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Organic Acid Lignin-based Polyurethane Films: Synthesis Parameter Optimization

Laurence Llovera,^a Bouchra Benjelloun-Mlayah,^{a,*} and Michel Delmas^{a,b}

Polyurethane (PU) films were prepared by solution casting using a three-component system, namely, a novel solvolytic lignin, polyethylene glycol (PEG), and tolylene 2,4-diisocyanate (TDI), with dibutyltin dilaurate as a catalyst. An important objective was to incorporate as much lignin as possible. To this end, PU film synthesis was optimized by varying the lignin content (30 to 70 wt.% with respect to PEG), isocyanate-to-hydroxyl (NCO/OH) stoichiometry (0.8, 1, 1.2, 1.5, and 1.8), and PEG molecular weight (400, 600, and 1000). The results showed that the films derived from PEG 600 and a NCO/OH ratio of 1.5 were synthesized with a maximum content of 70% lignin, with respect to PEG. The effects of lignin content on the tensile properties and the thermostability of the PU films were studied. The onset decomposition temperature (TOD) of the lignin PU films reached an average limit of 310 °C, regardless of the lignin content, and 260 °C for a PU film without lignin. Thus, the addition of lignin, as a PEG substitute in polyurethane films, leads to better thermal stability. Furthermore, breaking stress, Young's modulus, and Shore hardness of PU films increased constantly with lignin content, without reaching a maximum.

Keywords: Organic acid lignin; Polyurethane films; Tensile property; Thermostability

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INTRODUCTION

Lignin is found in the cell walls of plants, and it is the most abundant natural aromatic polymer, constituting about 15 to 30% of wood and 12 to 20% of annual plants (Cateto *et al.* 2011). Lignin is formed between the wood fiber walls and mainly acts as a cement-like material, imparting structural rigidity to the wood.

Recently, industrial lignin has attracted worldwide attention because it can be used as a sustainable alternative to petroleum-based, nonrenewable materials (Cateto *et al.* 2008). Lignin is a good raw material for polymeric synthesis because it is renewable and abundant, has intrinsic biodegradability, is a by-product of the pulp industry, and contains various reactive moieties, *e.g.*, free aliphatic and phenolic hydroxyl groups, which can be used in a wide range of chemical reactions.

The vast majority of lignin is produced through the kraft process; however, a small proportion of lignin production consists of liginosulfonates from sulfite pulping (Lancefield and Westwood 2015). In both cases, the extracted lignin is severely chemically altered compared with native lignin. Therefore, preliminary purification is necessary before lignin can be used extensively in polymeric materials. This purification can take the form of Indulin AT, a purified kraft pine lignin (Beis *et al.* 2010), or purified lignin from the LignoBoost process (Öhman *et al.* 2007a,b). Unconventional pulping methods such as

organosolv processes (Milox, Acetosolv, ASAM, Organocell, Alcell, CIMV) (Duval and Lawoko 2014) allow lignin to maintain a structural profile closer to native lignin than those produced using other industrial processes.

From a structural point of view, lignin can be characterized as an amorphous heterogenic polymer with high contents of aromatic units in its structure and three types of hydroxyl groups (aliphatic, phenolic, and carboxylic). These functional groups make the organosolv lignin used in the reactions serve as a donor of hydroxyl groups rather than just being incorporated as a filler in blends (Rösch and Mülaup 1994; Belgacem *et al.* 2003; Kubo and Kadla 2004; Xue *et al.* 2015). The groups can react with isocyanates to form polyurethanes (PU), where lignin serves as the hard segment in the polyurethane structure (Thring *et al.* 1997; Evtuguin *et al.* 1998; Thring *et al.* 2004; Saito *et al.* 2013) and provides mechanical strength to the polymer. The soft segment of the polyurethane structure, PEG for instance, provides rubbery flow characteristics (Sen *et al.* 2015).

The synthesis of Alcell[®] lignin-based polyurethane has been investigated (Thring *et al.* 1997; Vanderlaan and Thring 1998; Ni and Thring 2003; Thring *et al.* 2004). A three-component system of lignin, polyethylene glycol (PEG), and diisocyanate has been used to obtain polyurethane films (Vanderlaan and Thring 1998; Thring *et al.* 2004). Despite the more reactive properties of Alcell[®] lignin compared with lignosulfonates or kraft lignins, its structure does not allow a PEG substitution ratio beyond 30 wt.% (Thring *et al.* 2004) or 35 wt.% after fractionation (Vanderlaan and Thring 1998).

Due to its particular structure (Banoub and Delmas 2003; Banoub *et al.* 2007; Banoub *et al.* 2015), up to 40 wt.% (with respect to PEG) lignin resulting from the CIMV process, called Biolignin[™] (BL) (Delmas 2008; Snelders *et al.* 2014), has been included in the synthesis of polyurethane films (Wang *et al.* 2013). The CIMV process, which takes place in organic acid media, offers a new bio-refining alternative because it allows the separation of cellulose, lignin, and hemicelluloses, which are the main components of lignocellulosic biomass. Studies characterizing BL by APPI-MS have shown that the native lignin polymer is composed of a mixture of linear polycondensed coniferyl (G), syringyl (S), and p-hydroxyphenol (H) units (Banoub *et al.* 2015). Moreover, BL is characterized by a low molecular weight ($M_n = 933$ g/mol).

The properties of BL have allowed this macromolecule to be used as a co-reactant in the synthesis of different bio-materials, such as polyurethanes (Wang *et al.* 2013). Wang *et al.* (2013) demonstrated the feasibility of using BL as a source of hydroxyl groups in the synthesis of polyurethane with PEG 1000 and TDI. The tests were conducted with a NCO/OH ratio of 1.15, and the weight ratios of lignin to PEG were varied from 0 to 50%. Considering the mechanical and thermal properties, these results showed that BL can be used in a ratio of 40% with respect to PEG. Beyond this value, the obtained polyurethanes do not have the required properties.

The objective of this work is to optimize the synthesis of non-modified, BL-based polyurethane films to obtain a maximum degree of PEG substitution by lignin and then create value-added, high-performance polyurethanes with acceptable mechanical and thermal properties. The effects of lignin content (0 to 70 wt.% with respect to PEG), isocyanate-to-hydroxyl (NCO/OH) stoichiometry, and PEG molecular weight on the mechanical and thermal properties of the lignin-derived polyurethane were examined. Moreover, the solvent and the type of isocyanate were also studied.

EXPERIMENTAL

BL Extraction

Lignin was extracted from wheat straw using a pilot-scale CIMV organosolv process (Pomacle, France). The CIMV organosolv process consists of fractionation of lignocellulosic materials using an acetic acid/formic acid/water (55:30:15, w/w/w) solution at 105 °C and atmospheric pressure (Avignon and Delmas 2000; Benjelloun-Mlayah *et al.* 2006; Delmas 2008). After 3.5 h, around 90% of lignin and hemicelluloses were dissolved in the acid medium. The extracted lignin was separated from the hemicelluloses by adding water to the liquor (Delmas and Benjelloun-Mlayah 2011). Lignin was recovered by filtering, washing, and drying (95% DM) the liquid suspension.

BL Composition and Characterization

Ash content

Ash content was determined by the combustion of 1 g of sample (accuracy: 10⁻⁴) with a known moisture content. The sample was placed in an oven at 600 °C for 24 h.

Protein content

Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS/O elemental analyzer (Waltham, MA, USA). The protein content was deduced from the percentage of nitrogen using a specific nitrogen-to-protein conversion factor, which was 5.4 for wheat straw (Mariotti *et al.* 2008).

Residual hemicellulose content

The residual hemicellulose content in the organosolv lignin was determined according to standard method DIN 54361:1976-01 (1976), adapted to a lignin sample.

Lignin content

The total lignin content (Klason lignin) was determined as the sum of acid-insoluble lignin (AIL) (TAPPI 222 om-11 2011) and acid-soluble lignin (ASL), (TAPPI UM250 1985) adapting TAPPI standard methods to a lignin sample.

Gel permeation chromatography (GPC)

The molecular-average weights (M_w and M_n) of CIMV lignin were determined by gel permeation chromatography (GPC) using polystyrene standards for calibration. GPC analyses were carried out on a Waters 1515 isocratic HPLC pump (Milford, MA, USA) equipped with a Waters 2414 refractive index detector. Three stainless steel columns (Phenogel, 300 × 7.8 mm, 5 μm) connected in series and packed with a styrene-divinylbenzene copolymer (Phenomenex Inc., Torrance, CA, USA) of porosity 100, 500, and 103 Å were used.

Total hydroxyl group content

Total hydroxyl group content (phenolic and aliphatic) was obtained by GC analysis on propionylated lignin and benzyl hexanoate as an internal standard (Månsson 1983). The analysis utilized a DB-5 capillary column of fused silica and flame ionization detector (FID). The chromatographic conditions were as follows: speed of carrier gas (helium), 12 psi; injector temperature, 200 °C; temperature program, 60 °C for 1 min, 60 to 140 °C at

15 °C/min, and 140 to 250 °C at 5 °C/min; final temperature: 250 °C for 10 min; Detector temperature, 220 °C; speed of carrier gas (helium), 12 psi; and injection volume, 0.5 µL.

Phenolic hydroxyl group content

The content of phenolic hydroxyl groups was determined by GC analysis after aminolysis (Månsson 1983). Aminolysis is a direct method based on the fact that the rate of deacetylation of aromatic acetates in pyrrolidine, under mild conditions, is much greater than that of aliphatic acetates.

The analytical conditions for this assay were the same as those applied to the determination of total hydroxyl content. BL was dehydrated at 50 °C for 24 h before testing. The average particle size was determined by laser granulometry using a Mastersizer 2000 particle analyzer from Malvern Instruments (Malvern, UK).

PU Film Synthesis

A weighed quantity of lignin was initially solubilized in tetrahydrofuran (THF, 99%, extra pure, stabilized with BHT, purchased from Acros Organics (Fisher Scientific, Illkirch, France) or 1,4-dioxan (stabilized with approximately 25 ppm of BHT, purchased from Panreac (Castellar del Vallès, Spain) for 10 min in an ultrasonic bath.

Dibutyltin dilaurate catalyst (DBTDL, 95% Sigma-Aldrich, St. Louis, MO, USA), in concentrations of 2% of the total mass of TDI, BL and PEG, diisocyanate (MDI, 4,4'-diphenylmethane diisocyanate, 98% or TDI, 95%, Sigma-Aldrich), and PEG (400, 600, and 1000, Acros) were then added, and the resultant solution was stirred for 2 h at 30 °C.

The solvent was evaporated under vacuum (0.05 bar absolute) to create a flowable prepolymer, which was poured onto a rectangular Teflon mold with a lid. It was necessary to cover the mold with a 1-cm thick Teflon lid and place a heavy object on top to prevent the film from bending and to avoid the presence of small voids caused by rapid solvent evaporation. Cross-linking was first performed at room temperature for 48 h. The final curing was carried out in an oven at 50 °C for 24 h, then for an additional 12 h at 50 °C without the lid.

THF is the solvent normally used for polyurethane synthesis. However, BL is more soluble in 1,4-dioxan. When using THF, numerous cracks were formed during crosslinking, which was not observed with 1,4-dioxan. The saturated vapor pressure of THF was 193 mbar at 20 °C, while that of 1,4-dioxan was 38 mbar. For these reasons, 1,4-dioxan was selected as the solvent.

The choice of isocyanate for PU production is governed by the properties required for end-use applications. To prepare rigid PU, aromatic isocyanates are generally chosen. MDI and TDI are used almost entirely for the production of polyurethane polymers (Greim 2012). MDI exists in the form of white powder, while TDI is liquid. Because of the low solubility of MDI in 1,4-dioxan, white marks appear in polyurethane films after reticulation. The tests in this work were therefore been conducted with TDI.

Infrared Spectroscopic Analyses (ATR-FTIR)

The samples were analyzed using ATR-FTIR (Attenuated total reflectance system-Fourier transform infrared) spectroscopy on a PerkinElmer Spectrum 100 Universal ATR-FTIR instrument equipped with a diamond/ZnSe crystal single reflection (Waltham, MA, USA), in the wavenumber range of 600 to 4000 cm⁻¹, at a resolution of 2 cm⁻¹.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed on an ATG-DSC1 model (Mettler-Toledo, Columbus, OH, USA). Samples (2 to 13 mg) were heated from 18 °C to 500 °C at a heating rate of 20 °C/min in an Al₂O₃ crucible under a nitrogen atmosphere with a flow rate of 100 mL/min. The weight loss was recorded.

Mechanical Characteristics of PU Films

Shore hardness

A durometer is used to measure the hardness of rubber or rubber-like materials such as polyurethanes or plastics. Durometers measure hardness by penetrating an indenter into the PU sample. The calibrated reading is expressed as a number value, which is a whole number between 0 and 100 and the letter A or D. The hardness increases with this number; the letter A represents the most flexible grade. Type A is applicable to polyurethane films.

Young's modulus

Young's moduli were calculated according to standard NF EN ISO 527-1 (2012), with calculations made for 0.25% and 0.5% deformation.

Stress-strain characteristics

Breaking stress and elongation at break were evaluated using an Instron® Model 3367 series dual column system (Norwood, USA) with a load capacity 5 kN and a crosshead speed of 20 mm/min. The test specimens were conformed to the dimensions shown in Fig. 1 (Type I specimen), according to the standard test method for tensile properties of plastics (ASTM D 638-02a 2003). Tensile characteristics were calculated on the basis of the following dimensions: length, 165 mm; width, 13 mm; and thickness, 3 mm. Three specimens of each BL-PU film sample were used for tensile tests (Fig. 2).

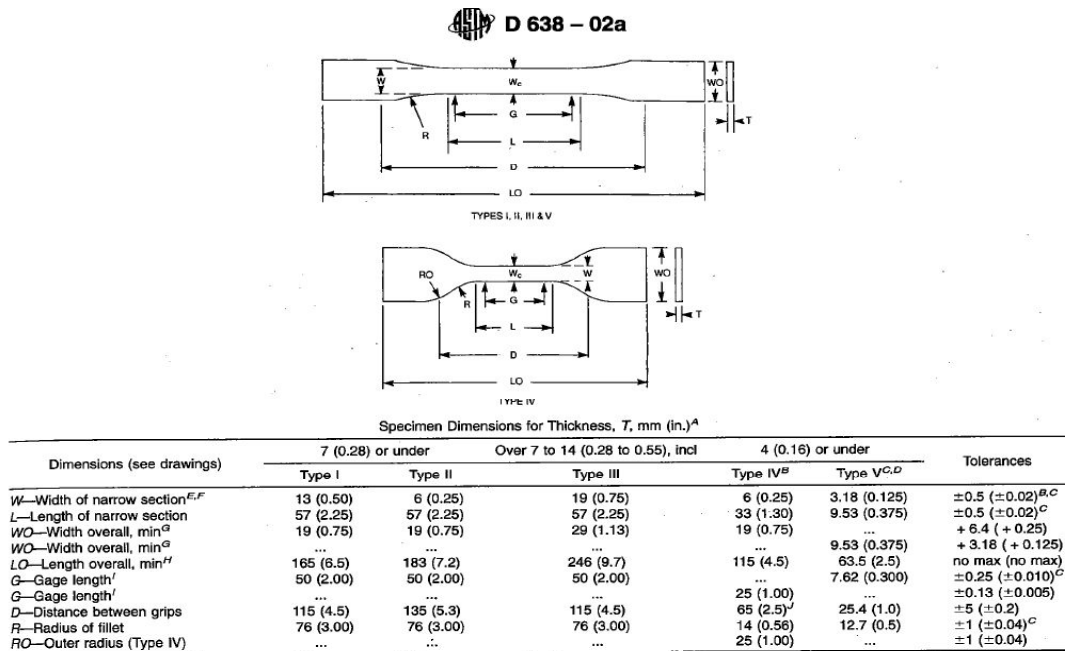


Fig. 1. Specimen standard characteristics (ASTM 2003)



Fig. 2. PU film sample for stress-strain testing

RESULTS AND DISCUSSION

BL Composition and Characterization

The composition of lignin used in polyurethane synthesis is shown in Table 1. Some residual pentoses were found in BL. These pentoses came from the hemicelluloses contained in biomass because of the soft hydrolysis conditions used in the CIMV process. Some biomass proteins were also found in lignin. The weight-average (M_w), number-average (M_n), and polydispersity P (M_w/M_n) values of the BL are given in Table 2.

Table 1. BL Composition

Dryness (%, DM)	Klason Lignin		Ash Content (%, DM)	Protein Content (%, DM)	Hemicelluloses Content (%, DM)
	AIL (%, DM)	ASL (%, DM)			
94	87.01	2.41	0.71	6.48	3.67

Table 2. BL Characterization

Molecular Weight			Aliphatic Hydroxyl Group	Phenolic Hydroxyl Group	Hydroxyl Group Acetylated	Hydroxyl Group Formylated
M_n (g/mol)	M_w (g/mol)	P (M_w/M_n)				
933	1951	2.09	(mmol/g Dried of Biolignin™)			
			1.5	2.1	0.6	0.9

These values are among the lowest observed in industrial lignins, such as kraft lignins, liginosulfonates, or Alcell lignins, which are between 1.6 and > 100 (Baumberger *et al.* 2007). The narrow distribution suggested that oligomers of CIMV lignin are more uniform than in typical industrial lignins.

As previously reported (Evtuguin *et al.* 1998), organosolv procedures are attractive because the organic-solvent-water media produces lignins with a high content of hydroxyl groups, low molecular weight, low polydispersity, and any sulphur-containing moieties. During the CIMV process, some hydroxyl groups are esterified. This feature gives BL a less dense structure than conventional organosolv and makes free hydroxyl groups more accessible to reactions with isocyanate.

Due to its enhanced reactivity coupled with a low average molecular size (44 μm), BL seems to be a macro monomer more appropriate than conventional lignins for lignin-based PU synthesis.

Effect of NCO/OH Ratio and PEG Molecular Weight

The selected solvent was 1,4-dioxan, and the diisocyanate was TDI. In a preliminary study, Wang *et al.* (2013) synthesized BL-based polyurethane films with PEG 1000, a NCO/OH ratio of 1.15, and TDI as the isocyanate source. Considering the thermal and mechanical properties, the lignin PU films performed the best with a 40% lignin substitution rate (with respect to PEG).

The effects of the chain length of PEG and the NCO/OH ratio have been reported in numerous publications. Thring *et al.* (2004) studied the effect of molecular weight (200, 400, 1000, 1500, and 2000) on the ultimate properties of Alcell lignin-derived PU. In another study (Thring *et al.* 1997), they investigated the effects of lignin content and NCO/OH ratio (from 1 to 2.75) on the mechanical properties of bio-based PU. Somani *et al.* (2006) examined both the effects of chain length of PEG (200, 400, and 600) and crosslink density (NCO/OH: 1, 1.3, and 1.7) on the properties of polyurethanes. These studies have shown that mechanical and thermal properties of lignin-derived polyurethanes are influenced by the degree of cross-linking as well as the amount of the soft and hard segments in the resin network.

In the current work, the combined influence of these two parameters was studied by varying the molecular weights of PEG (400, 600, and 1000) and the NCO/OH ratio from 0.8 to 1.8, with PEG substitution rates by CIMV lignin from 0 to 70 wt.%. The NCO/OH ratio (ratio of isocyanate to hydroxyl groups) is given by the following equation,

$$\text{NCO/OH} = W_{\text{TDI}} [\text{NCO}] / W_{\text{BL}} [\text{OH}]_{\text{BL}} + W_{\text{PEG}} [\text{OH}]_{\text{PEG}} \quad (1)$$

where W_{TDI} , W_{BL} , and W_{PEG} are the weight percentages of TDI, BioligninTM, and PEG 600, respectively. $[\text{OH}]_{\text{BL}}$ and $[\text{OH}]_{\text{PEG}}$ are the hydroxyl ion concentrations in the sample of BL (3.54 mmol/g) and in the polyethylene glycol (5 mmol/g, 3.3 mmol/g, and 2 mmol/g for PEG 400, 600, and 1000, respectively). $[\text{NCO}]$ is the concentration of isocyanate groups in the TDI (11.5 mmol/g).

There was first a visual pre-selection of BL-derived polyurethane films: those designated as “acceptable” were neither too brittle nor too flimsy to be tested. Nominally, films produced from the NCO/OH ratio of 0.8 were too weak or brittle to be tested. As the NCO/OH ratio increased, there was more cross-linking between the isocyanate and hydroxyl groups, thus giving PU films better mechanical properties. Suitable ratios were higher than 0.8.

Many works (Reimann *et al.* 1990; Thring *et al.* 1997, 2004) attest to the fact that lignin acts as a network-former due to its high functionality, and PEG is used as the soft segment in the polymer. Taking full of advantage of these two properties can lead to a maximum degree of substitution of PEG by lignin while obtaining polyurethane films with good mechanical properties.

For PEG 400, only ratios above 1.2 led to acceptable polyurethane films. The PEG substitution rate by BL was 40% with an NCO/OH ratio of 1.8. Other polymers were either too soft or too brittle. However, the objective was the synthesis of PU films with more than 50% lignin. It seemed that the PEG 400 chain length was not sufficient to introduce chain

mobility to the polymer (brittle polyurethane films), but at low lignin contents, it did not provide a 3-dimensional network (polyurethane films that were too soft).

BL based-polyurethane films obtained with PEG 600 were acceptable regardless of the NCO/OH ratio. The objective of a substitution rate greater than 50% was achieved with an NCO/OH ratio of 1.5.

To go beyond this value, PEG 1000 was tested. For each NCO/OH ratio (1 to 1.8), suitable polyurethane films were obtained without exceeding a lignin content of 50% (NCO/OH = 1.2). For very long PEG chains, the efficiency in creating dimensional PU networks decreased as a result of the increasing dilution of the hydroxyl chain-ends.

PEG 600 and an NCO/OH ratio of 1.5 allowed the synthesis of BL-based polyurethane films with a substitution rate greater than 50%. Therefore, the thermo-mechanical characteristics of the resulting PU (substitution rate from 0 to 70%) were determined through TGA analysis and tensile strength tests.

ATR-FTIR Analysis

ATR-FTIR spectra of BL and PU films with 0-30-50-70% BL contents with respect to PEG, are presented in Fig. 3.

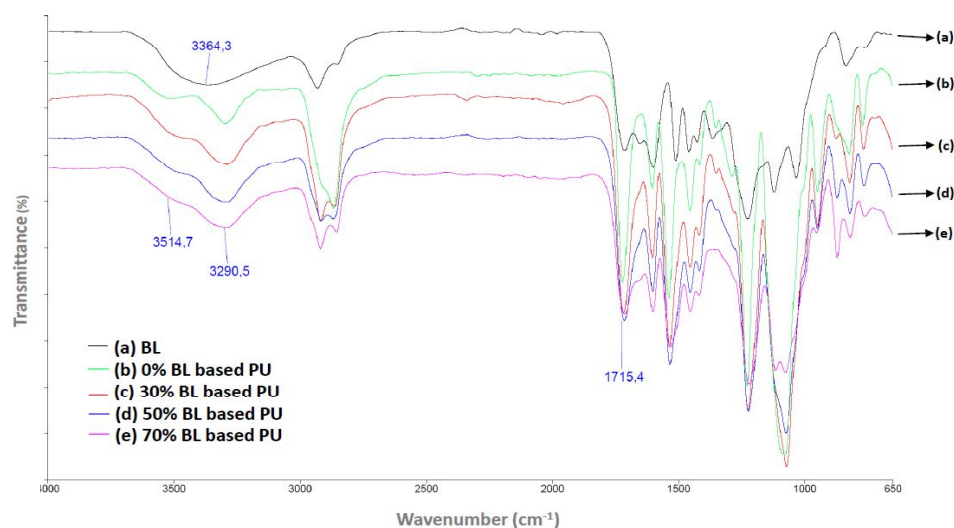


Fig. 3. ATR-FTIR spectrum of BL and PU films with 0-30-50-70% BL contents (with respect to PEG)

All PU films spectra (with and without BL) displayed several similar characteristics. The most important characteristic features of the PU are the presence of bands at 1720 to 1730 cm⁻¹ (C–O stretching and N–H bending), at 3290 to 3310 cm⁻¹ (bonding N–H groups with carbonyl oxygen) and at 3530 to 3550 cm⁻¹ (–OH vibration) (Badri *et al.* 2010; Ibrahim *et al.* 2015). These bands show that regardless of the BL content, the PU synthesis reaction had occurred.

Besides that, the BL spectrum showed a broad band at 3364 cm⁻¹, which corresponds to O–H stretching of aromatic and aliphatic OH groups. This broad band did not appear in the spectra of PU. This clearly shows that some or all of the BL –OH groups reacted with TDI. We can therefore say that BL, like PEG, played its role of polyol in PU synthesis and had been chemically incorporated in the PU matrix.

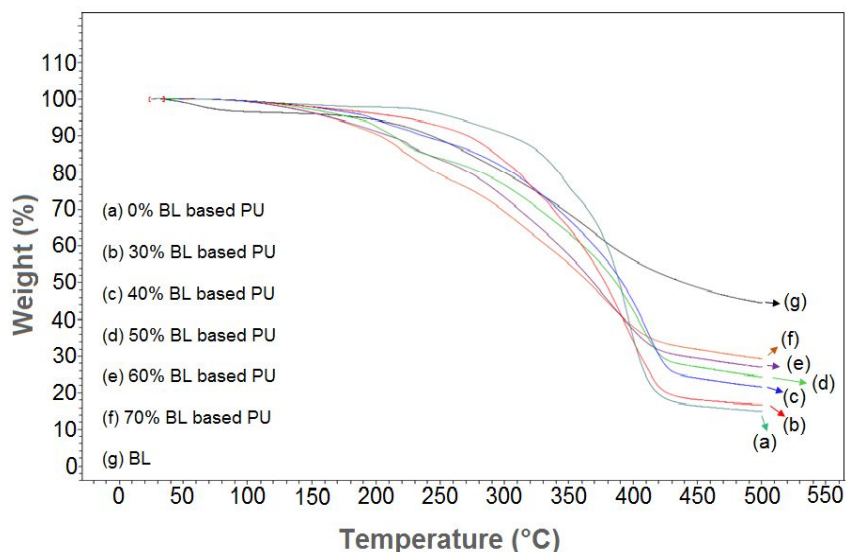


Fig. 4. TG curves of BL and PU films with 0-30-40-50-60-70% BL contents (with respect to PEG)

TGA

TGA was used to study the thermal stabilities of the lignin-based PU films (Fig. 4). These curves represent the weight percentage loss as a function of temperature. The lignin PU films experienced weight loss from 40 °C to 500 °C. The PU films degraded faster when the lignin content was increased. This phenomenon began at 220 °C for PU films without lignin (a), while degradation was initiated at around 100 °C for those containing 60% (e) and 70% (f) lignin, with respect to PEG.

However, the amount of char residue increased with lignin content. For example, at 500 °C, residues were 16%, 22%, and 31% for PU films with 0%, 40%, and 70% PEG substitution by lignin, respectively. Sen *et al.* (2015) reported that when the thermal stability of a polymer improved with increasing lignin content, it was due to the fact that the lignin added more aromatic structure to the resulting polymer.

The onset decomposition temperature (TOD) was approximately 260 °C for PU films without lignin. The corresponding BL-based PU (30 to 70% BL content, with respect to PEG), was stable up to about 310 °C, which was the limiting value obtained regardless of the lignin content. This result contradicted the findings of Wang *et al.* (2013); they found that the TOD of lignin PU films decreased with increasing lignin content. One explanation may be that the lignin PU polymers were synthesized in 1,4-dioxan in this study rather than in mixed DMF/acetone. However, the most suitable solvent for BioligninTM solubilization is 1,4-dioxan. Therefore, the lignin was better incorporated as a crosslinking agent in the urethane network, leading to a considerable improvement in the thermal stability.

Mechanical Properties of BL-Based PU Films

The mechanical properties of PU films synthesized with TDI isocyanate, PEG 600 as soft segment, and with a NCO/OH ratio of 1.5 were investigated. The PEG substitution extent by BL was varied according to the following values: 0, 30, 40, 50, 60, and 70%.

Shore hardness

By substituting PEG (soft segment) for lignin, which has a stiff backbone, the hardness was expected to increase with the lignin content (Fig. 5). As the BL content increased, the hardness also increased. Films with more lignin were more rigid than those with less lignin, demonstrating the active role of BL as a cross-linking participant. These results were in accordance with previous observations on the role of lignin in PU film synthesis.

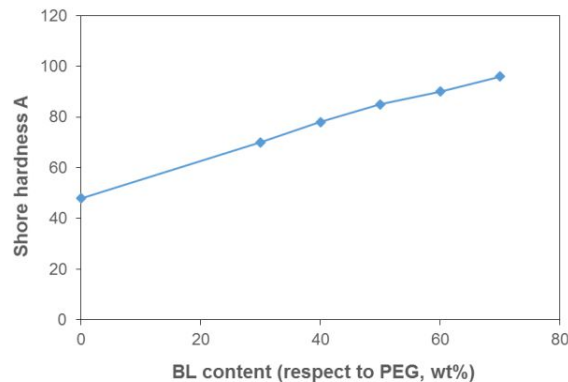


Fig. 5. Shore hardness as a function of BL content

Young's modulus

The Young's modulus increased with lignin content (Fig. 6). This result was explained by the fact that when a difunctional isocyanate molecule, such as tolylene 2,4 - diisocyanate (TDI), reacts with a difunctional diol, such as polyethylene glycol (PEG), a linear polyurethane chain is formed. When the polyhydroxy lignin is used as the source of all or some of the hydroxyl groups, a highly branched, 3-dimensional polyurethane is created (Thring *et al.* 2004). Lignin itself possesses a high modulus, but it is extremely brittle. Elder (2007) reported that the Young's modulus of lignin is 2.31 to 4.65 GPa. Thus, the incorporation of more lignin was expected to increase Young's modulus. These trends share similar characteristics to those previously discussed for shore hardness: at higher percentages of lignin, the PU becomes increasingly rigid due to a reduction in the amount of soft segment and an increase in the degree of crosslinking from the lignin hydroxyl group functionality.

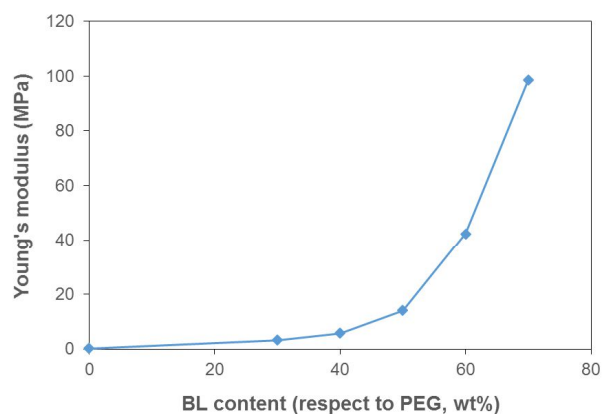


Fig. 6. Young's modulus as a function of BL content

Breaking stress and elongation at break

Breaking stress is the stress required to fracture a material, whether by compression, tension, or shear. As can be seen in Fig. 7, as the lignin content increased, breaking stress increased as well. These results were contrary to those obtained by Wang *et al.* (2013), where the tensile strength curve, as a function of lignin content, reached a maximum of 40% BL.

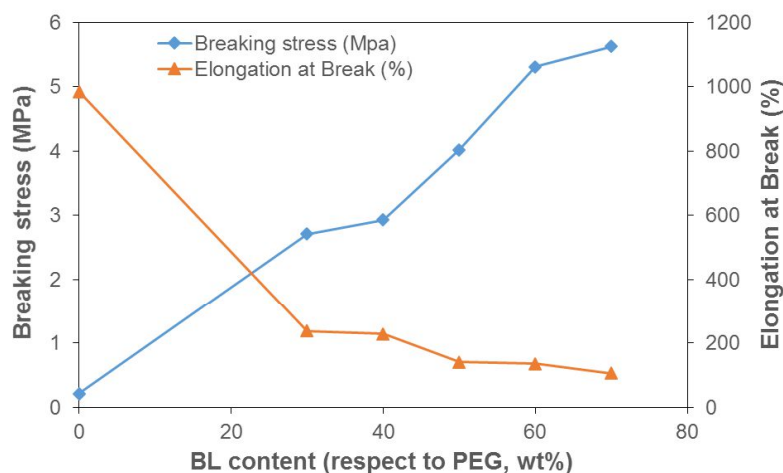


Fig. 7. Breaking stress and elongation at break as functions of BL content

As reported in studies of the shore hardness and Young's modulus, an increase of lignin content in the network results in additional crosslinking and greater mechanical strength in the polyurethane films.

The lignin structure is made of double bonds between the aliphatic carbons first and second away from the aromatic ring. The proximity of the stiff double bond to the aromatic ring contributes to the backbone of the lignin being rather crowded and far stiffer than the backbone of common flexible polymers such as polyethylene glycol, polyethylene, and even polystyrene. The stiffness of the lignin backbone is reflected in its glass transition temperature, T_g , which is in the range of 90 to 100 °C (Thring *et al.* 2004). This improvement in mechanical properties by the addition of lignin can also be explained by the fact that lignin contains many aromatic rings that restrict the movement of the backbone chain, producing a rigid material.

Conversely, the elongation at break decreased with lignin content. This effect was attributed to the increased rigidity of PU films as more lignin was incorporated with increased crosslink density. Indeed, with decreasing lignin content, it was necessary to increase the PEG (soft segment) content in the PU film network. The greater the content of the soft segment, the more flexible the ensuing PU film became. The PU films obtained at 70% lignin were thus more brittle. At 80% lignin, the PU films could not be analyzed because they were too breakable.

CONCLUSIONS

1. PU films with good mechanical characteristics were prepared from a three-component system, namely, Biolignin™ (BL) without any modifications or purifications, tolylene

2,4-diisocyanate (TDI), and polyethylene glycol (PEG 600). This system allowed the synthesis of BL-based polyurethane films containing, for the first time, a high rate of BL (*i.e.*, 70% PEG substitution). These results were achieved through the optimization of the synthesis parameters of polyurethane films and the intrinsic properties of the organosolv lignin.

2. The influence of the PEG molecular weight and the NCO/OH ratio with varying BL contents in polyurethane (PU) film synthesis was studied. Optimization of these two parameters was carried out to obtain polyurethane films containing an upper BL content of 50% (40% being the optimum rate obtained by Wang *et al.* (2013)). This objective was achieved by synthesizing polyurethane films with PEG 600 and a NCO/OH ratio of 1.5. Thus, polyurethane films with a PEG substitution rate by BL of 70% were created, which is equivalent to a rate of nearly 50% BL in the polymer. Beyond this value, the PU films were too brittle to be tested for thermal and mechanical properties.
3. ATR-FTIR analysis revealed that BL hydroxyl groups have reacted with TDI isocyanate to synthesize the polyurethane. BL is not therefore simply embedded in PU matrix but it has been chemically incorporated.
4. Considering the thermal stability, PU films containing more lignin begin to degrade more quickly but otherwise they lose less mass. Regardless of the PEG substitution rate by BL, TOD reached an average limit of 310 °C, which was much higher than that obtained for a PU film without lignin (260 °C). Thus, the addition of BL, as a PEG substitute in polyurethane films, leads to better thermal stability.
5. With increasing BL content, the breaking stress, Young's modulus, and shore hardness of PU films increased continuously without reaching a maximum. This was due to an increase of the crosslinking density, as well as the presence of numerous aromatic rings in the BL molecule. In contrast, the elongation at break decreased gradually with the BL content. This result is in line with previous observations on increasing stiffness of polyurethane films with the addition of lignin.

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