

Solid “Green” Polyurethanes Based on Rapeseed Oil Polyol and Modified with Glycerol and Microcellulose

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ABSTRACT: Solid biobased polyurethanes (PUs) were prepared from a rapeseed oil-based polyol (ROPO) synthesized by epoxidation reaction followed by oxirane ring-opening with diethylene glycol. The reference material was modified by replacement of the ROPO with glycerol in different proportions and also by addition of a commercial microcellulose (MC). The curing process of the reactive mixtures was monitored by rheological measurements and the analysis showed that both MC and glycerol increase the time of crossover between storage and loss modulus (liquid to solid transition in the response at 1 Hz) in the samples. The completely cured polyurethanes were characterized by physical, morphological and mechanical analysis. The results proved that the addition of glycerol and MC increases the modulus and ultimate stress. Despite the higher modulus of the composites, the ultimate deformation also increases with the incorporation of 3 and 5 wt% of MC, which was associated with the good interaction between the cellulose and its polymer matrix.

KEYWORDS: Rapeseed oil polyol, biobased polyurethanes, glycerol, microcellulose

1 INTRODUCTION

Polyurethanes (PUs) are very versatile materials that, like the majority of the polymers, depend on petroleum industry production [1]. They can be prepared as foamed or solid materials, the former type being the most important PU commercial product based on the volume of the production. In spite of this, the unfoamed PU market is on the rise because of the different types of materials that can be prepared, such as coatings, adhesives, sealants, elastomers and binders, among others, that can be used in different applications like flooring, electronic equipment, furniture, packaging, etc. [1–4].

Polyurethanes are prepared from polyols and isocyanates as main components of their formulations. As a world trend, the search for new raw materials to replace the synthetic ones for the production of polymers is constantly growing [5–7]. The use of natural products with renewable character can offer environmental and economic advantages. In this context, vegetable oils can be one of the alternatives to provide biobased monomers at a competitive cost. They are

chemically composed of three fatty acid chains joined to a glycerol framework. These fatty acid moieties present from 1 to 3 carbon-carbon double bonds that can be chemically modified to introduce one of a large variety of reactive groups, such as hydroxyl groups [8–14], as in the present work.

In particular, rapeseed oil (RO) is an edible oil that has around 61% oleic acid, 21% linoleic acid, 8% linolenic acid, and 10% other acids [4, 15]. Different paths of the reaction of the triglyceride double bonds for incorporating hydroxyl groups have been studied [8, 16–19]. One of the most reported methods is the transformation of the carbon-carbon unsaturated bonds to introduce hydroxyl groups through epoxidation with peroxy acids followed by oxirane ring-opening with different alcohols like diethylene glycol [2, 4, 18]. The structure of the resulting oil-based polyol depends on the chemical modification method and the distribution and position of the carbon-carbon double bonds in the fatty acid chain of an oil.

The aim of this work is to synthesize a rapeseed oil-based polyol to be further used in the production of solid biobased PUs. Commercial microcellulose was used as a filler, while glycerol was used as a reactive modifier in order to increase the crosslinking density and to improve the mechanical properties

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of synthesized materials. The characterization of the cured polyurethanes included density measurements, water and toluene absorption, morphological analysis and mechanical and dynamic-mechanical tests.

2 EXPERIMENTAL

2.1 Materials

A rapeseed oil-based polyol (ROPO) (prepared by epoxidation with peracetic acid generated "in situ," followed by oxirane ring-opening with diethylene glycol, as reported in a previous work [3]) has been used as a green polyol (hydroxyl value = 264.2 mg KOH/g) in the synthesis of PUs with polymeric diphenylmethane diisocyanate (pMDI – Rubinate 5005, Huntsman Polyurethanes, equivalent weight of 131 g/eq). Glycerol, Gly (FLUKA), was used as a reactive polyol to modify the reference formulation. The molar ratio of NCO to OH groups was adjusted to 1.1 for each formulation. The catalyst used was dibutyltin dilaurate, DBTDL (Aldrich). Moreover, commercial microcellulose (Arbocel UFC-100, Rettenmaier, with an average fiber length of 8 μm and an average fiber thickness of 2 μm) was added as a bio-derived filler.

2.2 Polyurethane Preparation

Solid polyurethane composites were prepared according to the formulations reported in Table 1. ROPO and glycerol as well as the MC were dehydrated until constant weight under vacuum before each reaction (80 °C for the polyols and 50 °C for the MC). The ROPO was mixed with the catalyst (1 wt% with respect to the polyol weight) and glycerol or MC using an overhead stirrer and then isocyanate was added. The reactive mixture was homogenized and placed in a closed aluminum mold under pressure applied with a hydraulic press (1 MPa) at 70 °C for one hour, then the temperature was raised to 120 °C

and kept for one hour to finally cool the system down to room temperature.

2.3 Curing Monitoring

The evolution of the storage (G') and loss modulus (G'') during curing was followed using an Anton Paar Rheometer (model Physica MCR-301) provided with a CTD 600 Thermo Chamber. Isothermal scans were performed at 25 °C without adding catalyst and using a parallel-plate configuration (diameter $D = 25$ mm, gap ≈ 1 mm) in oscillatory mode with a 1% amplitude at a frequency of 1 Hz.

2.4 Characterization of the Cured Polyurethane Materials

2.4.1 Density Determination

The densities were determined by the immersion in degassed and distilled water method in accordance with ISO 1183:1987.

2.4.2 Water Absorption

Determination of water absorption was performed by immersing the samples in distilled water according to EN ISO 62:1999. The weight of the samples was recorded at different periods of time until constant weight was achieved.

The diffusivity of moisture in the samples, D (mm^2/s), was calculated assuming as valid the single-phase Fickian moisture absorption according to the following equation (ASTM D5229-92):

$$D = \left(\frac{h}{4M_{\infty}} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (1)$$

where h is the average specimen thickness (mm); M_{∞} is the effective moisture equilibrium content (%); and $\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}$ is the slope of moisture absorption plot in the initial linear portion of the curve ($\text{seconds}^{-0.5}$).

Table 1 Polyurethane formulations.

	0MC 0Gly	1 MC	2 MC	3 MC	5 MC	5Gly	10Gly	15Gly
ROPO (g)	100	100	100	100	100	95	90	85
MC (g)	-	1	2	3	5	-	-	-
Gly (g)	-	-	-	-	-	5	10	15
DBLE (g)	1	1	1	1	1	1	1	1
pMDI (g)	66.4	66.4	66.4	66.4	66.4	85.6	104.8	124.0

2.4.3 Swelling in Toluene

Square samples of the films were weighed using an analytical balance and kept immersed in toluene in test bottles at 25 °C. Two parallel tests were run for each obtained PU material. Weight of the swollen sample was determined at various time intervals until it was constant. After the equilibrium swelling was achieved, the sample was dried in a vacuum oven (80 °C) up to a constant weight.

The results of the sorption experiments have been expressed as moles of toluene absorbed by the PU, mol percent uptake, Q_t , [%mol/g]:

$$Q_t = \frac{m_t - m_0}{m_0 \cdot M_t} \cdot 100 \quad (2)$$

where m_t is the weight of swollen sample after time interval t , [g]; m_0 is the initial weight of dry sample, [g]; and M_t is the molecular weight of toluene, [g/mol]. The sol fraction of the sample was calculated from the weight difference before and after immersion in toluene.

2.4.4 Scanning Electron Microscopy (SEM)

The materials were analyzed using SEM (SEC Philips model SEM 505) in order to evaluate the morphologies of the samples containing different contents of glycerol or MC. The samples used for the microscopy study were taken from the broken pieces of the tensile test specimens.

2.4.5 Dynamic-Mechanical Analysis (DMA)

The measurements were done using a PerkinElmer dynamic mechanical analyzer, DMA 7e, with tensile bar geometry (sample dimensions of $20 \times 5 \times 1$ mm³), under continuous nitrogen flow. The frequency of forced oscillations was 1 Hz, the heating rate 10°C/min and the dynamic and static stresses were kept at 200 and 240 kPa, respectively. At least two replicate determinations were made to ensure the reproducibility of results. The glass transition temperature, T_g , of each sample was determined as the temperature of the maximum in the peak of the loss factor ($\tan \delta$) curve.

To correlate the thermal and mechanical properties of the PUs with crosslinking density, the following equation was used:

$$\nu = \frac{E'}{RT} \quad (3)$$

where ν is the crosslinking density, [mol·m⁻³]; R is the gas constant, [J·mol⁻¹·K⁻¹]; and T is the absolute temperature, [K], at which the plateau E' was determined, [Pa].

2.4.6 Tensile Tests

Uniaxial tensile tests were carried out using an Instron 8501 Universal testing machine, according to ASTM D638-94. Specimens from each sample were cut using a dog-bone shaped driller and tested at a crosshead speed of 1 mm min⁻¹. Four specimens of each sample were tested. The elastic tensile modulus, the stress and deformation to rupture were calculated from the obtained stress-strain curves.

3 RESULTS AND DISCUSSION

3.1 Curing of the ROPO/pMDI Analysis

Figures 1 and 2 show typical examples of the evolution of the shear storage (G') and shear loss (G'') modulus as a function of the time for the ROPO/pMDI, reference system (0MC0Gly) and ROPO/pMDI with the addition of 5 wt% of MC and 15 wt% of glycerol, respectively, during a heating at 25 °C. Table 2 summarizes the time of crossover between the storage and loss modulus curves and the modulus value at this time for all the compositions. It is important to note that although the mentioned crosspoint is not exactly the gel time because the test was carried out at a constant frequency (1 Hz), this time can be related to the moment where the elastic contribution became more important in comparison to the viscous contribution. The reference system requires 3.1 h of curing to achieve the crosspoint between G' and G'' . All composites modified with MC show significantly longer crossover G' - G'' times and much higher shear storage and shear loss modulus during the whole curing time. The incorporation of rigid particles to the polyurethane reactive mixture can produce a delay in the

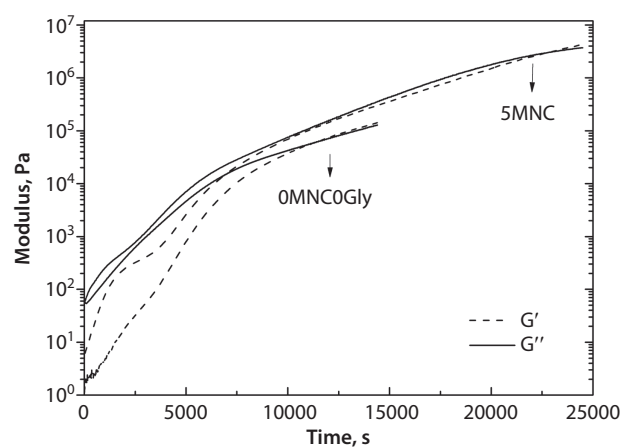


Figure 1 Evolution of storage modulus (G') and loss modulus (G'') of the reference material (0MNC0Gly) and the material with 5 wt% of micro/nanocellulose (5MNC).

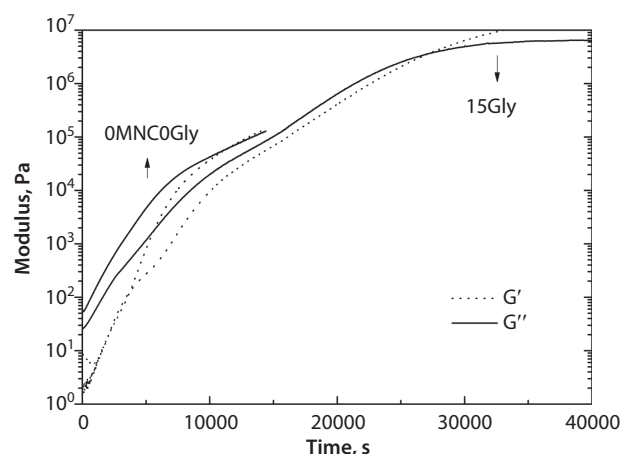


Figure 2 Evolution of storage modulus (G') and loss modulus (G'') of the reference material (0MC0Gly) and the material modified with 15 wt% of glycerol (15Gly) with respect to the ROPO mass.

Table 2 Rheological measurements during curing and T_g of postcured sample obtained by rheometry.

	$t_{\text{crossover}}$ (h)	$E_{\text{crossover}}$ (MPa)
0MC0Gly	3.16	0.06
1 MC	6.41	2.05
2 MC	5.66	1.91
3 MC	5.66	1.83
5 MC	6.30	2.96
5 Gly	5.00	1.89
10 Gly	5.16	1.87
15 Gly	7.50	3.52

gel time in comparison with the unfilled system. The particles seem to be an obstacle in the reaction process and, in this way, the crosspoint between the storage and loss modulus curves occurs after longer times as the MC increases. Moreover, the high stiffness of the particles results in the increased value of the storage modulus of the composite (as compared to the unfilled system) during the whole time interval considered. A similar trend is observed in the case of the partial substitution of the rapeseed oil-based polyol with glycerol. Generally, as more glycerol is incorporated into the formulation, the crosspoint time increases as well as the modulus reached at that time. The substitution of ROPO by glycerol of lower molar mass increases the OH group concentration in the initial reactive mixture and thus to maintain the same ratio of NCO/OH more pMDI is required. Consequently, higher concentration of reactive groups per unit mass of the initial mixture is obtained, but since the hydroxyl groups of the glycerol are not all equally reactive, changes in the rate of

crossover can be detected. As it is known, the primary hydroxyl groups are usually more reactive than the secondary OH ones, although obviously some reaction of the secondary hydroxyls can occur before all of the most reactive primary ones have been consumed [20]. However, the fast reaction of the primary hydroxyls in the Gly can give this monomer the initial behavior of a chain extender to finally behave as a crosslinker with the reaction of the secondary hydroxyl at longer times. This behavior would result in a longer time to reach the crossover when glycerol is added. Besides, the addition of glycerol that has higher functionality per unit of mass than the ROPO generates higher amounts of crosslinking points that are reflected in higher storage modulus.

3.2 Characterization of the Cured Materials

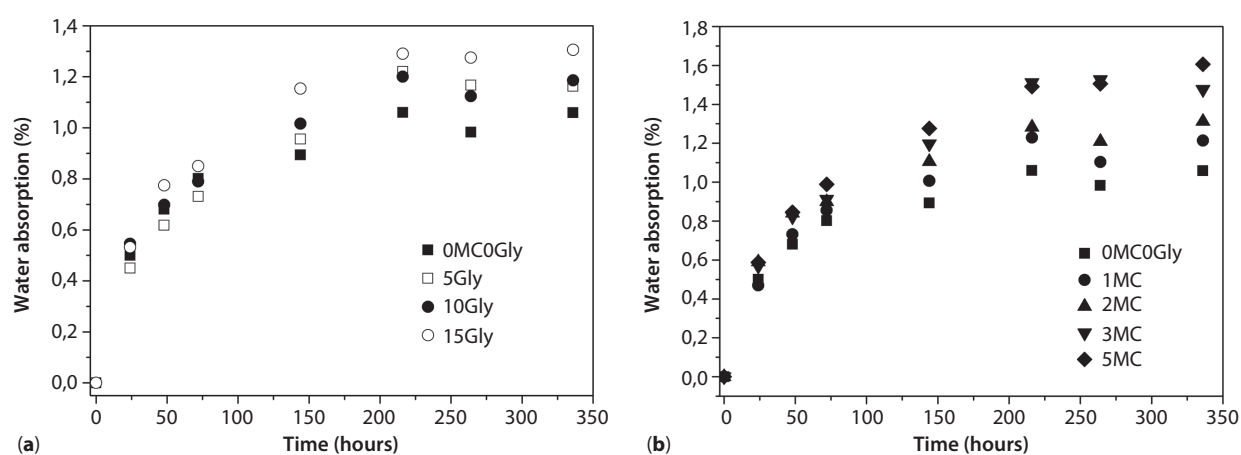
Table 3 shows density, water absorption and toluene mol percent uptake values of the cured polyurethanes. The density of the materials increases with the incorporation of MC. The experimental values of the density of the filled materials were found to be between the values of the densities of the commercial MC ($\sim 1.5 \text{ g/cm}^3$) [21] and that of the reference material, 0MC0Gly (1.126 g/cm^3). However, the increase is much more important than can be calculated from the rule of mixtures, which may indicate some changes also occurring in the polymer due to the presence of the MC.

The water absorption also increases with MC content, which is associated with the hydrophilic character of the cellulose particles. On the contrary, the toluene mol percent uptake decreases with MC content (Table 3 and Figure 3a). This behavior is associated with the highly polar hydroxyl groups in the cellulose surface that keep away the nonpolar toluene, decreasing the solvent organic absorption as more MC is incorporated into the material.

Similarly, the incorporation of glycerol in the polyurethane formulation generates an increase in density, although the largest differences appear at low glycerol concentration and a leveling off trend is observed at higher concentrations. These changes in formulation also lead to the increase of water absorption, while significantly decreasing the toluene absorption (Table 3 and Figure 3b). As the rapeseed oil-based polyol is replaced by the reactive glycerol (small molecule with three reactive groups), an increase of the crosslinking density in the network occurs, leading to the increase of material density and the reduction of the capability of absorbing the organic solvent. On the other hand, the hydrophilic character of PU samples is increased with the addition of glycerol and thus the water absorption is increased.

Table 3 Density, water absorption and toluene mol percent uptake of the polyurethanes.

Sample	Density (g/cm ³)	Water absorption at equilibrium (wt. %)	Q _t (% mol/g)
0MCOGly	1.1260 ± 0.0005	1.06 ± 0.02	0.3389 ± 0.0039
1MC	1.1491 ± 0.0014	1.21 ± 0.02	0.3141 ± 0.0004
2MC	1.1436 ± 0.0013	1.31 ± 0.02	0.3170 ± 0.0011
3MC	1.1540 ± 0.0007	1.48 ± 0.04	0.3100 ± 0.0006
5MC	1.1601 ± 0.0000	1.61 ± 0.12	0.2983 ± 0.0001
5Gly	1.1576 ± 0.0092	1.16 ± 0.09	0.1124 ± 0.0102
10Gly	1.1813 ± 0.0053	1.19 ± 0.08	0.0213 ± 0.0009
15Gly	1.1816 ± 0.0091	1.31 ± 0.06	0.0132 ± 0.0024

**Figure 3** Moisture absorption as a function of time for the materials modified with MC (a) and Gly (b).

The level of absorption and swelling by action of solvents is directly related to the crosslinking density of the investigated materials. Reduced absorption of organic solvents supposes importance, since most polymers worsen their physical-mechanical properties after swelling in the presence of a solvent. Therefore, polymers for commercial applications should be chemically resistant and retain their mechanical strength and dimensional stability. On the other hand, the retention of organic solvents could be related to the crosslinking density of the analyzed material.

The diffusion coefficients of water absorption calculated using Equation 1 and Figures 3a and 3b do not show a clear trend as an effect of the addition of glycerol or MC, however, all the values are in the range of 1×10^{-9} – 1.6×10^{-9} cm²/s.

3.3 Morphological Analysis

Figure 4 shows micrographs obtained by scanning electron microscopy at different magnifications of the fracture surfaces resulting from tensile testing. The

images show non-foamed matrices for all the analyzed materials.

The micrograph corresponding to the reference polyurethane (0MCOGly) presents the features of fragile fracture. With the incorporation of MC, the roughness of the surfaces increases and plastic deformation can be observed, indicating that the particles are an impediment to the progress of the advancing crack. For the highest percentages of MC (3 and 5 wt%) in the composites, zones with particle agglomeration could be observed at the highest magnifications (x5000 and x10000).

Inversely, as more glycerol is introduced in the reactive mixture of the polyurethane formulation, the smoothness of the surfaces increases and the same happens with the fragility of the material.

3.4 Dynamic-Mechanical Analysis

Figures 5 and 6 show the dynamic mechanical response of the polyurethanes with different content of MC and glycerol, respectively. The storage modulus in the glassy and rubbery regions of the material,

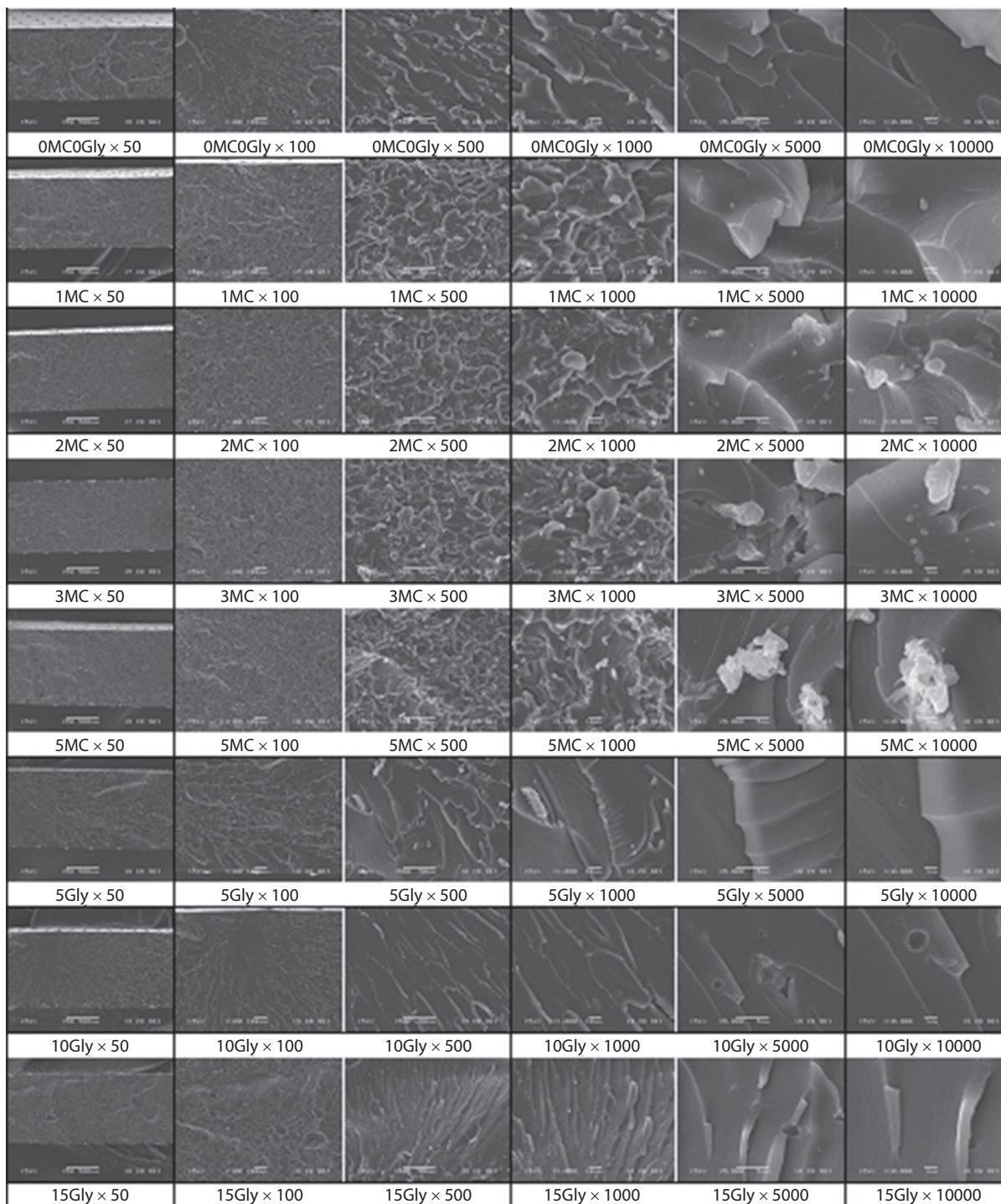


Figure 4 Scanning electron microscopies for the materials modified with MC and Gly.

in general, increases with the MC content (Figure 5a), which is attributed to the addition of high modulus particles.

On the other hand, $\tan \delta$ vs temperature curves (Figure 5b) show that the maximum in the glass transition temperature corresponds to the unreinforced material, while all the composites present lower

values. Although the introduction of a small MC concentration causes the reduction of T_g of the sample, there is a trend of increasing T_g as the MC concentration is increased.

The MC contains reactive OH groups that can consume a part of the NCO groups of the pMDI. In such case, the incorporation of MC can lead to a less

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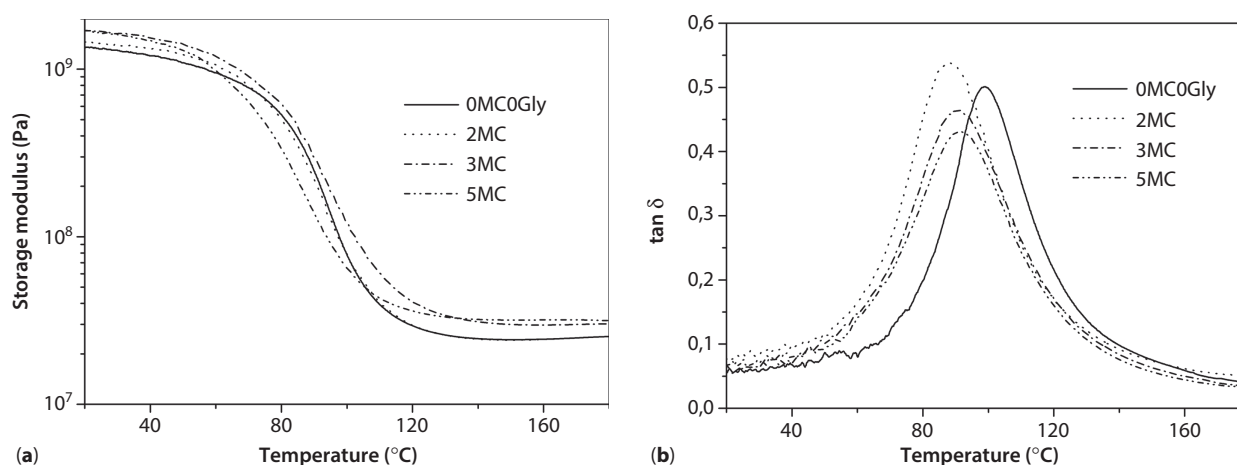


Figure 5 Storage modulus E' (a) and $\tan \delta$ (b) as a function of temperature for the polyurethanes filled with MC.

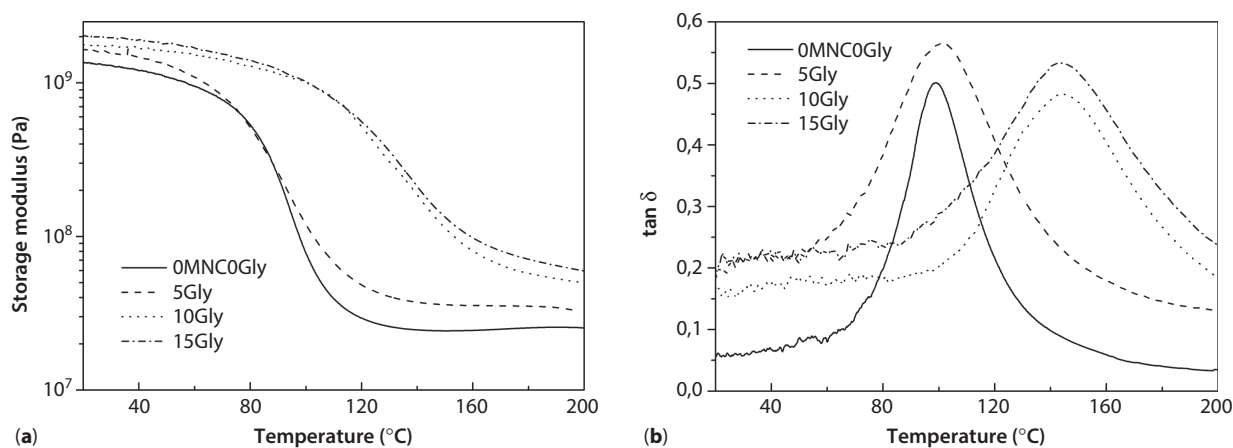


Figure 6 Storage modulus E' (a) and $\tan \delta$ (b) as a function of temperature for the polyurethanes modified with Gly.

crosslinked polyurethane, thus, a network with more dangling chains that relax at lower temperatures. With the addition of higher percentages of MC, a second and opposite effect of rigid particles that restrict the mobility of the materials starts to become the most important effect and thus the T_g increases.

Figure 6a shows the storage modulus for materials with different percentages of glycerol as a replacement of ROPO. The storage modulus increases in all the analyzed range of temperatures as more glycerol content is incorporated as the replacement of ROPO. The glycerol acts as a crosslinking agent of low molecular weight that produces an increase in the crosslinking density and consequently, the rigidity of the material increases. In addition, as a result the calculus of the crosslinking density (Equation 3) gives values of

$9.6 \cdot 10^3$, $11.8 \cdot 10^3$, $42.8 \cdot 10^3$ and $46.4 \cdot 10^3$ mol/m³, for the samples with 0, 5, 10 and 15% of Gly, respectively. The use of glycerol is more effective in increasing the modulus of these systems than the addition of MC that is micro (standard) filler.

The curves of $\tan \delta$ as a function of temperature illustrate the effect of increasing the glycerol concentration in the PU formulation (Figure 6b). The higher crosslinking density is the reason for the shift of T_g towards higher temperatures. The incorporation of the low molecular weight of crosslinking agent also modifies the structure of the network that, according to the wider relaxation observed in the temperature DMA scan, is a more heterogeneous structure (in agreement with the use of two polyols of different chemical structure and molecular weight).

3.5 Mechanical Properties

The observed increase of the tensile modulus of the materials with increasing MC content confirms the effect of the addition of the highly rigid particles on the polymer matrix, as was discussed in the analysis of DMA results. Additionally, the strength also increases with MC content, denoting a reinforcing effect of the particles that can be explained by strong interactions developed between them and the matrix through physical and chemical bonds formed between the isocyanate groups of the pMDI and the hydroxyl groups of the particle surfaces. The elongation at break also increases mainly for the formulations with percentages of MC of 3 and 5 wt%. This unusual observation for microcomposites has been previously reported by Mosiewicki *et al.* [22], who found that deformation at break increases in tung oil-based polyurethanes with 10 wt% of wood flour. The typical failure of microcomposites (initiation of the failure by interfacial debonding at multiple sites, followed by the coalescence of the cracks and catastrophic crack growth [23–25]) is not present because of good interfacial adhesion particle-matrix, which delays the final breakage of the material. Besides, the MC added to the composites and covalently linked to the polyurethane networks can act as a chain extender, behaving as the short diols used in the formulation of segmented polyurethane [20, 21].

Table 4 also presents the effect on the tensile properties of the glycerol use in the PU formulations. The tensile modulus and strength increase with increasing content of glycerol, while the elongation at break is mostly unaffected. This behavior is related to the more crosslinked structures that generate polymers of higher stiffness and strength.

4 CONCLUSIONS

A polyol based on rapeseed oil (ROPO) was a viable monomer for use in the formulation of solid

Table 4 Tensile properties of the polyurethanes modified with addition of MC and glycerol.

Sample	E (MPa)	σ_{break} (MPa)	ϵ_{break} (%)
0MC0Gly	430 ± 17	36.9 ± 1.3	19.5 ± 1.9
1MC	439 ± 21	36.4 ± 0.8	20.0 ± 2.5
2MC	465 ± 15	37.9 ± 0.6	19.0 ± 0.4
3MC	476 ± 6	38.0 ± 0.6	25.1 ± 1.2
5MC	502 ± 21	38.8 ± 0.7	25.9 ± 4.9
5Gly	478 ± 45	40.1 ± 1.4	20.2 ± 7.3
10Gly	571 ± 20	45.1 ± 5.9	21.2 ± 5.8
15Gly	598 ± 29	52.6 ± 3.1	18.2 ± 0.7

polyurethanes. The properties of a reference formulation were tuned by addition of commercial microcellulose as filler and glycerol as a reactive modifier.

In general, the rigidity and glass transition temperatures increased with the incorporation of MC and glycerol into the polyurethane. An unusual increase in deformation at break was found for the polyurethanes modified with MC. The variation of the properties was related to the high stiffness of the MC and its strong interaction with the polyurethane matrix, and to the higher crosslinking density of the polyurethane materials prepared with glycerol replacement.

An increase in the materials water absorption was observed as the content of any of the two hygroscopic modifiers was increased, while swelling in toluene was significantly reduced when glycerol was incorporated into the polyurethane formulation.

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