

Effect of the biobased polyols chemical structure on high performance thermoset polyurethane properties

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ABSTRACT

The sustainability of the polymeric materials has become a fundamental challenge; therefore, the development of new biobased formulations has gained increasing interest. Thermoset polyurethanes (PURs) present high performance and are a competitive solution for structural composites. However, polyols used in the PUR synthesis are typically from petrochemical origin. Nowadays, a broad range of biobased polyols is available in the market, but there is not yet a specific formulation for high performance PURs composites. The aim of this work was to study the effect of biobased polyols' characteristics in the PUR processing and final properties. In addition, biobased polyol features to synthesize BIO-PURs suitable for structural applications were established. The viscosity and reactivity were studied by means of rheology and differential scanning calorimetry (DSC). Thermal and mechanical properties were studied through thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and flexural tests. The results obtained demonstrated the dramatic influence of polyols' nature on BIO-PUR/PUR properties and their effect on the crosslink density. It was observed that using a high functionality and high hydroxyl index biobased polyol, it was possible to synthesize high performance BIO-PUR suitable for structural composites.

1. Introduction

Polyurethane resins (PURs) represent an interesting alternative to the commonly used epoxy resins for structural composites, thanks to their higher toughness and fatigue resistance that allow to further extent the service life of the composites [1–4]. For that reason, in recent years the use of polyurethane thermosets as a matrix for high-performance composites in both the automotive and wind energy sectors is being explored [5,6]. For instance, the PUR resin system suitable for wind blade manufacturing developed by Covestro [7,8] or Henkel's PUR formulation for automotive structural components resin transfer moulding (RTM) [9].

PU's represent an interesting alternative to the commonly used epoxy resins in structural composites due to their higher toughness and fatigue resistance combined with a fast curing [10–12]. In automobiles, materials with a high fatigue tolerance are essential to exploit lightweight potential to its fullest extent. However, in the mass-production of

automobiles, speed is paramount, and the newly developed materials should allow high production rates.

Resins based on this technology could therefore be a particularly interesting solution for structural applications such as automotive leaf springs manufactured by RTM. However, the PUR resin systems used for this application show some environmental drawbacks, such as the petrochemical origin of their components.

In general, the interest on developing PUR formulations based on renewable resources is significantly increasing due to environmental, geopolitical and economical concerns derived from the commonly used fossil-based starting materials [13–15]. Vegetable oils are one of the cheapest and most abundant sustainable source available in the world [16–18]. Nowadays, there are different routes for the synthesis of polyols from these oils, which provide the possibility to produce a wide variety of biobased polyols [19,20] for the synthesis of BIO-PURs. The most used oils are castor, soybean, sunflower, palm, canola and eucalyptus.

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BIO-PURs based on biobased polyols are being developed for a huge variety of applications [21]. For instance, polyurethanes (PUs) are gaining increasing interest for biomedical applications due to their tunable properties and the possibility of obtaining shape memory materials [22–24]. In this context, BIO-PU's have shown great biocompatibility and degradation properties compared to petrochemical based ones [25,26]. However, currently the main BIO-PURs developed are for foams [27–30], coatings [31–33] and adhesives [34–36]. However, despite the intensive investigation on BIO-PURs, there is not yet a high-performance formulation suitable for structural automotive applications. A biobased alternative suitable for structural composites should have low initial viscosity, latency and fast curing to allow fast and low-cost manufacturing processes, together with high mechanical properties [12]. These characteristics are directly correlated to the nature of the components, so a good selection of the biobased polyol is critical [37].

The aim of this work was to study the effect of the characteristics of biobased polyols (viscosity, hydroxyl index, functionality, type of hydroxyl group) on the reactivity, viscosity evolution during processing and final properties of the BIO-PUR resin systems in order to find the keys to formulate biobased systems suitable for high-performance composites. More specifically, the formulation for a leaf spring for the automotive sector has been optimized.

For this purpose, several BIO-PUR based on biobased polyols with different characteristics, were formulated, and compared to PURs based on petrochemical polyols. The biobased polyols were selected from those of low functionality and low hydroxyl index, with high viscosity to polyols of high functionality and hydroxyl index, with lower viscosity, to further study the effect of these variables in aspects such the density of urethane groups, the final thermal and mechanical properties or reactivity.

The viscosity and reactivity of the different BIO-PUR/PUR systems were studied by means of rheological tests and differential scanning calorimetry (DSC). Thermal and mechanical properties were evaluated by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and flexural tests. The results obtained are promising and it has been possible to determine the type of polyols suitable for structural composites. However, some of the properties, such as the elastic modulus are inferior to those of the reference petrochemical PUR, not fulfilling the requirements for the target application. Nevertheless, these properties could be further enhanced by the addition of other components in the formulation, such as crosslinking agents, to increase the stiffness of the network.

2. Experimental

2.1. Materials

Different renewably sourced commercial polyols were employed in the synthesis of BIO-PURs. Their renewable content, hydroxyl index (I_{OH}), functionality (f), equivalent weight and viscosity values, provided

Table 1
Properties of polyols.

	I_{OH} mg KOH g ⁻¹	f	Viscosity at 25 °C mPas	Renewable content%	Equivalent weight g OH eq ⁻¹	Commercial name (supplier)
Polyol-1	60	3.1	24600	73	935	Emerox 14060 (Emery)
Polyol-2	86	2.5	5000	80	652	Emerox 14090 (Emery)
Polyol-3	71	>2	11000	86	790	Priplast 3186 (Croda)
Polyol-4	203	4	27050	60	276	Priplast 4F (Croda)
Polyol-5	400	3	1500	80	141	Polycin 400 (Vertellus)
Polyol-6	330	4	3000	80	170	Polycin 12 ^a (Vertellus)
Polyol-7	280	4	1385	80	200	Polycin 280 (Vertellus)
Polyol-8	400	3	373	0	140	Lupranol 3300 ^b (BASF)
Polyol-9	490	5	22750	0	114	Lupranol 3422 ^b (BASF)

^a 25% of secondary OH groups.

^b 100% of secondary OH groups.

by the supplier or determined in their absence, are summarized in Table 1. Moreover, two petrochemical origin polyols were also used for comparative purposes (Table 1). The second component was an isocyanate (Voraforce TR1500-Isocyanate from Dow Chemical, NCO equivalent weight = 136 g·eq⁻¹ and viscosity = 130 mPa s). NCO equivalent weight was determined according to the ASTM D2572-97.

2.2. Synthesis

Nine BIO-PUR/PUR systems were synthesized, seven with biobased polyols, BIO-PUR1 to BIO-PUR7, and two with petroleum derived polyols, PUR8 and PUR9, as references. The isocyanate index was maintained (equal to 1.2) for all the PUR/BIO-PUR systems studied. The designation, composition and renewable content of the BIO-PUR/PUR systems are summarized in Table 2. All formulations are based on 100 parts by weight of polyol (pbw).

The renewable content of BIO-PURs was determined according to the weight percentage and renewable content of the biobased components. All BIO-PURs have a renewable content higher than 33%.

BIO-PUR/PURs were synthesized using a one-step bulk polymerization process, according to the reactant's ratios shown in Table 2. Before the BIO-PUR/PUR synthesis reaction, all components, polyols and isocyanate, were degassed under vacuum to remove any trace of moisture. The components of the reaction were prepared as shown in Fig. 1a.

The BIO-PUR/PUR plates were manufactured by casting the resin into a mould and curing it in an oven at 120 °C for 1 h (Fig. 1b).

3. Characterization

Rheological tests were carried out on a HAAKE RheoStress 6000 Rheometer (Thermo Fisher Scientific, Massachusetts, USA), running in an oscillating stress mode at a frequency of 1 Hz. Amplitude was held constant in the Linear Viscoelastic Range (LVR) throughout the test. A gap separation of 1 mm and disposable parallel plates of 60 mm diameter were used. Experiments were performed at dynamic or temperature sweep test conditions. Temperature sweep tests were performed from 25 to 200 °C at a constant heating rate of 5 °C min⁻¹. Storage and loss moduli, G' and G'' respectively, and complex viscosity, η^* , were

Table 2
Summary of synthesized BIO-PUR/PUR systems.

System	Polyol (pbw)	Isocyanate (pbw)	Renewable content %
BIO-PUR1	100 (Polyol-1)	17.5	63.1
BIO-PUR2	100 (Polyol-2)	25.1	63.9
BIO-PUR3	100 (Polyol-3)	20.7	71.3
BIO-PUR4	100 (Polyol-4)	80.6	33.2
BIO-PUR5	100 (Polyol-5)	116.7	36.9
BIO-PUR6	100 (Polyol-6)	96.3	40.8
BIO-PUR7	100 (Polyol-7)	81.7	44.0
PUR8	100 (Polyol-8)	116.7	0
PUR9	100 (Polyol-9)	143.0	0

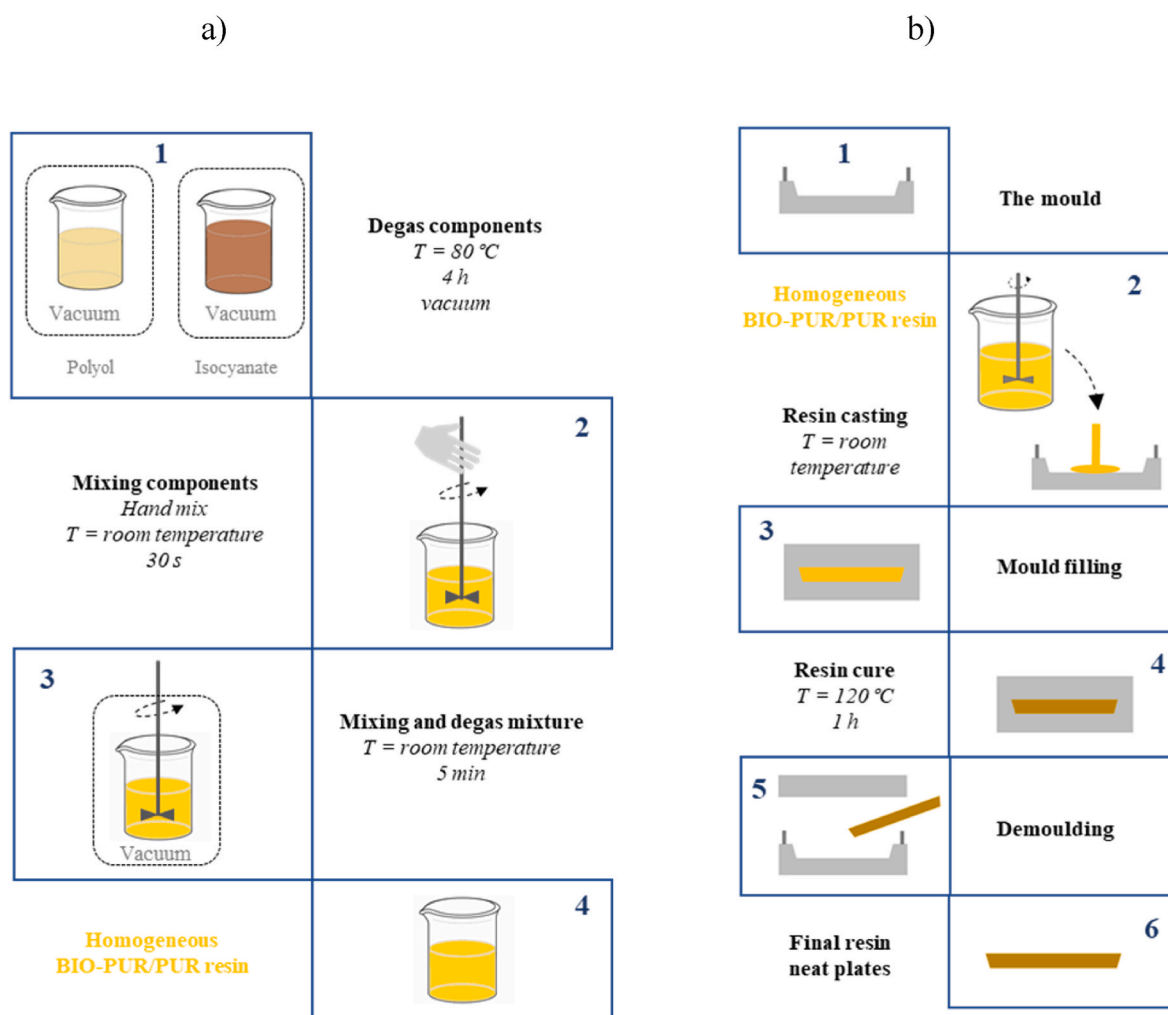


Fig. 1. a) BIO-PUR/PUR sample preparation and b) resin plates casting process.

measured over temperature.

Differential scanning calorimetry (DSC) tests were carried out on a TA Instruments DSC Q100 (TA Instruments, New Castle, USA) calorimeter in dynamic conditions. The experiments were performed from -90 to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate. All samples were subjected to a subsequent dynamic scan from -90 to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ to evaluate the presence of residual curing.

Dynamic mechanical analysis (DMA) tests were carried out using the Gabo Eplexor100 N (Netzsch, Selb, Germany) dynamic mechanical analyser, working in flexural mode. Temperature scans were performed from -40 to $200\text{ }^{\circ}\text{C}$ at $2\text{ }^{\circ}\text{C min}^{-1}$ heating rate and at a frequency of 1 Hz. The sample dimensions were $2.2 \times 5 \times 50\text{ mm}^3$. The T_g of the PUR resin systems was taken at the temperature value of the maximum of $\tan \delta$, T_{α} [38,39].

The colour parameters of BIO-PUR/PUR were measured by X-rite 962 spectrophotometer (Grand Rapids, Michigan, USA). L^* (lightness-darkness), a^* (red-green), b^* (yellow-blue) were calculated as an average of five different tests.

The thermal stability of the cured PURs was analyzed by thermogravimetric analysis (TGA) using a Mettler Toledo TGA/SDTA851 (Mettler Toledo, Columbus, USA) equipment. Temperature scans were performed from room temperature to $600\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, under nitrogen atmosphere.

The presence of insaturations in the biopolyol was analyzed by Fourier transform infrared (FTIR) spectroscopy using a Nicolet Nexus FTIR spectrometer equipment with an ATR Golden Gate (Specac)

accessory. The spectra were performed averaging 32 scans in a range from 4000 to 650 cm^{-1} with a 2 cm^{-1} resolution.

The flexural tests were carried out at room temperature using a Instron 5967 (Instron, Norwood, USA) equipment, with a 3-point bending device, according to ISO 178 standard.

4. Results and discussion

Liquid composite moulding (LCM) process in its different versions, such as RTM, H-RTM, C-RTM or infusion, is used more and more to produce structural composites because of its numerous advantages.

In these processes the viscosity is a critical factor. Some latency is needed in the first part of the process to maintain a low viscosity and to facilitate the fibre impregnation. Then, high reactivity is desired to reduce curing times and allow fast production cycles.

Before curing, the BIO-PUR systems showed in general higher viscosity values than the two petroleum derived reference PURs (Fig. 2). This can be related to i) the lowest content of low viscosity isocyanate and ii) the different polyol nature.

Among the different BIO-PURs, BIO-PUR1 showed the highest initial viscosity value and BIO-PUR5 showed the lowest one, due to their lowest and highest isocyanate content, respectively. On the other hand, the polyol's properties such as, functionality, hydroxyl number and molecular weight also directly affected the component's viscosity. The viscosity of the polyols depends on the functionality or hydroxyl number due to their quantity of hydroxyl groups capable of forming hydrogen

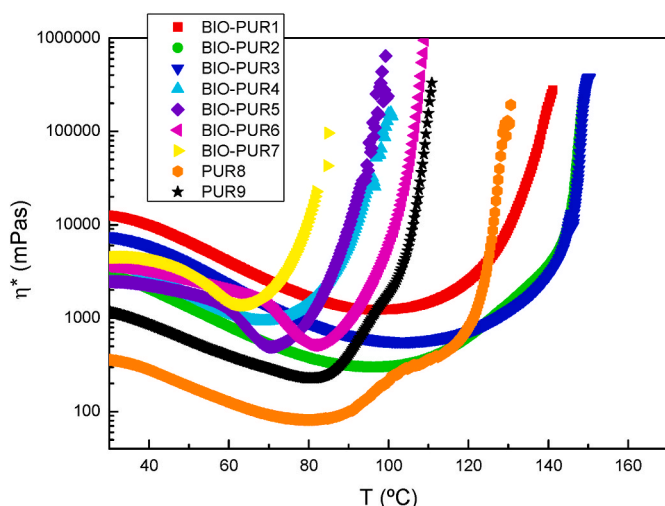


Fig. 2. Complex viscosity evolution with temperature of the different BIO-PUR and PUR.

bonds [40]. This is the reason why Polyol-4 and Polyol-9 showed very high viscosity values (22750 and 27050 mPa s, respectively). However, after mixing them with isocyanate, the hydrogen bonds' concentration decreased and the viscosity values decreased down to 3990 and 1140 mPa s respectively. The effect of the molecular weight of the polyol could be observed on BIO-PUR1, this system presents the highest viscosity value because of the effect of the high molecular weight of Polyol-1 [41,42].

Fig. 2 shows results of the complex viscosity evolution for the different BIO-PUR/PURs resins. At low temperatures, the viscosity decreased with temperature until the curing started accompanied by an abrupt increase in viscosity and subsequent resin gelling. The gelation times determined by the crossing point of the G' and G'' curves (Fig. S2-S10) are shown in Table 3. The results showed a wide variety of systems, formulation with low gelation times with high reactivity and formulation with high gelation times with moderate reactivities. Regarding the effect of hydroxyl index value and polyol functionality in the reactivity, it can be observed that in the case of biobased polyols with the lowest hydroxyl index value (IOH < 100 mg KOH g⁻¹), BIO-PUR1, BIO-PUR2 and BIO-PUR3, the curing started at higher temperatures, showing a higher latency. At these hydroxyl indexes, the increase of the functionality results in an increase of the reactivity of the system, showing lower curing starting temperature as for BIO-PUR1. For higher hydroxyl index values (IOH > 200 mg KOH g⁻¹), there was a decrease of reaction starting temperature, as for BIO-PUR4 with functionality 4. This effect was observed even for the lowest functionality system, BIO-PUR5, where its lower functionality (f = 3) was compensated by its higher hydroxyl value (IOH = 400 mg KOH g⁻¹).

However, these were not the only factors affecting the resins viscosity evolution. In addition to IOH and functionality, the type of hydroxyl group, primary or secondary, has to be considered. In this way, if

Table 3
Total heat reaction and gelation times of different BIO-PUR/PUR's systems.

System	Total heat of reaction (J g ⁻¹)	Gelation times (min)
BIO-PUR-1	72 ± 1.8	20.5 ± 0.6
BIO-PUR-2	99 ± 2.4	22.5 ± 0.5
BIO-PUR-3	73 ± 1.6	22.7 ± 0.7
BIO-PUR-4	164 ± 2.8	13.3 ± 0.5
BIO-PUR-5	121 ± 2.3	13.3 ± 0.3
BIO-PUR-6	109 ± 2.9	15.3 ± 0.4
BIO-PUR-7	211 ± 1.1	11.1 ± 0.5
PUR-8	207 ± 3.2	18.9 ± 0.8
PUR9	278 ± 1.5	16.0 ± 0.7

we compare BIO-PUR6 and BIO-PUR7, both with the same functionality, it can be observed that although BIO-PUR6 has a higher hydroxyl index, the curing started at higher temperature. This can be attributed to the fact that the polyol employed in BIO-PUR6 has a secondary hydroxyl group, which is less reactive than a primary hydroxyl group [43–45]. The same effect can be seen in the reference PUR8 and PUR9 systems, which contain only secondary hydroxyl groups. Regarding PUR9, it can be also observed that an increase of IOH and functionality results in a faster curing.

Comparing the different options, it can be seen that BIO-PURs based on polyols with high functionality (f = 4) and high OH index (200 mg KOH g⁻¹ < IOH < 330 mg KOH g⁻¹) like BIO-PUR4, BIO-PUR6 and BIO-PUR7, or polyols with f = 3 and IOH = 400 mg KOH g⁻¹, like BIO-PUR5, could provide promising viscosity and reactivity to formulate systems for LCM processes.

The curing reaction of each BIO-PUR was also characterised by dynamical DSC tests (Fig. 3). The obtained thermograms were in accordance with rheological tests results. The resin systems formulated with polyols with high functionality and OH index higher than 200 mg KOH g⁻¹ presented the fastest curing. BIO-PURs based on polyols with OH index lower than 100 mg KOH g⁻¹ exhibited significantly slower curing reactions. As can be seen in Fig. 3, the exothermic peaks corresponding to the curing of BIO-PUR1, BIO-PUR2 and BIO-PUR3 started and finished at higher temperatures. Furthermore, BIO-PUR6 and PUR8 and PUR9 presented slower curing than their counterparts with similar functionality and OH index, due to the different hydroxyl group type. These results demonstrate that BIO-PUR/PURs reactivity is directly correlated with the polyol OH index, functionality and secondary hydroxyl group content.

The total heat of reaction is summarized in Table 3. For the different BIO-PUR/PUR systems, the total heat of reaction increased with the increase of IOH, which is mainly related with the total hydroxyl or isocyanate groups' content, thus the formed urethane groups' density. However, other factors should also be considered, such as the functionality and hydroxyl group type. BIO-PURs showed in general lower total heat release than PURs, which is of interest for structural composite manufacturing processes, in order to avoid overheating due to exothermic processes, especially in the case of thick laminates.

BIO-PUR/PURs plates for DMA were prepared by casting and curing them 1h at 120 °C. BIO-PUR1, BIO-PUR2 and BIO-PUR3 presented high flexibility, while the other systems were stiffer at room temperature (Fig. 4).

Fig. 5 shows tan δ and storage modulus, E', as a function of temperature for the synthesized BIO-PURs and PURs systems.

Flexible BIO-PURs with low OH index (IOH < 100 mg KOH g⁻¹),

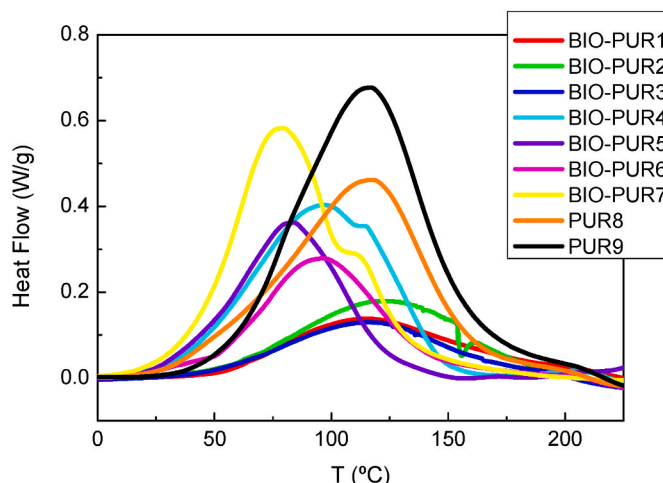


Fig. 3. Dynamic DSC thermograms.

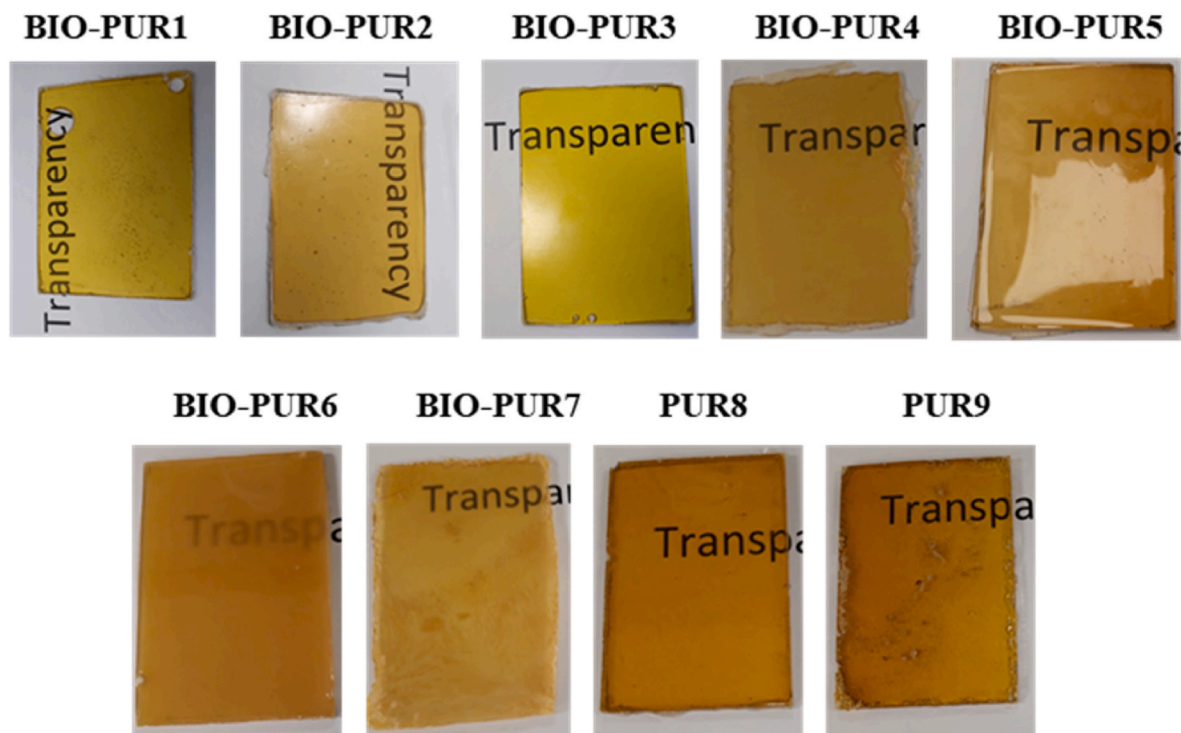


Fig. 4. BIO-PURs and PURs plates.

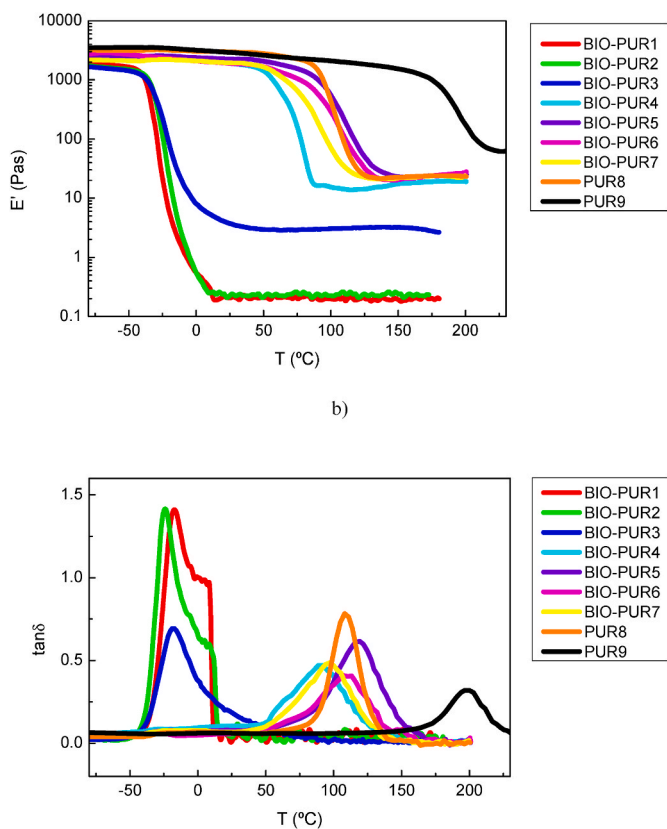


Fig. 5. a) Storage modulus (E') and b) loss factor ($\tan \delta$) vs temperature for BIO-PUR/PUR formulations.

showed T_g values below room temperature, while BIO-PURs with IOH >200 mg KOH g^{-1} showed T_g values above room temperature.

The cross-linking density was calculated from the storage modulus in

the rubbery interval according to equation (1) [38,39].

$$v(\text{mol m}^{-3}) = \frac{E'_{T_{\alpha}+50}}{3 R (T_{\alpha} + 50)} \tag{1}$$

where $E'_{T_{\alpha}+50}$ is the storage modulus in the rubbery region (at $T_{\alpha} + 50$ °C), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T_{α} is the glass transition temperature in Kelvin.

As it can be observed in Table 4 and Fig. 6, which schematically represents the structures of the synthesized BIO-PUR/PURs, the BIO-PUR1-3 systems showed T_g values below room temperature, which is associated with a low crosslinking density network. In addition, above the T_g value, these formulations were very flexible, especially BIO-PUR1 and BIO-PUR2, and showed very low storage modulus, resulting in very high elongation and low resistance during the DMA tests. Despite not shown here, the same results were obtained in tensile geometry. BIO-PUR1-3 systems could be interesting for flexible components, but they are not suitable for the target structural composite applications.

In contrast, BIO-PUR4-7, PUR8 and PUR9 presented higher T_g values, due to their higher crosslinking density network and their lower chain mobility. If we compare BIO-PUR 4-7, BIO-PUR5 showed the highest T_g value and storage modulus (E'). This is due to its higher urethane density, which is comparable to the PUR8 reference system

Table 4

Crosslinking density, storage modulus at 25 °C and $T_{\alpha}+50$ and T_g values of different BIO-PUR/PUR systems.

System	v (mol m^{-3})	E' ($T_{\alpha}+50$) (MPa)	T_g (°C)	E' (25 °C) (GPa)
BIO-PUR-1	27	0.2	-17	0.2
BIO-PUR-2	33	0.3	-17	0.3
BIO-PUR-3	351	2.7	-25	2.7
BIO-PUR-4	1516	15.6	90	1.8
BIO-PUR-5	2145	23.7	119	2.3
BIO-PUR-6	1938	20.5	101	2.1
BIO-PUR-7	1992	20.9	97	2.0
PUR-8	1830	23.3	108	2.9
PUR9	8020	106.3	187	3.0

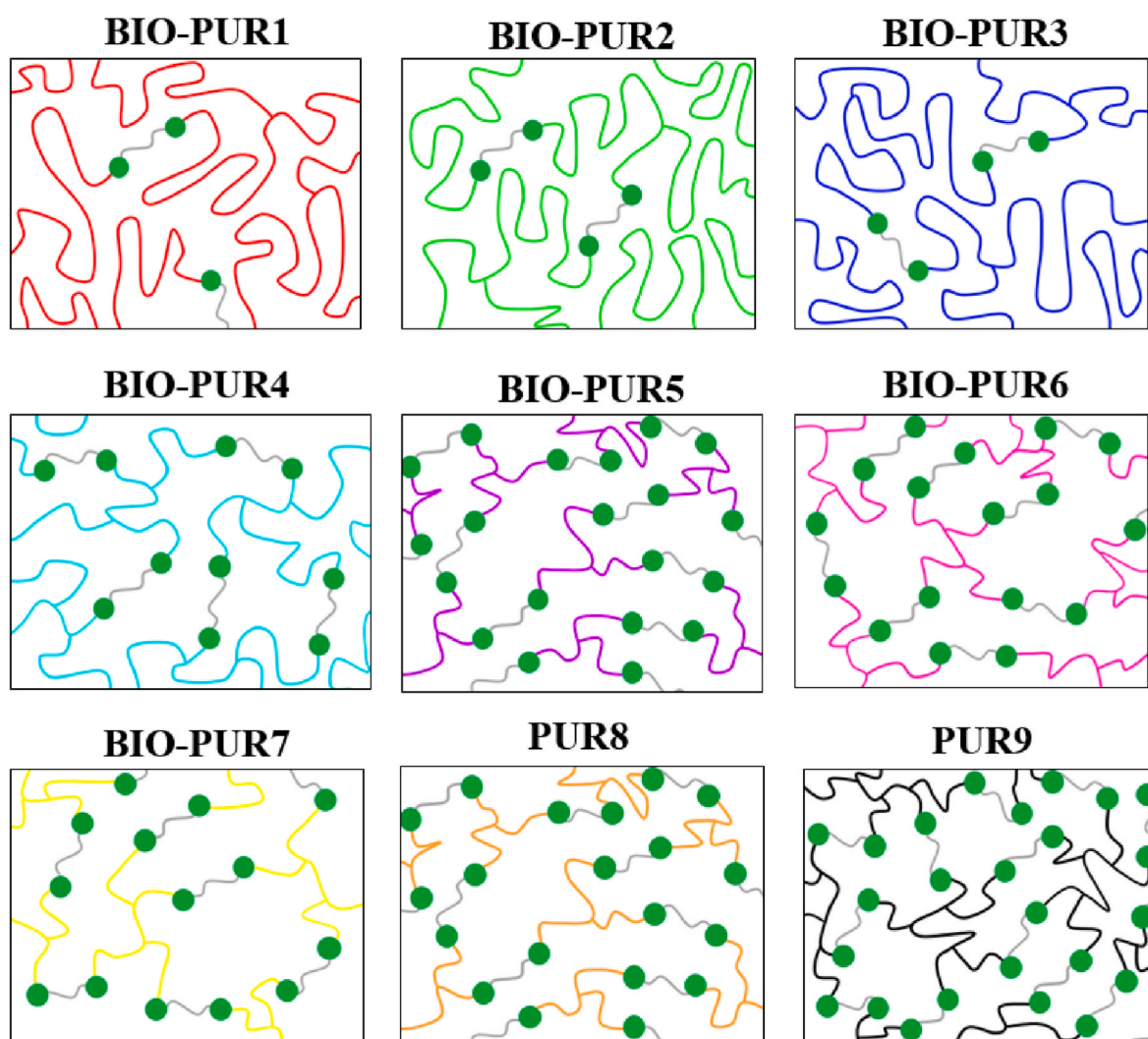


Fig. 6. Scheme of the different three-dimensional networks of the BIO-PUR/PUR systems.

with a slightly lower T_g and crosslink density. PUR9 ref system showed the highest T_g and storage modulus values according to higher crosslinking density.

According to these results, the following systems were selected to compare the final properties of the cured resins: one flexible system (BIO-PUR1), two BIO-PUR rigid systems with different crosslink density (BIO-PUR4 and BIO-PUR5), and the petrochemical origin reference system with the highest properties (PUR9).

The colour parameters of the representative BIO-PUR and PUR systems were evaluated (Table 5). The values of L^* , a^* , and b^* were characteristics of the brown materials. Moreover, the colour differences between samples and white standard (ΔE^*) and whiteness index (WI) were calculated using the following Equations (2) and (3) [46]:

Table 5

L^* , a^* , b^* , and ΔE^* colour values as well as WI of selected BIO-PUR/PUR systems.

System	L^*	a^*	b^*	ΔE^*	WI
BIO-PUR-1	65.2 ± 1.2	11.5 ± 1.1	69.9 ± 2.3	73.7 ± 3.3	21.1 ± 1.9
BIO-PUR-4	66.5 ± 2.6	4.7 ± 3.1	71.5 ± 3.2	76.7 ± 3.4	20.8 ± 3.3
BIO-PUR-5	68.1 ± 3.0	4.1 ± 0.6	66.9 ± 2.7	71.9 ± 3.5	25.6 ± 2.7
PUR9	63.4 ± 1.9	9.9 ± 1.6	73.7 ± 1.0	80.3 ± 1.2	17.2 ± 1.3

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

$$WI = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}} \quad (3)$$

The final colour of BIO-PUR and PUR is directly related to the initial components, polyol and isocyanate (Fig. S11). The characteristic brown colour of the plates is mainly due to the isocyanate. Consequently, PUR9, which was formulated with the highest amount of isocyanate presented a high value of the a^* factor related to the red colour. In addition, biobased polyols also exhibit a colour that also has an influence on the final material. BIO-PUR1 based on the polyol with the highest intensity of brown colour also showed a high value of a^* factor. The plates were brown in colour but also showed transparency. The whiteness index was low (far from 100), which indicated that the surface of the formulations investigated absorbed and transmitted visible light. However, colour or its absence is not a necessary characteristic for the target application and brown colour of the systems is not a drawback.

Fig. 7 shows the results of the thermogravimetric curves for the selected BIO-PUR and PUR systems.

The thermal stability of PURs was related with the structural differences in their reactants. Two regions were clearly appreciated in the decomposition of all analyzed systems. The first one corresponds to the dissociation of urethane bonds (200–350 °C) and the second region (370–500 °C) to the polyol degradation and the residues formed during

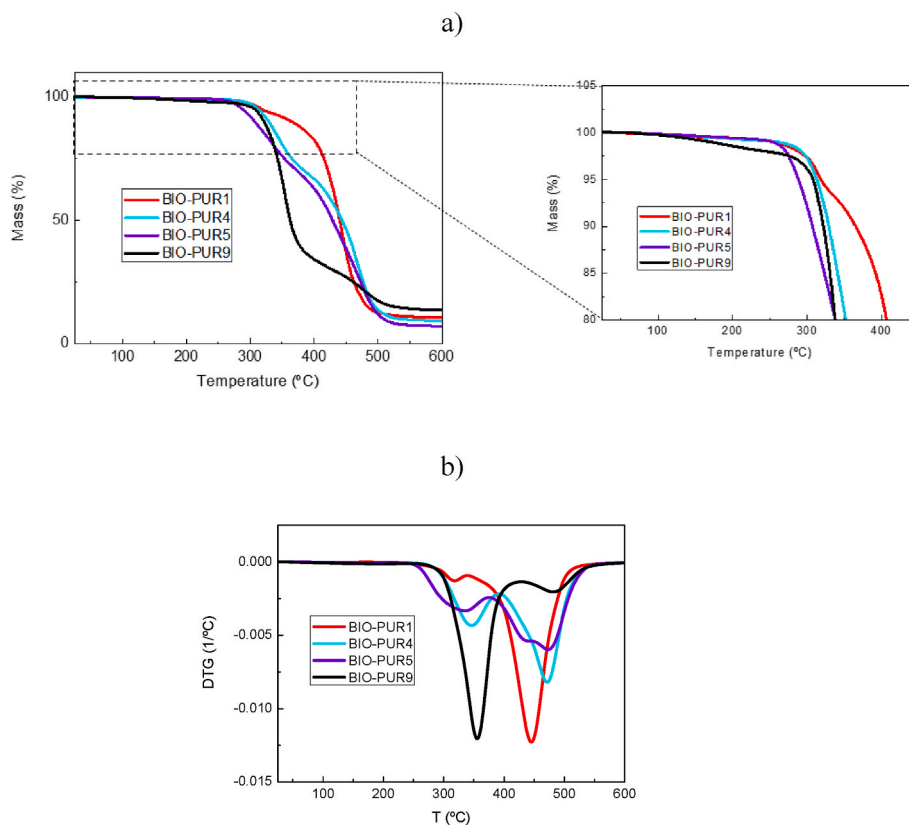


Fig. 7. a) TG curves b) DTG curves for the BIO-PUR and PUR systems.

the previous degradation steps that further degrade to form char residue [47].

As shown in Fig. 7, in all studied formulations the weight loss started at temperatures higher than 200 °C, so it can be concluded that all BIO-PUR/PURs systems had a suitable thermal stability. The onset of weight loss was similar for all studied systems except for BIO-PUR5 and PUR9, where the degradation started at a slightly lower temperature. It is reported that the onset degradation temperature of PURs depends both on the urethane groups density and structural differences [48,49]. The degradation onset temperature shifts to lower temperatures as the polyol's IOH and functionality increases. Javni et al. analyzed the thermal stability of different polyurethanes synthesized from polyols derived from different vegetable oils and observed that those synthesized with polyols containing double bonds in their structure presented lower thermal stability and more complex degradation mechanism [48,50,51]. Therefore, the lower thermal stability observed for BIO-PUR5 could be attributed to its high urethane density (Fig. 6 and Table 4) and to its unsaturated chain as shown in the FTIR spectra of the selected polyurethanes polyol (Fig. 8).

Moreover, several differences between the different systems in terms of percentage in weight loss of each region could be appreciated. Fig. 7a-b shows that in the urethane cleavage temperature region, the PUR9 presented the largest mass loss (around 62%). This system was based on the polyol with the highest OH index and, as previous results demonstrated, the higher crosslinking density (Fig. 6). The BIO-PUR4 and BIO-PUR5 also presented large mass loss in the urethane cleavage region (27% and 31%). Conversely, when the crosslink density is significantly lower, the mass loss is not large (6%) as for BIO-PUR1 with IOH <100 mgKOH g⁻¹.

In the second degradation region, the opposite effect could be appreciated. The mass loss in that region decreased with increasing crosslinking density. In this step, the degradation of the polyol occurred as well as the oxidation of the char residue. Therefore, system based on a

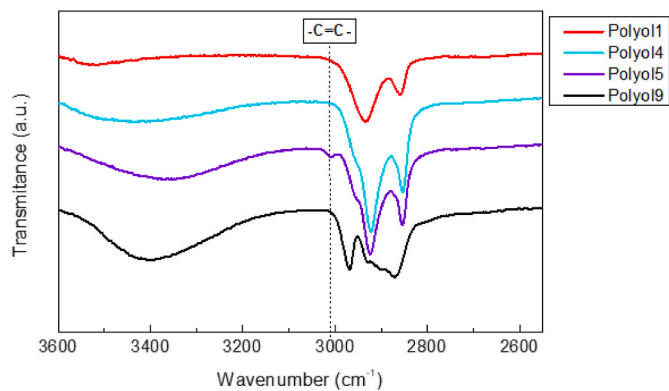


Fig. 8. FTIR spectra of selected polyurethanes' polyols.

low OH index polyol (BIO-PUR1), showed a significant mass loss. Moreover, PUR9 presented the highest residue due to the higher content of aromatic isocyanate used in its synthesis.

Table 6 summarizes the results of flexural tests for the selected BIO-PUR/PUR systems. Flexural modulus values are in accordance with the DMA tests results. BIO-PUR1 system presented low flexural strength and modulus and a high elastic deformation. Samples did not break during the test and they recovered the initial deformation.

In general, the properties for the rest of the BIO-PURs were satisfactory, with BIO-PUR5 presenting the most promising results. However, the modulus was still lower than that of the reference petrochemical origin based PUR. Nevertheless, these properties could be further enhanced by the addition of other components on the formulation, such as crosslinking agents to increase the network rigidity [39,52].

Table 6
Flexural properties of BIO-PUR/PUR systems.

Systems	Flexural strength	Flexural modulus	Flexural strain to failure
	MPa	GPa	%
BIO-PUR1	10.8 ± 1.6	0.01 ± 0.00	No break
BIO-PUR4	73.7 ± 2.0	1.85 ± 0.01	6.4 ± 0.3
BIO-PUR5	92.8 ± 4.3	2.17 ± 0.07	6.6 ± 0.7
PUR9	115.0 ± 1.3	3.13 ± 0.02	6.0 ± 0.0

5. Conclusion

In this work different BIO-PUR/PUR systems based on different biobased polyols and petrochemical based polyols were investigated in order to understand the effect of the characteristics of the biobased polyols on the resins' viscosity evolution, reactivity and final properties.

Rheological tests, DSC, DMA, TGA and flexural test results showed that a wide variety of systems can be formulated, from resins with low reactivity and high flexibility to fast curing and low viscosity resins with high strength and rigidity. In this work, it was demonstrated that BIO-PUR/PURs behaviour are closely related to the polyol's hydroxyl index value, functionality and hydroxyl group type. The initial viscosity of the resin depends on the polyol's initial viscosity, which in turn is associated to their chemical structure. The BIO-PURs showed wide variety of reactivities, including fast curing when the functionalities and hydroxyl index values were high. In the same way, high functionality and high hydroxyl index polyols led to high crosslinking density BIO-PURs, with high modulus and high Tg values.

Formulations based on polyols with low functionalities ($f < 3$) and low hydroxyl index value (IOH < 200 mg KOH g⁻¹) like BIO-PUR1-3, presented high initial viscosity, low reactivity and very high flexibility. Thus, this type of biobased polyols are not suitable for structural applications.

On the other hand, due to the good balance of biobased polyol's functionality ($f \geq 3$) and hydroxyl index value (IOH > 200 mg KOH g⁻¹) BIO-PUR4-7 showed high reactivities. Moreover, all these systems showed Tg values higher than 90 °C. Among all BIO-PURs, BIO-PUR5 presented a promising combination of low viscosity before curing, high reactivity, high Tg and good mechanical properties for the target application. The flexural modulus seemed to be the only factor to be improved in order to achieve properties equivalent to those of the petrochemical origin based structural PUR system (PUR9). However, this property could be further enhanced by the addition of other components on the formulation, which could potentially be achieved by the addition of biobased crosslinking agents.

CRedit authorship contribution statement

O. Echeverría-Altuna: Methodology, Investigation, Visualization, Formal analysis. **O. Ollo:** Methodology, Investigation. **I. Larraza:** Methodology, Investigation. **N. Gabilondo:** Methodology, Investigation. **I. Harismendy:** Conceptualization, Methodology, Supervision, Visualization, Formal analysis, Funding acquisition. **A. Eceiza:** Conceptualization, Methodology, Supervision, Visualization, Formal analysis, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2022.125515>.

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