPRE, Department of Chemical Engineering, University of Coimbra, Pólo II, Pinhal de Marrocos, 3030-790 Coimbra, Portugal

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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 biobased UPs, 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 9837[®]). 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 (ItAc) presented very close thermomechanical properties compared to the commercial resin.

Keywords: thermosetting resins, biobased unsaturated polyester, thermomechanical properties

1. Introduction

Unsaturated polyester resins (UPRs) are currently one of the most important types of thermoset polymers in the industry. These polymers are well-known for their excellent balance between mechanical, electrical and chemical properties. They have found applications in diverse sectors, including: coatings, reinforcement materials in construction, marine and automotive industries [1–3]. The petroleum-based maleic anhydride (MA), phthalic anhydride (PhA) and PG are the most regularly employed monomers in the industrial synthesis of UPRs [4, 5]. 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 biobased UPRs (BioUPRs). In the

market, there are already a considerable number of available renewable monomers for the synthesis of UPs and UPRs [6–8] and, in the last years, some authors have focused their work on the development of UPRs partially based on these raw materials [4, 9–11]. The work of Gonçalves *et al.* [4] reports the preparation of UPRs for microstereo-thermal-lithography (μ STL), with a biobased content between 24 and 47 wt%. 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 a good thermal stability and a glass transition temperature (T_g) that has shown to be dependent on the formulation compositions. In another study, Fonseca *et al.* [12] prepared UPRs with high biobased content

*Corresponding author, e-mail: anafs@eq.uc.pt

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using the biobased monomers FuAc, ItaAc, SeAc, PG, 1,3-propanediol (PDO) and isosorbide (Iso). After the crosslinking reaction of biobased UPs 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.* [13] 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 biobased UPs 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 biobased content lower than 20 wt%.) and compared their properties with a fossil based commercial UPR. Sadler and co-workers 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[®] [5, 9]. 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 a 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 [14, 15]). It should be pointed out that, to the best of our knowledge, the synthesis of an UP totally based on renewable monomers has never been reported to afford UPRs (crosslinked with Sty) that have thermal and mechanical properties similar to those of a commercial UPR.

2. Experimental section

2.1. Materials

FuAc (99%), SeAc (94.5%), PG (99%), Iso (98%), Sty (>99%) and tetrahydrofuran (THF, >95%) were purchased from Sigma-Aldrich (St. Louis, USA). AdAc (>99%) and PDO (>98%) were purchased from TCI Europe (Zwijndrecht, Belgium). SuAc (99%), ItaAc (99%), BDO (>99%) and potassium hydroxide solution (1N, in ethanol) were purchased from Acros Organic (Geel, Belgium). Cobalt Octoate (CoO) was purchased from AGAMI (Moreira, Portugal), phenolphthalein was obtained from Riedel-Häen (Bucharest, Romania), methyl ethyl ketone peroxide (MEKP) from Algarplás (Sta Bárbara de Nexe, Portugal) and hydroquinone (HQ, >99%) was purchased from Analar (Radnor, USA). Deuterated THF (THF-d₈, 99.5%) was purchased from Eurisotop (Saint-Aubin, France). All the reactants were used as received, unless otherwise stated.

2.2. Synthesis of the UPs

The biobased UPs 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 (determined according to ASTM 109-01). Table 1 presents the molar amounts

Table 1. Reaction conditions for the synthesized biobased UPs

Formulations	$n_{\text{saturated acid}}$ [mol]	$n_{\text{unsaturated acid}}$ [mol]	n_{glycols} [mol]	t [h]
Resipur 9837 [®]	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 [mol]; t : reactions time [h]

of monomers, as well as the reaction times used in the different polycondensations.

2.3. Preparation of the UPRs

The biobased UPs (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 [16]. The formulations were cured in a Teflon mold (16×7×0.5 mm) at room temperature for 24 hours and post-cured at 80 °C for 3 hours [17, 18].

2.4. Characterization

2.4.1. Chemical structure identification

ATR-FTIR analysis of UPs was carried out with a Jasco FT-IR-4200 spectrometer, from Jasco Inc. (Easton, USA) 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 (Billerica, USA) using a 5 mm TIX triple resonance detection probe, in THF-d₈, at room temperature. Tetramethylsilane (TMS) was used as the internal reference.

2.4.2. Molecular weight distribution

The molecular weight and molecular weight distribution 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 (Malvern, UK). HPLC pump was set with a flow rate of 1 mL/min. The system was also equipped with an online degasser. The tests were carried out at 30 °C 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). THF was used as the eluent. Conventional calibration was done with narrow polystyrene standards (M_n [(g/mol)] = 1980; 4290; 10050; 30300; 52220 and 96000).

2.4.3. Thermal properties

The differential scanning calorimetry (DSC) studies were performed in a TA Instruments Q100 model, equipped with a RCS90 cooling unit, from TA

Instruments (New Castle, USA). The heat flow and the heat capacity were calibrated at 5 °C/min 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 °C/min and a dry nitrogen purge flow of 50 mL/min were used in all measurements. The samples were heated at 5 °C/min from –80 to 200 °C, after performing a cycle in which the samples were heated from room temperature to 120 °C and cooled to –80 °C 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 (Keyworth, UK). 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 to 200 °C temperature range, at frequencies of 1 and 10 Hz, using a heating rate of 5 °C/min. The T_g of the UPs and UPRs was determined from the maximum of $\tan \delta$, at 1 Hz.

2.4.4. 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 °C. 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]).

2.4.5. Gel content

The degree of curing of UPRs was determined by the gel content test (according to ASTM D2765). 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, and weighed. Gel content was calculated according to the Equation (1):

$$\text{Gel content [\%]} = \frac{w_f}{w_0} \cdot 100 \quad (1)$$

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

2.4.6. 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 10 μL drop of distilled water was dispensed, at a rate of 0.5 $\mu\text{L/s}$, and the final WCA was determined as the average of four different drops deposition measurements.

3. Results and discussion

3.1. Polycondensation of UPs based on renewable monomers

In this work, new biobased UPs 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 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). SuAc, AdAc and SeAc can be considered as potential candidates to replace PhA. The use of different chain lengths allows the design of UPs that, after crosslinking, originate materials with different flexibilities and tensile strength [21]. 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 [22–25]. 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 double bonds, and the influence

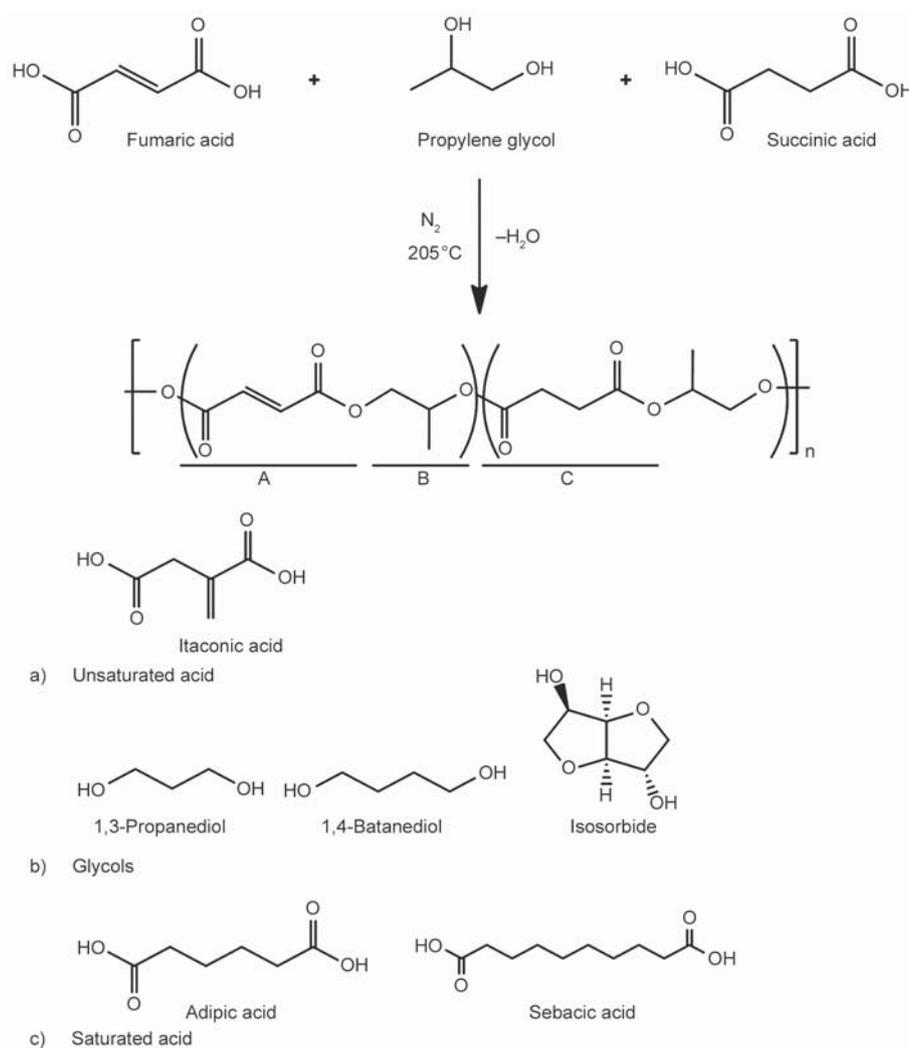


Figure 1. Synthesis of biobased UPs. The remaining structures (a, b, c) correspond to the different monomers used to prepare the different UPs

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 ^1H NMR.

All the BioUPs presented similar FTIR spectra, being possible to identify the band corresponding to the stretching vibration of the carbonyl group of the ester linkage [26], at 1722 cm^{-1} , and a band in the region $1280\text{--}1240\text{ cm}^{-1}$, related to the stretching vibration of the C–O–C and C–O groups of the ester linkage [27]. A band at *ca.* 1650 cm^{-1} was also identified and can be ascribed to the stretching vibration of C=C bond in FuAc [28]. Two other bands, at *ca.* 2980 , 2930 and 2860 cm^{-1} , are due to the vibrational modes of the CH stretching [27].

Table 2 summarizes the main bands observed in the BioUPs prepared in this work.

Further insights onto the chemical structure of bio-based UPs were obtained by ^1H NMR spectroscopy. Figure 2 presents the ^1H 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.

In all spectra (Figure 2), it is possible to identify the peaks belonging to the $-\text{CH}_3$ protons of PG, at $1.25\text{--}1.30\text{ ppm}$ (d) [4]. The signals of the $-\text{CH}_2$ protons belonging to this diol are seen at $3.7\text{--}4.3\text{ ppm}$ (b) and the $-\text{CH}$ 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 FuA moieties [29]. 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 $-\text{CH}_2$ due to the SuAc structure at $2.4\text{--}2.8\text{ ppm}$ (e) [4]. The BioUP_2 presents the signals of AdAc at 2.29 ppm (e) and 1.62 ppm (f), corresponding to the $-\text{CH}_2\text{CH}_2\text{C}=\text{O}$ and $-\text{CH}_2\text{CH}_2\text{C}=\text{O}$ protons, respectively [4]. Furthermore, the characteristic

peaks of SeAc can be identified in the spectrum of BioUP_3 with the $-\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{O}$ protons at 1.32 ppm (g), $-\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{O}$ protons at 1.59 ppm (f) and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{O}$ protons at 2.27 ppm (e) [30].

The chemical composition of formulations containing different biobased glycols were also studied by ^1H NMR spectroscopy. The corresponding spectra is presented in Figure 3. As expected, both UPs spectra show the characteristic resonances attributed to the $-\text{HC}=\text{CH}-$ of FuAc at $\delta \sim 6.8\text{ ppm}$ (a) and the SuAc units at $2.5\text{--}2.7\text{ ppm}$ (e) [31]. For BioUP_4, the proton resonances are in accordance with the anticipated chemical structure, with the OCH_2 protons of FuAc-PDO and SuAc-PDO at 4.27 ppm (b) and 4.13 ppm (d), respectively, and OCH_2CH_2 protons at $2.00\text{--}1.93\text{ ppm}$ (c) [13]. The BioUP_5 spectrum shows peaks at 3.5 ppm (b') and 1.53 ppm (a'), corresponding to unreacted BDO. This unexpected result was confirmed by repeating the polymerization two times and showed the low reactivity of this monomer. Also, the ^1H NMR spectrum of BioUP_6 revealed the presence of some unreacted Iso. 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 [10, 12, 31].

Figure 4 presents the ^1H NMR spectrum of BioUP_7, with ItaAc. As expected, when compared to the ^1H NMR spectrum of BioUP_1, the main difference concerns the resonances corresponding to the protons of ItaAc. The resonances ascribed to the unsaturated diacid can be identified at 6.3 ppm (a₁), 5.7 ppm (a₂) and 3.35 ppm (a₃) [31, 32]. It should also be pointed out the presence of the protons characteristic of mesaconate moieties at *ca.* 6.71 ppm (*), resulting from the isomerization of itaconate moieties [31].

The relative molar amount of the incorporated monomers in the UPs structure was evaluated taking into account the integral values of the signals corresponding to the different monomers in the structure. The results are shown in Table 3.

The data presented in Table 3 reveals some differences between the molar amount of the monomers in the feed and their incorporation in the final structure of the UPs. These discrepancies can be due to the loss of more volatile monomers during the synthesis, causing a stoichiometric imbalance, and/or to the different reactivities of the monomers [4, 12].

Table 2. Main IR bands and respective assignments of the synthesized BioUPs

Formulation	Infrared Bands [cm^{-1}]		
	VC=O, ester	VC-O, ester	VC=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

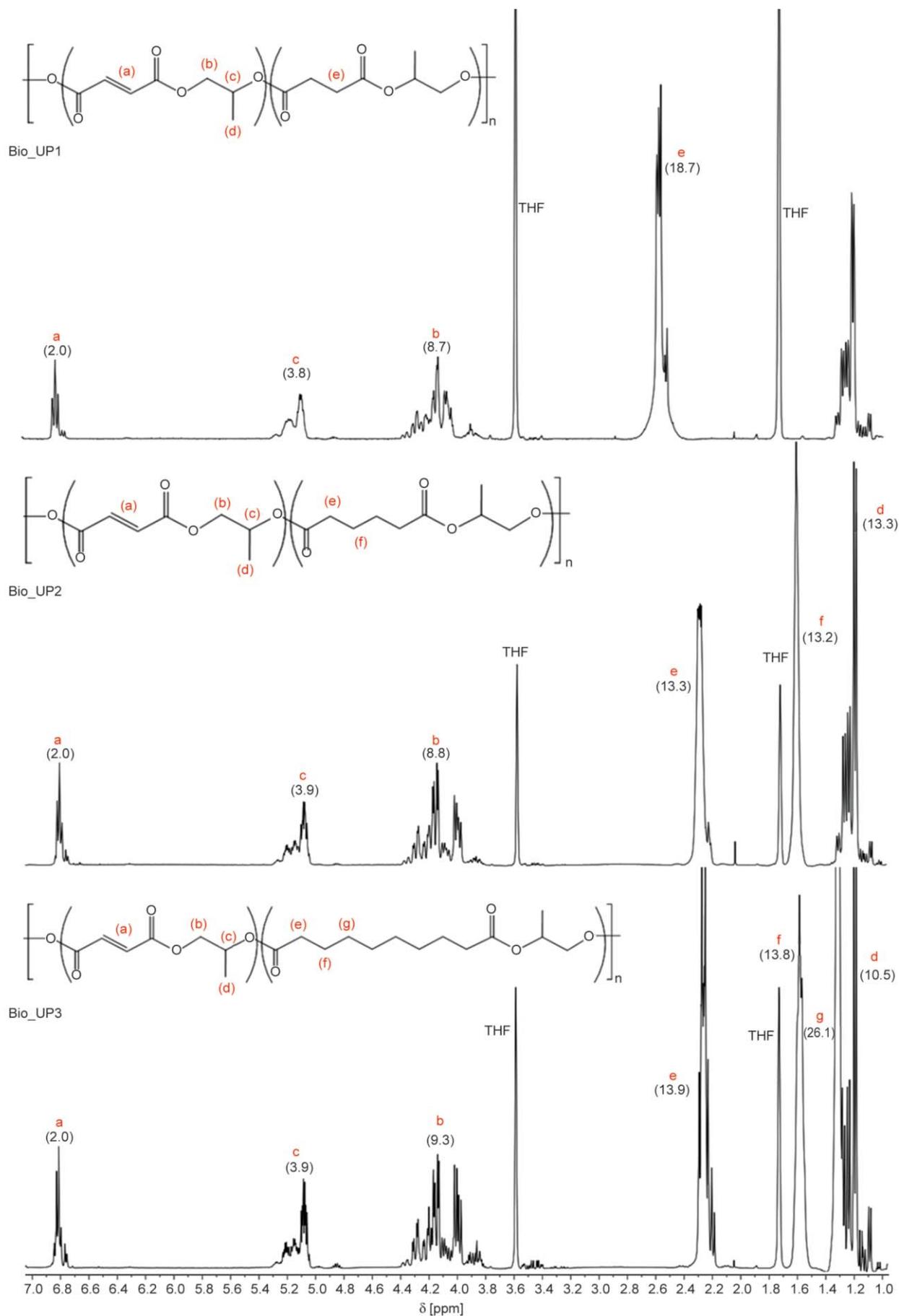


Figure 2. ^1H NMR spectra of BioUP₁, BioUP₂ and BioUP₃

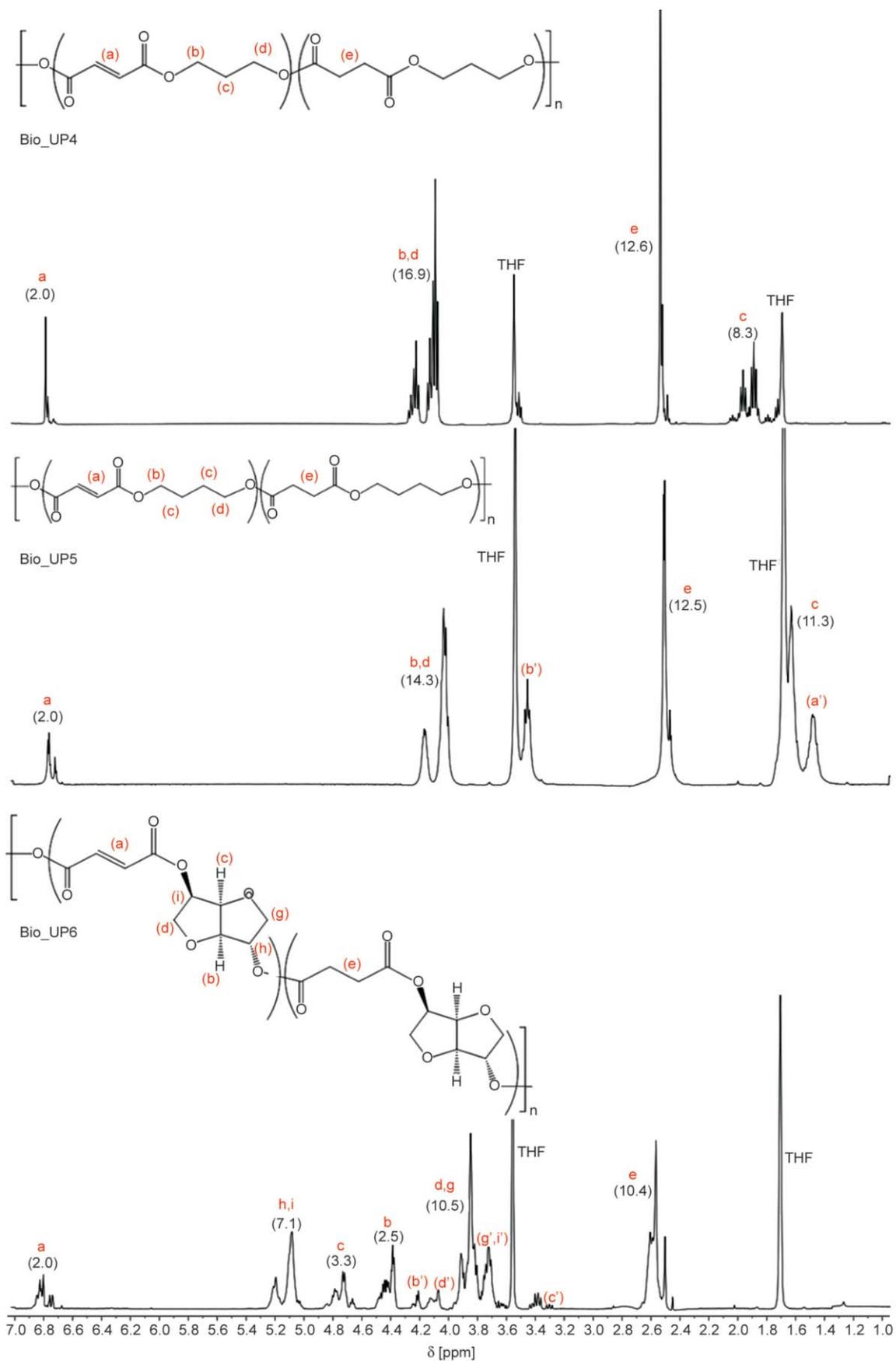


Figure 3. ^1H NMR spectra of BioUP₄, BioUP₅ and BioUP₆

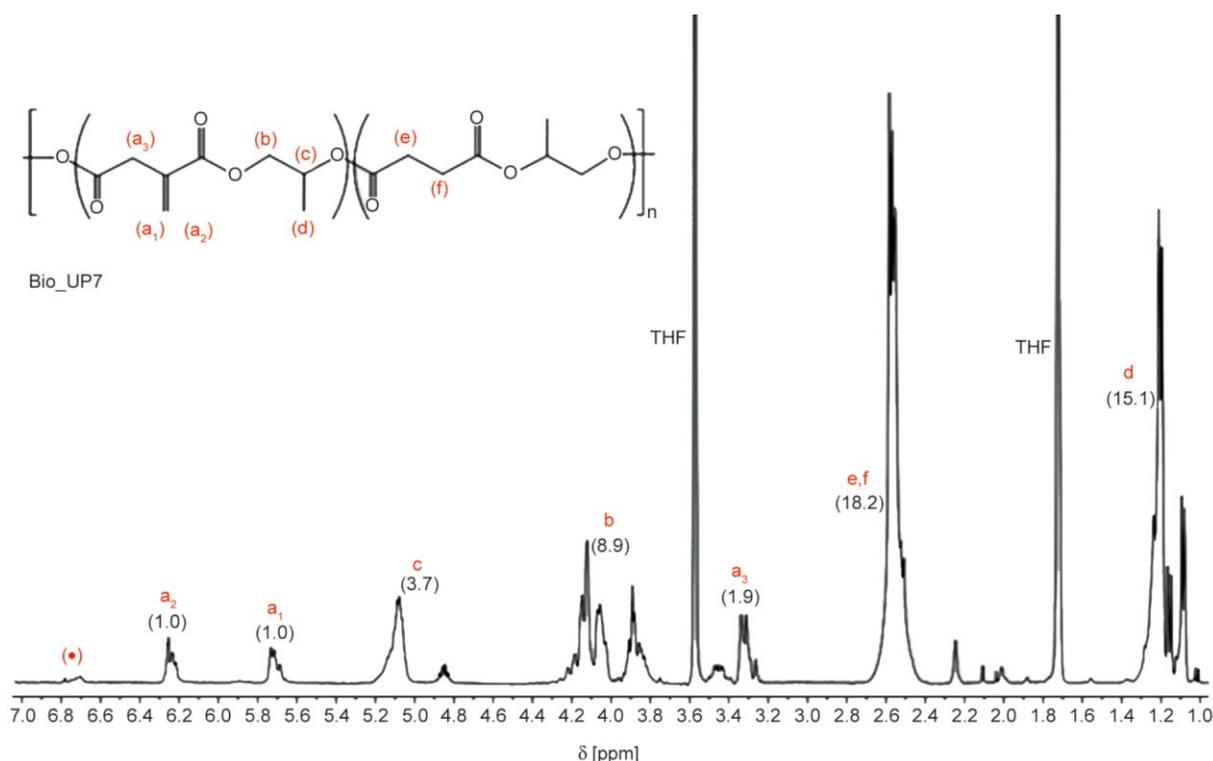


Figure 4. ^1H NMR spectrum of BioUP_7. The integration area of the peaks is indicated in brackets in all spectra

Table 3. Comparison between the feed amounts of the different monomers and their relative percentages in the final structure of the UPs, determined by ^1H 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

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 °C) when compared to the boiling point of PDO (215 °C). On the other hand, the PG can also suffer from some steric hindrance, which might render its incorporation in the UP difficult.

In addition, Iso and BDO presented intermediate incorporation values. Indeed, despite its higher boiling point (235 °C), BDO presented lower incorporation than PDO namely due to the high amount of unreacted

monomer at the end of the reaction. 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 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 [33] and this was the range that was found for the BioUPs prepared in this work. Table 4 summarizes the values of AV, molecular weight (M_n), the polydispersity (\mathcal{D}) as well as the Gardner viscosity values of the BioUPs.

According to Table 4, the BioUPs are characterized by molecular weights ranging from 2700 to 4400 g/mol, and \mathcal{D} between 1.4 and 2.5. These results are in the range of values reported in the literature for UPs [34–37]. Besides molecular weight, 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 higher mobility of the polymeric chains is achieved [38]. As expected, the value of viscosity of the different formulations can be easily tuned by varying the monomers in the

Table 4. Molecular weight, polydispersity and viscosities of the synthesized BioUPs

Formulation	AV [mg KOH/g]	M_n [g/mol]	D	Gardner viscosity [St]	Viscosity [Pa·s]**
BioUP_1	31	4062	1.85	4.85 (RS)	0.51
BioUP_2	32	4401	2.50	4.00 (P)	0.41
BioUP_3	32	4170	2.38	2.31 (I+J)	0.23
BioUP_4	29	2708	1.40	**	**
BioUP_5	25*	n.d. ¹⁾		**	**
BioUP_6	31*	<1980	n.d. ²⁾	7.56 (UV)	0.88
BioUP_7	32	3999	1.82	1.91 (GH ⁺)	0.20

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

***The viscosity from St to Pa·s was obtained by the following relationship: v [Pa·s]= μ [St]/ ρ (the density, ρ , was determined by the method of pycnometer)

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 mobility of the polymeric chains provided by the diacid with longer aliphatic chains [4, 5]. For these formulations, similar molecular weights were achieved and, consequently, M_n does not have a significant effect on the viscosity of UPs. Regarding the UPs with different glycols, it was not possible to determine the molecular weight 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 [10, 39]. It is 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 [5] 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 4 also revealed that BioUP_3 and BioUP_7 have viscosities very close to the commercial polyester (2.38 St (0.27 Pa·s)).

The thermal transitions were evaluated by DSC and DMTA. Figure 5 presents the heat flow curves (from the second heating cycle) of the different UPs.

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 °C), with an associated enthalpy of 82 J/g. 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 to the absence of a T_g . A similar result was obtained for a UP prepared from FuAc and BDO by Farmer and co-workers [31]. The T_g of the BioUPs was also determined by DMTA. Table 5 presents the values of T_g obtained with both techniques.

Regarding the results summarized in Table 5, 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

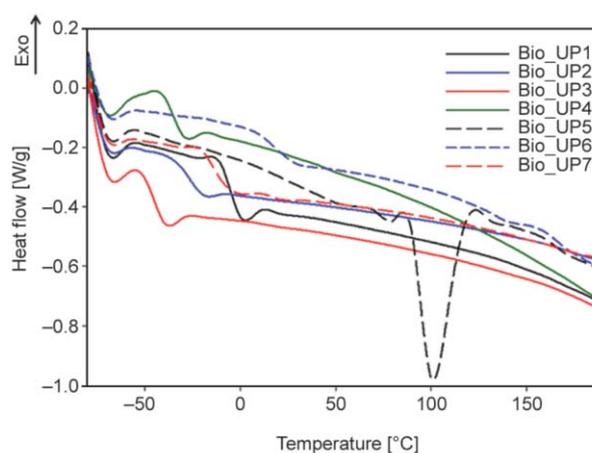


Figure 5. Heat flow curves (from the second heating cycle) of the BioUPs

Table 5. T_g of the biobased UPs obtained from DMTA and DSC

Formulation	T_g [°C]	
	DMTA	DSC
Commercial UP	34.0	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

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 [31]. 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 UM, it can be seen that BioUP_7 (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 [37]. In spite of the differences between the T_g values determined by the two techniques (DSC and TGA) [40], the T_g values follow the same trend in both.

3.2. 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 for industrial applications, and the mixture was thermally cured in the presence of an initiator and an accelerator [5, 41].

Table 6. Gel content and water contact angles (CA) on the resins

	Gel content [%]	CA [°]
Resipur 9837 [®]	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

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 5), which could limit its solubility in Sty [31]. The low solubility of Iso based UP can be ascribed to the high polarity of this particular monomer, as described by Sadler and co-workers [9].

Table 6 presents the gel content and the water contact angles for the commercial resin and the obtained BioUPRs

The results suggest that the BioUPRs have high gel content values, which are very similar to the value obtained for the Resipur 9837[®]. The results indicate that the composition of the UPRs can be changed without jeopardizing the extent of the crosslinking reactions. The water contact angle (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 6, only the resins BioUPR_1, BioUPR_2 and BioUPR_3 present clearly hydrophobic surfaces, with WCA higher than 90°. 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 contact angle, being this conclusion more evident for the formulation BioUPR_7.

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 °C. The tests were carried out in multifrequency mode since it allows to distinguish between the frequency dependent processes (e.g., α transition, T_g , and secondary transitions, γ and β) and those that are non-frequency dependent (e.g., melting, crystallization). The T_g of the UPRs was determined from the maximum of the $\tan \delta$ curve, at 1 Hz. The T_g of the

materials is important to be determined since it is directly related with their mechanical properties and with their service temperature. Typically, the toughness of a material attains its maximum at a temperature slightly below or at the polymer's T_g , temperature at which the polymer chains increase their molecular motion, allowing the material to sustain larger strains without compromising the strength [42]. The DMTA traces of the UPRs, at 1 Hz, are presented in Figure 6.

According to the results presented in Figure 6 it is possible to observe that the changes in the monomers used had a significant impact on the thermomechanical properties. Figure 6a 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 °C, 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 6b) 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 $\tan \delta$ curve are expected. Figure 6c presents the $\tan \delta$ 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 [2, 13]. 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

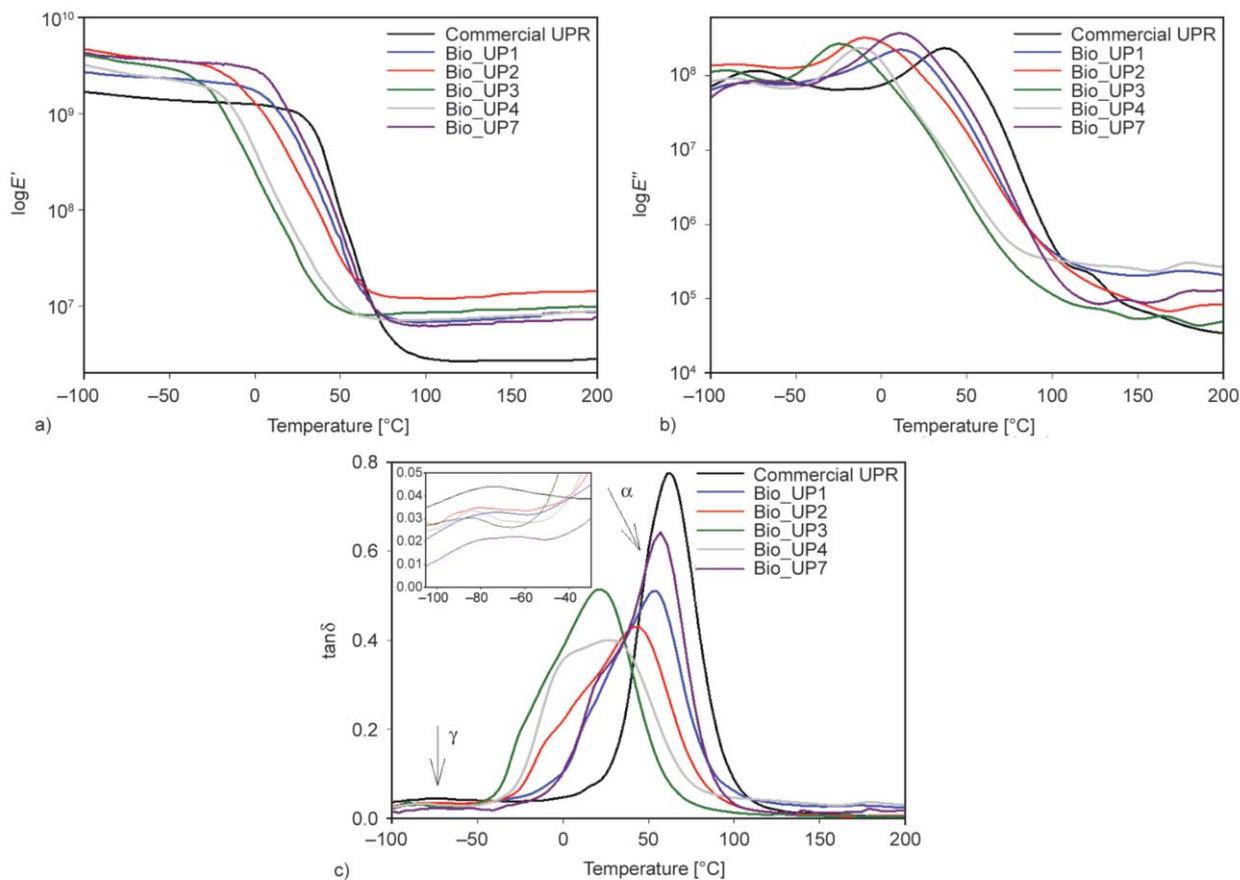


Figure 6. DMTA traces of the commercial and biobased UPRs in terms of E' (a), E'' (b) and $\tan \delta$ (c)

the UPs composition. In literature, it is described that this transition (denoted as γ transition) can be explained by the motions of the aromatic group in poly(styrene) or oligo(styrene) moieties [2, 43]. On the other hand, it is also possible to observe that the $\tan\delta$ traces are relatively broad. This feature could be interesting for some applications that require similar properties in a wide range of temperatures. It is also worth to note that $\tan\delta$ peaks have different amplitudes, which indicates that the UPRs have different capacities to dissipate energy. According to the $\tan\delta$ traces, the Resipur 9837[®] is the resin with the highest capacity to dissipate energy, followed by BioUPR_7. This result can be particularly relevant since the capacity to dissipate energy has a decisive impact on different mechanical properties (e.g. impact strength).

In Table 7 are summarized the main values obtained from DMTA data.

Looking at the values presented in Table 7, some conclusions can be drawn regarding the influence of composition in the elastic and viscous properties of the materials, at 25 °C. Concerning the influence of the diacids, it is clear that the biobased UPRs made from UPs with diacids with shorter chain lengths are more rigid ($E'_{\text{BioUPR}_1} > E'_{\text{BioUPR}_2} > E'_{\text{BioUPR}_3}$). 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 translates to a higher rigidity (higher E') and also to 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 [44]. 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 biobased UPR 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 9837[®], which suggests that this Bio_UPR is a reliable candidate to replace the commercial resin in its common applications.

4. 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 9837[®].

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 ¹H 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 °C, respectively).

Regarding the BioUPRs, prepared using Sty as reactive solvent, high gel content values were obtained and their 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.

Table 7. Thermomechanical parameters of the studied UPRs

Formulation	$E'_{25^\circ\text{C}}$ [MPa]	$E''_{25^\circ\text{C}}$ [MPa]	T_γ [°C]	T_{shoulder} [°C]	T_g [°C]	$\tan\delta_{\text{max}}$
Resipur 9837 [®]	100·10 ¹	102.0	-75.4	–	62.9	0.77
BioUPR_1	523.0	163.0	-76.3	13.3	53.4	0.52
BioUPR_2	240.0	83.3	-82.5	-10.7	45.6	0.45
BioUPR_3	32.7	16.3	-84.3	-24.6	21.8	0.52
BioUPR_4	51.8	21.0	-84.1	-1.0	27.1	0.40
BioUPR_7	657.0	232.0	-74.5	19.2	58.0	0.67

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