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Lignin-based polyurethane materials

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Abstract

Four technical lignins (Alcell, Indulin AT, Sarkanda and Curan 27-11P) were used as macro-monomers in the synthesis of polyurethane materials following two global approaches. In the first one Alcell and Indulin AT lignins were used directly as co-monomers in combination with a linear polycaprolactone (PCL) in order to produce polyurethane elastomers where lignin content varied between 10 and 25% (w/w) with respect to polyol mixture (PCL+lignin). The thermomechanical properties of the resulting materials were determined by dynamical mechanical analysis (DMA), differential scanning calorimetry (DSC) and swelling tests. In lignin-based elastomers Indulin AT showed to be more efficiently incorporated in the polyurethane network compared with Alcell lignin. Elastomers prepared with Indulin AT lignin exhibited a cross-linking density and storage modulus (rubbery plateau) higher than those of Alcell lignin-based counterpart and a lower soluble fraction. For both Alcell and Indulin AT based elastomers the glass transition temperature increased and extended over a wide temperature range with the increase of lignin content.

The second approach consisted of producing rigid polyurethane foams (RPU) using lignin-based polyols obtained after chemical modification by an oxypropylation procedure. Two polyol formulations (20/80 and 30/70, in what concerns the weight ratios between lignin and propylene oxide, PO), were used in RPU formulations and their content varied from 0 to 100% (w/w with respect to a commercial polyol, used as a reference). The resulting RPU foams were characterized in terms of density, mechanical properties, conductivity and morphology. The prepared RPU foams with lignin-based polyols presented properties, very similar to those obtained from conventional commercial polyols. RPU foams prepared with 30/70 polyols exhibited improved properties comparatively to those arising from 20/80 formulations. Exceptions were however detected in RPU foams prepared with all Sarkanda lignin based polyols and Curan 27-11P 30/70 formulation, which were found to be inadequate for RPU formulation.

1 Introduction

Polyurethanes are considered as one of the most versatile polymeric materials offering a wide range of products with various applications in diverse sectors. Rigid polyurethane (RPU) foams and elastomers belong to this class of products. Nowadays, due to economical and environmental concerns, the utilization and development of low-cost polyols from abundant and renewable biomass resources has gained an increasing attention in polyurethane industry. Lignin belongs to these biomass resources, and its application as a macro-monomer in polyurethane synthesis, has been the subject of several studies (Yoshida et al., 1990; Thring et al., 1998; Gandini et al., 2000).

Lignin is defined as a random, amorphous three-dimensional polymeric network, which does not possess a uniform, homogenous, well defined structure with well established repeating

units. Commercially available lignins are, most often, Kraft or lignosulfonates associated to the corresponding most commonly used industrial processes for wood delignification and fibres isolation (Kraft and sulphite, respectively). These lignins are largely used in dispersing and binding applications and a small part is employed in the production of specialty chemicals like vanillin and dimethylsulfoxide (Gosselink et al., 2004). Recently, sulphur-free lignins are becoming an emerging class of lignin products, partly motivated by environmental policies, but also, by less capital intensive associated technologies (Lora and Glasser, 2002). The utilization of lignin as a macromonomer in polyurethane synthesis often follows two global approaches: (i) the direct utilization of lignin without any preliminary chemical modification, alone or in combination with other polyols (Yoshida et al., 1990, Evtuguin et al., 1998, Cateto et al., 2008) or, (ii) by making hydroxyl functions more readily accessible by chemical modification, such as esterification and etherification reactions (Glasser, 1989, Gandini et al., 2002, Nadji et al., 2005).

In this work, the two approaches were studied. Four technical lignins (Alcell, Sarkanda, Indulin AT and Curan 27-11P) representing softwood and non-wood lignin types and three pulp processes: Kraft, soda and organosolv (properties shown in table 1) have been used. In the first approach Alcell and Indulin AT were used directly as a co-monomer in combination with a linear PCL. PCL was introduced into the formulation to provide flexibility and enable polymerization in bulk. In the second approach the four lignin samples were oxypropylated and the resulting liquid polyols incorporated into RPU foams, alone or in combination with other commercial polyether-polyol.

Table 1. Properties of the technical lignins used in this work

Lignin Sample	Total OH (mmol/g)	Phenolic OH (mmol/g)	COOH (mmol/g)	Ash content (% w/w)
Alcell	5.26	3.81	0.23	0.05
Sarkanda	5.26	2.41	0.62	3.26
Indulin AT	6.99	3.95	0.39	3.06
Curan 27-11P	6.21	3.63	0.47	17.0

2 Material and Methods

2.1 Rigid polyurethane foams

Materials The lignin-based polyols used in this work were obtained from the oxypropylation of four technical lignins (Alcell, Indulin AT, Curan 27-11P and Sarkanda) as described elsewhere (Cateto et al., 2007). The following terminology will be used to identify the polyol formulations used in this work: L/PO/C (ratio between lignin, PO and catalyst content). The commercial polyether polyol (Lupranol® 3323), polymeric MDI (PMDI with a functionality of 2.7), silicone surfactant (SR-321 NIAX) and the catalysts NIAX and DMCHA were kindly supplied by Elastogran-BASF (France). Glycerol and n-pentane were obtained commercially.

Foam Preparation Polyurethane foams were prepared by mixing, during 1 minute, the polyol or polyol mixture in combination with glycerol (10%, w/w), surfactant (2%, w/w), water (2%, w/w) and a catalyst combination (2%, w/w of a mixture with equal amounts of DMCHA and NIAX). Thereafter, n-pentane was added (20%, w/w) and the mixture was stirred during 30 s. Finally, the polymeric isocyanate was added and the resulting mixture vigorously stirred until the foam started to grow. Foams were left to cure during 24 hours at room temperature. The weight percentage of glycerol, surfactant, water, catalysts and, n-pentane are given relatively to total weight of polyol. The isocyanate/hydroxyl ratio (NCO/OH) chosen was of 1.1.

Foam Characterization For density and compression tests, foams were cut into cube specimens of 50×50×50 mm^3 dimensions and thereafter conditioned during 40 hours at 23ºC and 50% of humidity. The densities of the foams were determined according to ASTM D1622 standard method. The specimens were weighted and its dimensions measured. Density was calculated by dividing the mass and volume obtained for each specimen. Compression tests were conducted according to ASTM D1621 standard. Measurements were performed using a tensile instrument (Instrom model 4501) in the direction perpendicular to foam growth. A load

was applied at a crosshead speed of 5 mm/min until the specimen was compressed to approximately 15% of its original thickness. Conductivity measurements were conducted according to ASTM C177 standard. Specimens with a diameter of 90 mm and thickness of 4 mm were cut and placed in an apparatus developed to measure the thermal conductivity of insulating materials. This apparatus is composed of two plates maintained with a temperature differential. The thermal conductivity of the samples was determined when the thermal equilibrium was reached and a uniform temperature gradient thought the sample was attained. Morphology analysis of RPU foams was performed on a Quanta 200 FEI field emission scanning electron microscope (SEM). The samples were cut and gold coated before scanning. The used accelerating voltage was of 12.5 Kv and the sample was observed both in the free-rise and free-rise perpendicular directions.

2.2 Polyurethane elastomers

Materials and Formulations The lignin-based polyurethanes were prepared starting with 4,4'-methylene-diphenylene diisocyanate (MDI), policaprolactonediol (PCL) with an average molecular weight of 750 (PCL750) and two different technical lignins, Indulin AT from Meadwestvaco (South Carolina, USA) and Alcell from Repap, with different weight contents (10, 15, 20 and 25%). PCL was kindly supplied by Solvay Interox (Cheshire, UK) and MDI was commercially obtained from Aldrich.

Elastomers Preparation Lignin and PCL were degassed overnight under vacuum at 60 ºC. MDI (Aldrich) was purified by heating at 60 ºC and filtered through a heated filter just prior use. Lignin and PCL were weighed in an analytical balance in the desired proportions and the mixture homogenised by stirring during 1 hour at 80 ºC. Then, molten MDI was added and the reaction mixture thoroughly stirred during 30 s and rapidly transferred into a Teflon mould. The obtained films were left to cure during 24 hours at 80 ºC.

Elastomers Characterization Differential Scanning Calorimetry (DSC) experiments were performed using a DSC Q100 differential calorimeter (TA Instruments) working in modulated mode. Analyses were carried out from -60 to 200 ºC with a heating rate of 5 ºC/min. The oscillation period and the amplitude were 60 s and ± 1 ºC, respectively. Dynamical Mechanical Analysis (DMA) of lignin-based elastomers was carried out using a RSA3 (TA Instruments) equipment working in tensile mode. The measurements were performed at a constant frequency of 1 Hz, strain amplitude of 0.03% and a distance between the jaws of 10 mm. The heating rate was 5°C.min^{-1} and the temperature ranged from -100 to 200 ºC. The width of the samples varied from 3 to 5 mm.

3 Results and Discussion

3.1 Rigid polyurethane foams from lignin- based polyols

Oxypropylated lignin was incorporated into RPU foams formulations without performing any purification concerning the homopolymer and catalyst (KOH) contents removal. Thus, several RPU foams were prepared by varying the lignin-based polyol content from 0 to 100% (w/w). Additionally, for the 20/80/5 based formulation a more detailed study was performed. RPU foams with 25, 50, 75 and 100% (w/w) of lignin-based polyol were prepared. For the 30/70/2 formulations only foams containing 50 and 100% (w/w) of lignin-based polyol were produced. Table 2 summarizes some of the data obtained for the lignin based RPU foams produced with 20/80/5 and 30/70/2 polyols. The properties of the RPU foams produced with the commercial polyol are also shown as a reference.
The produced lignin-based RPU foams (particularly those based on 20/80/5 polyols) exhibit lower mechanical properties and density to compare with reference foams (those obtained from the commercial polyol). Additionally, it was also observed that RPU foams based on Alcell and Indulin AT polyols showed higher mechanical properties and density values to compare with those produced with Sarkanda and Curan 27-11P polyols. In fact, RPU foams prepared with 20/80/5 Sarkanda based polyols were found to be brittle presenting quite large cells, as observed in SEM micrographs (Figures not shown). For Sarkanda lignin 30/70/2

polyol, the generated mixtures were so heterogeneous that the production of RPU foams was not possible, probably because of the complex rheological properties of this polyol.

Foams produced with 30/70/2 Curan 27-11P based polyol also showed some brittleness. For RPU foam samples including 100% (w/w) Curan 27-11P based polyol no defined cells were observed by SEM. For those including 50% (w/w) irregular size and deteriorated cells were observed. In conclusion, the studied Sarkanda based polyols and the 20/80/5 Curan 27-11P seems to be unsuitable for RPU formulations.

Table 2. Density, thermal conductivity and compressive modulus of lignin based RPU foams.

L/PO/C (w/v/(%w/w))	Lignin sample/ % Lignin polyol (w/w)	Density (Kg/m^3)	Conductivity (mW/mK)	Compressive Modulus (MPa)
30/70/2	Alcell/100	22.3	25.7	3.1
	Alcell/50	25.1	26.9	3.0
	Indulin AT/100	23.1	27.4	4.0
	Indulin AT/50	23.7	29.1	3.6
20/80/5	Alcell/100	20.9	26.7	2.5
	Alcell/50	23.9	30.5	3.3
	Indulin AT/100	19.2	26.8	2.6
	Indulin AT/50	22.4	32.9	2.4
	Curan 27-11P/100	18.4	28.5	2.3
	Curan 27-11P/50	19.4	31.3	2.7
Reference Foam (100% commercial polyol)		31.1	30.3	4.6

For thermal conductivity it was observed that RPU foams produced with 100% (w/w) lignin-based polyols present the lowest conductivity values. RPU foams prepared with 20/80/5 based formulations presented cells with an elongate hexagonal well defined shape and a quite homogeneous size distribution. For comparison, foams prepared with different lignin based polyols contents, are presented in Figure 1. The observed elongate form can explain the low density and compressive modulus obtained for these RPU foam formulations. As a consequence of lower density, mechanical properties are influenced (anisotropy effect) (Hawkins et al., 2005). In fact, SEM micrographs showed that with the increase of commercial polyol content, the cells tend to become smaller and less elongate, thus explaining the observed increase of density and compressive modulus. For the studied lignin-based RPU foams, cells with very large size are often detected thus contributing to less homogeneous structures. This heterogeneity can justify the reason why no relation was found between RPU foam lignin content and the conductivity. Nonetheless, compressive modulus and density were found to correlate relatively well.

Foams produced with 30/70/2 formulations presented cells with smaller size (approximately 370 µm instead of 550 µm obtained with 20/80/5 based RPU foams) and with a more pronounced spherical form comparatively to those produced with 20/80/5 based polyols (see Figure 2). This can explain the higher density and the improved thermal conductivity and mechanical properties of the latter formulations (20/80/5 lignin-based polyols). Also, this could be associated with higher hydroxyl number and lignin content and a decrease of KOH and homopolymer contents in the final 30/70/2 polyol mixture.
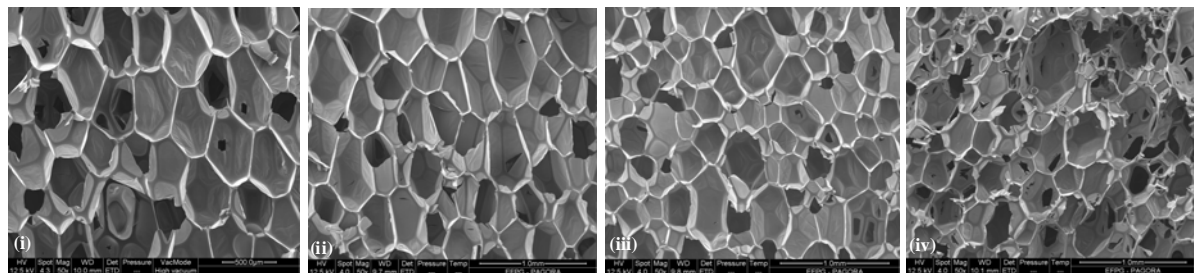

Figure 1 Scanning electron micrographs obtained for RPU foams containing 100% (w/w) for (i), (ii) 20/80/5 and (iii),(iv) 30/70/2 for Alcell and Indulin AT based polyol, respectively (free-rise direction).

3.2 Lignin-based elastomers polyurethanes

The obtained data showed that Alcell and Indulin AT produced elastomers with quite distinct properties. Figure 2 shows the effect of Alcell and Indulin AT content on the storage modulus (E´) and loss tangent (tan δ) with temperature. As can be observed for both Alcell and Indulin based elastomers, the maximum of tan δ shifts towards higher temperatures and the peak become broader as the lignin content increased. This trend was also confirmed by DSC analysis. Thus, glass transition temperature (Tg) increases with the increase of lignin content and the associated transition temperature range also increases with the increase of lignin content. Yoshida et al. (1990) pointed out that the increase of the transition temperature range may reflect structural heterogeneities in the network structure, e.g., a broad distribution of molecular weights between cross-linking points may exist. Also, the shift observed for Tg with the increase of lignin content must be due to an increasing of lignin incorporation. It is well know that increasing of cross-linking density introduces restrictions on the molecular motion thereby increasing the Tg value.

The dependence of storage modulus with temperature observed for lignin-based elastomers corresponded to that obtained for typical cross-linked polymers. For Alcell lignin elastomers the E´ in the rubbery region remained approximately constant with the increase of lignin content. Cross-linking density, determined from DMA data and soluble fraction also exhibit the same trend, i.e., the increase of lignin content did not yield significant modification neither concerning the cross-linking density nor that related to soluble fraction with. Soluble fraction and cross-linking density values were found to be approximately 0.085 and 0.28 × 10^{-3} mol/cm^3, respectively.

The E´ (rubbery region) of Indulin AT based elastomers increased with the lignin content until a value of 20% (w/w). Among the prepared materials incorporating 20 and 25% (w/w) no significant difference was noticed. The same trend was observed for cross-linking density, which increases from 0.6 × 10^{-3} to 1.0 × 10^{-3} mol/cm^3, as the lignin content increases. Regarding the soluble fraction a slight linear increment was observed from 4.4 to 7.5% (expressed in w/w %). Nevertheless, for a given lignin content the percentage of the soluble fraction was always lower than those obtained for Alcell based elastomers. This indicates that the incorporation of Indulin AT lignin in the polymer network was more effective than that of Alcell counterpart. The increase of cross-linking density and E´, for Indulin AT-based samples, can reflect more effective reactions between lignin hydroxyl groups and isocyanate functions. In fact, in comparison with Alcell, Indulin AT lignin presents higher hydroxyl group content, particularly, a higher aliphatic hydroxyl content (known to be more reactive with isocyanates to compare with phenolic ones). Also, Yoshida et al. (Yoshida et al., 1990) found that medium and high molecular lignin fractions act as cross-linking points, whereas low molecular weight fractions act more like a chain extender. This can also explain the different properties observed with Alcell and Indulin AT based elastomers since Alcell lignin has a weight average molar mass (M$_W$) much lower that that of Indulin AT homologue, i.e., 7281 and 13979 g/mol (determined from DMF/LiBr solutions using a GPC and based on polystyrene calibration), respectively.
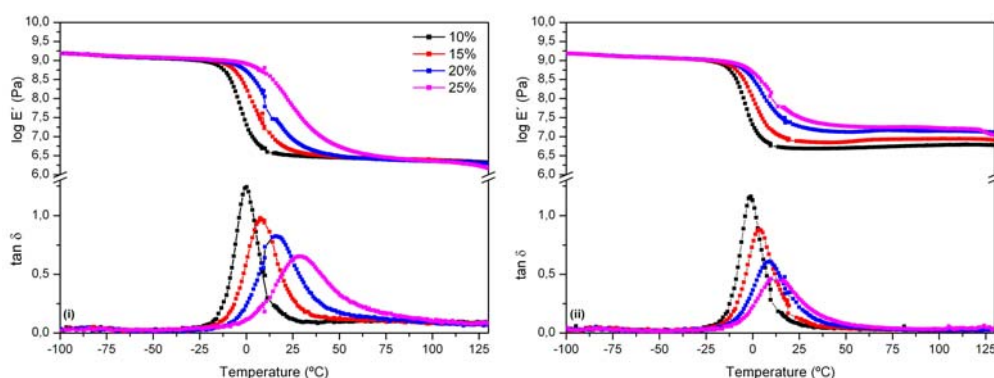

Figure 2 Storage modulus and tan δ as a function of temperature for elastomers containing 10, 15, 20 and 25% (w/w) of (i) Alcell and (ii) Indulin AT lignin.

4 Conclusions

This study provides irrefutable evidence about the possibility to incorporate lignin in polyurethane materials. A wide range of polyurethane materials presenting properties which depended on the lignin type and content introduced. Moreover, both approaches of using lignin (as such or after chemical modification, oxypropylation) yielded materials with very promising properties. In most cases, these materials exhibit properties similar to those of conventional ones, thus presenting a viable option to rationally valorise an abundant renewable industrial by- product.

Acknowledgements

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