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Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethanes synthesis

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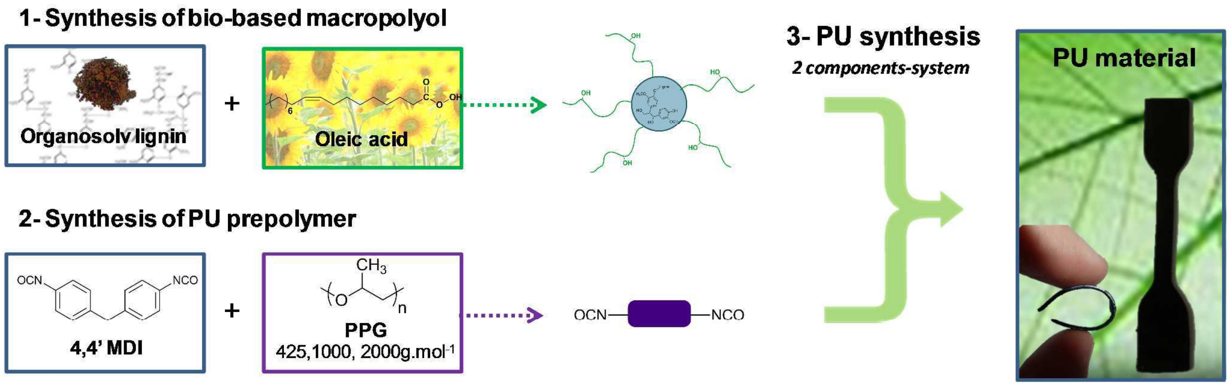


Abstract

A macropolyol was successfully prepared through combining two different biomolecules from biomass i.e., lignin and oleic acid, using a solvent-free and catalyst-free method. The chemical structures of this original lignin-fatty acid based polyol and its intermediates were determined by ^{1}H NMR and FT-IR analyses. A serie of polyurethanes (PUs) were then prepared on a two-step procedure. Three linear isocyanate prepolymers were first synthesized from 4,4' methylenebis(phenyl isocyanate) and different molecular weight poly(propylene) glycol (PPG - 425, 1000 and 2000 g.mol^{-1}). These intermediates were used to obtain different PUs macromolecular architectures by varying reaction parameters in presence of the lignin-fatty acid based macropolyol. The final lignin-based polyurethanes were thoroughly chemically characterized by FT-IR studies, whereas the properties of these polymers were assessed through DSC, TGA, DMTA, and tensile tests experiments. All this was performed in order to evaluate the influence of NCO:OH molar ratio (from 0.2 to 1.0) as well as the influence of PPG chain length. These new polymers with controlled architectures presented advanced properties. The high biobased content (until 89%) depicts an important output for the valorisation of the lignin and then may be an optimal alternative to conventional PUs.

1. Introduction

Renewable resources have recently gained interest as a petroleum substitute in chemical and polymer applications[1]. Biomass can also be the starting point of innovative pathways for designing new tailor-made building blocks and then original macromolecular architecture[2]. Among the multitude of resources which are extracted from the biomass, vegetable oils and lignocellulosic components represent a great potential and have attracted a lot of researches, notably to design monomers (mainly polyols) for the synthesis of bio-based polymers[3].

Lignin, a lignocellulosic component, represents after cellulose the most abundant biopolymer on earth. It is a substituted hyperbranched polyphenol and constitutes a natural aromatic polymer that accounts for up 18-35% by weight of wood[4]. Lignin can be extracted from lignocellulosic biomass (wood, annual plants such as wheat straw and agricultural residues) by different extraction processes but its chemical structure still remains under investigation. It is an amorphous polymer consisting of phenylpropane units, originating from three aromatic alcohol precursors (monolignols), *p*-coumaryl, coniferyl and sinapyl alcohols[5]. Given its unattractive structure, lignin possesses therefore significant potential for being a source of macromolecular materials due to its huge availability and variety of functional groups. In fact, the numerous sites on the lignin backbone offer many opportunities for chemical modifications. Several studies have tried to take advantage of this aromatic structure by performing reactions that would confer to lignin higher reactivity and suitability for industrial applications, e.g. for the synthesis of polymers[6]. In that frame, chemical modification of lignin can be used to introduce reactive sites such as available hydroxyl groups and improve the capacity of hydrogen bonding with other components. The production of lignin-based polymers is however limited by its hindered structure i.e. its high crosslink density and the highly polydisperse molecular weight of the molecule. Development of new advanced lignin-derived polymer is thus related to chemical modifications that can be carried out on this macromolecule. Similarly to thermoplastic cellulose ester derivatives, one method adopted to improve the properties and use of lignin as a thermoplastic polymer is by esterification. This procedure is an effective way to solubilise it in a common solvent and to easily characterize it. Various studies have been performed on lignin esterification by using organic acids such as acid anhydrides or acyl chlorides in presence of suitable acid or basic catalysts (sulphuric acid or pyridine). Lignin esterification using diacids has already been done[7, 8] but the use of fatty acid has only been seen for the functionnalisation of wood to enhance its thermoplastic properties, flexibility and melting temperature [9, 10].

Recently, with the rapid development of green chemistry and engineering, a large quantity of polymeric materials mainly derived from plant oil and its derivatives have been reported[11-13]. During the last decades, a plentiful literature has been dedicated to the synthesis of polyol based on vegetable oil functionalization through their double bonds[14, 15]. These latter are generally performed by epoxidation and direct hydroformylation reactions whereas the ester bonds can be derivatized by e.g., transesterification or amidation. Those functionalization processes require the epoxidation of double bonds followed by the oxirane ring-opening by ozonolysis[16], hydroformylation[17] and more recently metathesis[18, 19] and thiol-ene coupling reactions[20-22] offer a new and green approach to modify fatty acids derivatives. In this way, a great variety of polyols based on vegetable oils have been synthesized and suggests interesting intermediates for designing e.g., polyurethanes (PUs) with new macromolecular architectures.

PUs represent one of the most important and versatile classes of polymeric materials. They can vary from thermoplastic to thermosetting materials with broad applications such as flexible or rigid foams, thermoplastic elastomers, adhesives and coatings[23]. The production of PUs is based on a polyaddition reaction between oligomeric polyol with terminal hydroxyl groups and a diisocyanate (or polyisocyanate)[24]. Thanks to the high variety of design for oligomeric polyols, it is possible to modulate the architecture and then final properties of PUs. Among them, we have mainly focused our investigations on segmented polyurethanes (PUs), well-known for their versatility with a wide range of behaviours and applications. They are multi-phase copolymers structured with soft and hard segments. The soft block is built out of a polyol responsible for the flexibility and elastomeric character of the PU whereas the hard block, constructed from a chain extender and isocyanate gives its toughness and physical performance properties.

Through an original approach we have used vegetable oils derivatives (triglycerides and fatty acids) as a raw material for lignin chemical modification. This methods depicts an innovative way for designing new tailor-made bio-based building blocks an then new macromolecular architectures[25].The aim of this study is focused on the esterification of lignin with chlorinated fatty acid (oleoyl chloride) in a solvent-free system to develop a new polyol. The resulting biobased polyester, with an original core-shell structure, can represent a promising precursor for polymer synthesis.

This paper also reports the PUs synthesis in a two-step procedure with synthesized prepolymers. A total of three isocyanate prepolymers intermediates were produced with different molecular weight poly(propylene) glycol (PPG) i.e 425, 1000 and 2000 g.mol^{-1}. Final PUs were performed between the biobased macropolyol and the different isocyanate prepolymers. Properties of the resulting PUs were modulated by varying NCO:OH molar ratio from 0.2 to 1.0, and the PPG chain length. The synthesized chemicals (intermediates and lignin-based polyurethanes) were first analysed by FT-IR and DSC. To further investigate the thermo-mechanical properties and their thermal stability, TGA, DMTA and tensile test were performed to define the structure and determine the behaviour of the resulting polymers.

2. Experimental section

2.1 Raw materials

Organosolv lignin (Alcell) from hardwood was supplied by Lignol Company (Canada) and used as received without any further purification. Specific techniques for lignin characterization have been carried out according different methods previously reported[6] (Table 1). Priolene 6936 mainly based on oleic acid (91% C18:1, 4% C18:2, 2% C16, 2% C18) was purchased from Croda. It is a yellowy transparent viscous liquid with an acid number of 199 mg KOH.g^{-1}.

Peracetic acid (35%wt in an acetic acid solution), dichloromethane (DCM - 99.9%), methanol (99.6%), Tetrahydrofuran (THF - 99.8%), *para*-toluene sulfonic acid (PTSA) and Dibutyl Tin Dilaurate (DBTDL - 95%) were all obtained from Sigma Aldrich. Poly(propylene) glycol polymers (PPG) of 425, 1000 and 2000 g.mol^{-1} were obtained from Acros and were dried under reduced pressure at 100°C before using. All of the solvents were distilled before their utilization for chemical synthesis.

Moisture content (%)		3.83
SEC analysis[a]	M_n *(g.mol^{-1})*	1000
	M_w *(g.mol^{-1})*	2275
	PDI *(M_w/M_n)*	2.28
^{1}H NMR analysis	Total OH *(mmol.g^{-1})*	2.26
	OH phenolic *(mmol.g^{-1})*	1.30
	OH aliphatic *(mmol.g^{-1})*	0.96
	Average hydroxyl groups/ mol of lignin	2.26
Tappi method	Methoxy content *(mmol.g^{-1})*	2.07
DSC analysis	T_g (°C) *crude lignin*	76

Table 1. Analysis results performed on organosolv lignin.

2.2 General methods and analysis

^{1}H NMR were recorded in $CDCl_3$ on a Bruker UltraShield 300 spectrometer operating at 300Hz. Chemical shifts (δ-ppm) are reported in parts per million relative to the internal standard tetramethylsilane (TMS, $\delta = 0.00$ ppm). Polymer analysis was performed with a size exclusion chromatography (SEC) system from Shimadzu equipped with a pre-column PLGel 5µ, two PLGel 5µ Mixed-C 300mm columns, one PL 100 Å 300mm column and refractive index (RI) and ultra-violet (UV) detectors. Chloroform ($CHCl_3$) was used as the eluent at a flow rate of 1mL.min^{-1}. All determinations of molar mass were performed relative to linear Polystyrene standards from 580 to 1,650,000 g.mol^{-1}.

Fourier Transformed Infra-Red spectroscopy was carried out with a Nicolet 380 FT-IR spectrometer working in Attenuated Total Reflectance Mode (FTIR-ATR). This analysis was used to detect specific chemical groups which provide direct evidence of different reactions performed onto lignin.

Differential scanning calorimetry (DSC) experiments were carried out with a TA DSC Q200 calorimeter, under nitrogen atmosphere using a sample mass in the range 2-5 mg. The samples were heated until 120°C with a heating rate of 10°C.min^{-1} (first heating scan), then cooled to -80°C at 10°C.min^{-1} and finally re-heated to 120°C at a heating rate of 10°C.min^{-1} (second heating scan). The glass transition temperature, T_g, is reported as the midpoint of the heat capacity change. These values were determined on the second heating scan in order to erase the previous thermal history of the samples during the first scan.

Thermogravimetric analyses (TGA) were performed on a Hi-Res TGA 2950 apparatus from TA Instruments at a heating rate of 10°C min^{-1} up to 750°C under a nitrogen atmosphere (flow rate = 25 mL.min^{-1}).

Dynamic mechanical thermal analysis (DMTA) was performed on polymers (with dimensions around 23 x 4 x 1 mm^3) with RSA-II apparatus from TA Instruments equipped with a liquid-nitrogen cooling system. Experiments were recorded on PU films with traction mode at a maximum strain from 0.003% to 0.9% and a frequency of 1Hz. The sample was heated from -100°C to 200°C at a heating rate of 2°C.min^{-1}.

Dynamic rheological analyses (DRA) were performed by using a strain-controlled rheometer (ARES, Rheometric Scientific) with parallel-plate geometry (25 mm in diameter). The dynamic storage modulus (G’) and dynamic loss modulus (G’’) were measured as a function of the temperature ranging from 0°C to 200°C. A fixed strain was used to ensure that the measurements were taken well within the linear viscoelastic range of the material investigated. Results of rheological experiments are only presented in Supplementary Information section.

From uniaxial tensile tests, Young’s modulus (E), ultimate strength (σ_{max}) and strain at break (ε_{max}) were obtained using a Zwick/Roell machine. The experiments were performed at room temperature, using a crosshead speed of 20 mm.min^{-1} and a load cell of 200N sensitivity. After adjusting the parameters, experiments were carried out 5 times for each sample.

2.3 Synthesis and characterization of lignin-fatty acid based polyol

Lignin-fatty acid based polyol (LOAP) is performed in a multistep synthesis involving the esterification of lignin with oleic acid, followed by the epoxidation of the fatty acid double bond and then the oxirane ring-opening.

2.3.1 Esterification of organosolv lignin

Lignin esterification has been performed with oleic acid from sunflower oil (Figure 1). In order to improve reactivity of the oleic acid, a chlorination step of the compound has been carried out before esterification. According the procedure established by Thiebaud et al.[9, 10] , esterification has been then performed by a solvent-free and catalyst free reaction using oleoyl chloride.

Chlorination step

The reaction took place into a three-necked 500 mL round-bottomed flask equipped with a magnetic stirrer, a nitrogen-gas bubbling system and an outlet connected to a wash-bottle containing an aqueous sodium hydroxide solution to trap the hydrogen chloride formed. The chlorination step is carried out with an excess of oxalyl chloride, oleic acid: oxalyl chloride (1:2). Oleic acid (40 g; 0.14 mol) was first dissolved into ethyl acetate (300 mL) and was cooled to 0°C under nitrogen flow. An excess of oxalyl chloride (36.02 g; 0.28 mol) was then added drop by drop at 0°C (15 min) and finally heated at 50°C during 5h. The solvent and the excess of oxalyl chloride were then distilled out from the reactive mixture.

Oleoyl chloride (OC) was obtained as a yellow viscous product.

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.88 (3H, t, CH_3), 2.87 (2H, t, CH_2-COCl), 5.32-5.38 (vinylic protons).

IR (cm^{-1}): 3005 (C=C-H), 1799 (C=O chloride group).

Esterification step

The esterification procedure was carried out in a 500 mL reactor having a mechanical stirrer, a nitrogen-gas bubbling system and an outlet connected to a wash-bottle containing an aqueous sodium hydroxide solution. Organosolv dried lignin (30 g; 67.8 mmol OH) and OC (40.7 g; 135.6 mmol) were successively introduced in the reactor. The reaction was then conducted at 130°C under agitation and a continuous nitrogen stream for 15h. At the end of the reaction a brown viscous but homogeneous product was obtained. The esterified lignin (EL) was washed with cold methanol in order to remove the excess of acid chloride.

The esterification reaction was confirmed by NMR and IR analyses and the remaining fatty acid has been quantified.

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.88 (3H, t, CH_3), 2.29 (2H, t, CH_2-$COOCH_3$), 2.54 (2H, t, CH_2-COO-lignin), 3.88 (3H, OCH_3 lignin methoxy) 5.32-5.38 (vinylic protons).

IR (cm^{-1}): 3005 (C=C-H), 1761 and 1737 (ester band).

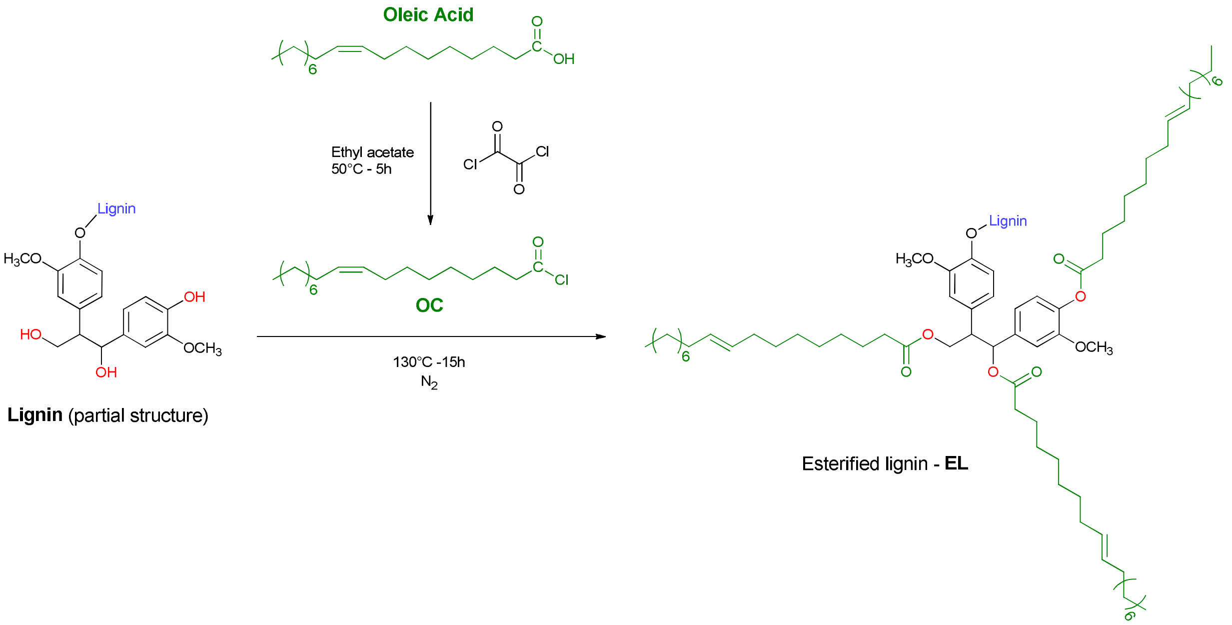


Figure 1. Reaction schemes for the synthesis of the esterified lignin – EL

2.3.2 Epoxidation of oleic acid double bond

A 500 mL round-bottomed flask was charged with esterified lignin (EL) (45 g, 72 mmol of double bonds) dissolved into DCM (250 mL) and stirred until obtain homogenous solution. Peracetic acid (10.95 g; 144 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 5 h. The organic layer was washed three times with brine and dried over sodium sulfate. The solvent was evaporated under reduced pressure and then dried under vacuum at 35°C for one night to obtain the epoxy-lignin oleate (ELO).

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.87 (3H, t, CH_3), 1.20-1.70 (methylene protons), 2.29 (2H, t, CH_2-$COOCH_3$), 2.54 (2H, t, CH_2-COO-lignin), 2.89 (2H, epoxy ring proton).

IR (cm^{-1}): 1740 ($COOCH_3$ – ester bond), 841 (epoxy).

2.3.3 Oxirane Ring-Opening synthesis

A 500 mL round-bottomed flask was charged with epoxy lignin oleate (ELO), methanol, and PTSA (2 wt % vs. ELO) as the catalyst. The reaction mixture was stirred under reflux and nitrogen flow for 15h. After completion of the reaction, the methanol was distilled out under reduced pressure. The product was then dissolved in DCM and washed three times with brine to remove the catalyst. The organic layer was dried over sodium sulfate, filtered and evaporated under reduced pressure to obtain the lignin-oleic acid polyol (LOAP).

^{1}H-NMR (300MHz, $CDCl_3$, δ (ppm)): 0.88 (3H, t, CH_3), 120-1.70 (methylene protons), 2.29 (2H, t, CH_2-$COOCH_3$), 2.54 (2H, t, CH_2-COO-lignin), 2.99 (1H, dd, CH-OCH_3), 3.41 (3H, s, OCH_3), 3.49 (1H, m, CH-OH).

IR (cm^{-1}): 3480 (OH), 1740 ($COOCH_3$)

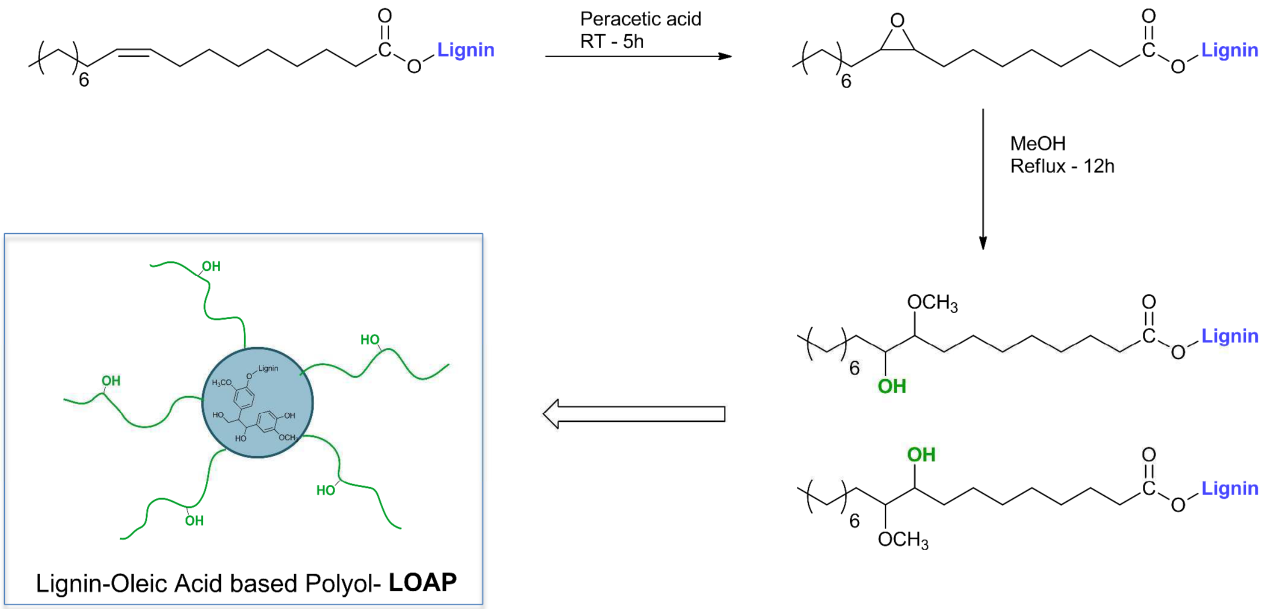


Figure 2. Synthetic pathway to macropolyol - LOAP (Lignin Oleic Acid Polyol) - from lignin and oleic acid. Schematic representation of lignin-fatty acid based polyol.

2.4 Polyurethane synthesis

Before the PU synthesis, the synthesized lignin-fatty acid based polyols have been characterized. A standard method has been developed to evaluate the amount of hydroxyl groups available for the reaction with isocyanates. This parameter is defined as the hydroxyl number or as the hydroxyl index (the procedure used for I_{OH} determination is described in Supporting information).

The general procedure followed for polyurethane (PU) synthesis is based on a two-step procedure. Firstly, three isocyanate prepolymers have been synthesized by varying the diol (PPG) molar mass while the molar ratio of isocyanate and hydroxyl groups remains constant. Then in a second step, different PUs are synthesised with the bio-based polyol building blocks and the prepolymers (Figure 3).

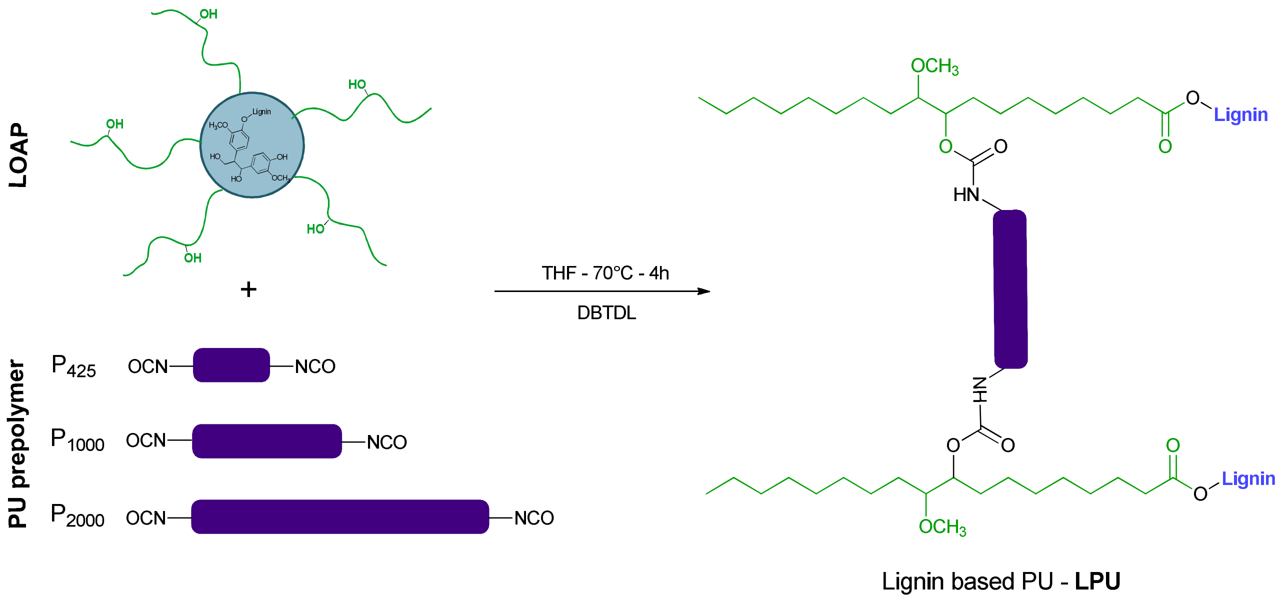


Figure 3. Synthesis of lignin based PU – LPU[26-28].

2.4.1 Prepolymer synthesis

A three-necked 250 mL round-bottomed flask was fitted with a nitrogen inlet tube and a mechanical stirrer. Poly(Propylene Glycol) and 4,4' MDI (f=2) were added into the flask and stirred at 70°C during 5 hours to yield isocyanate prepolymer with a 1.8 molar ratio of NCO:OH. The ensuing isocyanate prepolymers were coded as P_{425}, P_{1000} and P_{2000} for syntheses with PPG with molecular weights of 425, 1000 and 2000 $g.mol^{-1}$, respectively. The exact concentration of free isocyanate functions on the prepolymer was then determined.

NCO content determination

This method allows determining the amount of isocyanate which reacts with one equivalent of N-Dibutylamine, and gives NCO content by weight per cent.

$$(1) \qquad \% \, NCO = \frac{(V_{blank} - V_S) \times 42 \times 0.1}{W_P}$$

Where V_{blank} (mL) is the hydrochloric acid volume required for blank titration, V_s (mL) is the HCl volume required for polyol sample titration and W_P (g) is the polyol weight.

2.4.2 Polymer synthesis

The typical procedure used is as follow: three-necked 100 mL round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and condenser was charged with LOAP and around 40 mL of anhydrous THF. The solution stirred at 70°C under nitrogen flow until the complete dissolution of polyol. Then, the isocyanate prepolymer previously dissolved in THF (P_{425}, P_{1000} or P_{2000}) and DBTDL (5 wt % based on lignin monomers) were added. The NCO:OH molar ratios, also known as isocyanate index, were calculated on the basis of hydroxyl index of the polyol and NCO content from the prepolymers. Five different molar ratios were used for the syntheses: 0.2, 0.4, 0.6, 0.8 and 1.0. The reaction mixture was stirred at 70°C for 4h. After completion of the reaction, THF was evaporated and the PU was dried over one night at 35°C under vacuum. It may be noticed from Table 2 that in PU series, up to 89 wt.% of lignin/oleic acid based macropoyol (LOAP) could be incorporated, highlighting the high content of biobased products in PU formulations. The resulting PUs were characterized to determine their structures and their physicochemical and mechanical properties by IR, DSC, DMTA, DRA and uniaxial tensile tests. Rheological and mechanical tests were performed on PUs processed into films obtained by compression moulding between two plates, at 100-120°C.

Samples	Isocyanate prepolymer	NCO:OH molar ratio	% LOAP [a] (w/w)	PU formulation		
				OH of LOAP (mol)	PPG (mol)	NCO (mol)
LPU-1	P_{425}	0.2	89	3.67	1	1.8
LPU-2		0.4	81	1.83	1	1.8
LPU-3		0.6	74	1.22	1	1.8
LPU-4		0.8	68	0.92	1	1.8
LPU-5		1.0	63	0.73	1	1.8
LPU-6	P_{1000}	0.2	82	4.02	1	1.8
LPU-7		0.4	69	2.02	1	1.8
LPU-8		0.6	60	1.35	1	1.8
LPU-9		0.8	53	1.00	1	1.8
LPU-10		1.0	47	0.80	1	1.8
LPU-11	P_{2000}	0.2	78	5.35	1	1.8
LPU-12		0.4	64	2.70	1	1.8
LPU-13		0.6	54	1.80	1	1.8
LPU-14		0.8	47	1.35	1	1.8
LPU-15		1.0	42	1.10	1	1.8

Table 2. Synthesis of the different PUs with the corresponding designations and formulations.
[a] : % of biobased content (LOAP is composed by lignin and oleic acid)

3. Results and discussion

The results are presented in six sections. First lignin has been characterized to clearly define its chemical properties in view of chemical modification. Afterwards, the polyol building block and PU were analysed by FT-IR and ^{1}H NMR to confirm reaction and the properties of the resulting materials are discussed subsequently. The influence of reaction parameters such as NCO:OH molar ratio and PPG molar mass on PU materials are further investigated. In the last section, thermal stability of PU is also studied by TGA experiments.

3.1 Lignin characterization

The lignin was produced from an ethanol-water pulping (Alcell process) as already described elsewhere[29]. The main characteristics of this lignin have been reported in Table 1. These data were found to be in the same range as that of others reported in the literature[30] and were also in good agreement with the values given by the supplier. The chemical data constitute a key point since the hydroxyls functions were functionalized. Total and phenolic hydroxyl contents were quantified according different techniques including chemical titration and ^{1}H NMR based on acetylated lignin and SEC in chloroform[31-33]. As can be observed from Table 1, results found for Alcell lignin showed low hydroxyl content of 2.26 mmol.g^{-1} with a low number average molecular weight (M_n = 1000 g.mol^{-1}), compared to kraft lignin and lignosulfonate. Therefore, SEC results should be taken as "relative values". This lignin is well known to present a high purity (low ash and sugar content) and also presents a good solubility in most solvent, particularly in THF and pyridine which must be considered as a great advantage for chemical modifications.

3.2 Synthesis and characterization of macropolyol

The main objective of this part was to synthesize a macropolyol. The resulting LOAP macropolyol with secondary hydroxyl groups was designed to react in a second time with isocyanate functions. LOAP was synthesized in a four step pathways (Figures 1 and 2). The structures of all the intermediates were analysed. The targeted chemical structures were confirmed by FT-IR and ^{1}H NMR spectroscopy (Figures 4 and 5).

In the first step, chlorination of oleic acid with oxalyl chloride yield OC. FT-IR of oleic acid shows a band at 1708 cm^{-1} linked to the carbonyl group (C=O) from carboxylic acid function and a broad band from 3100 to 3500 cm^{-1} corresponding to the hydroxyl groups, while a C=C-H stretching vibration band is observed at 3005 cm^{-1}. The chlorination of oleic acid was confirmed by the shift of the carbonyl group band from 1708 to 1798 cm^{-1} due to the formation of a more withdrawing chloride group and disappearance of hydroxyl band in the region of 3100-3500 cm^{-1}.

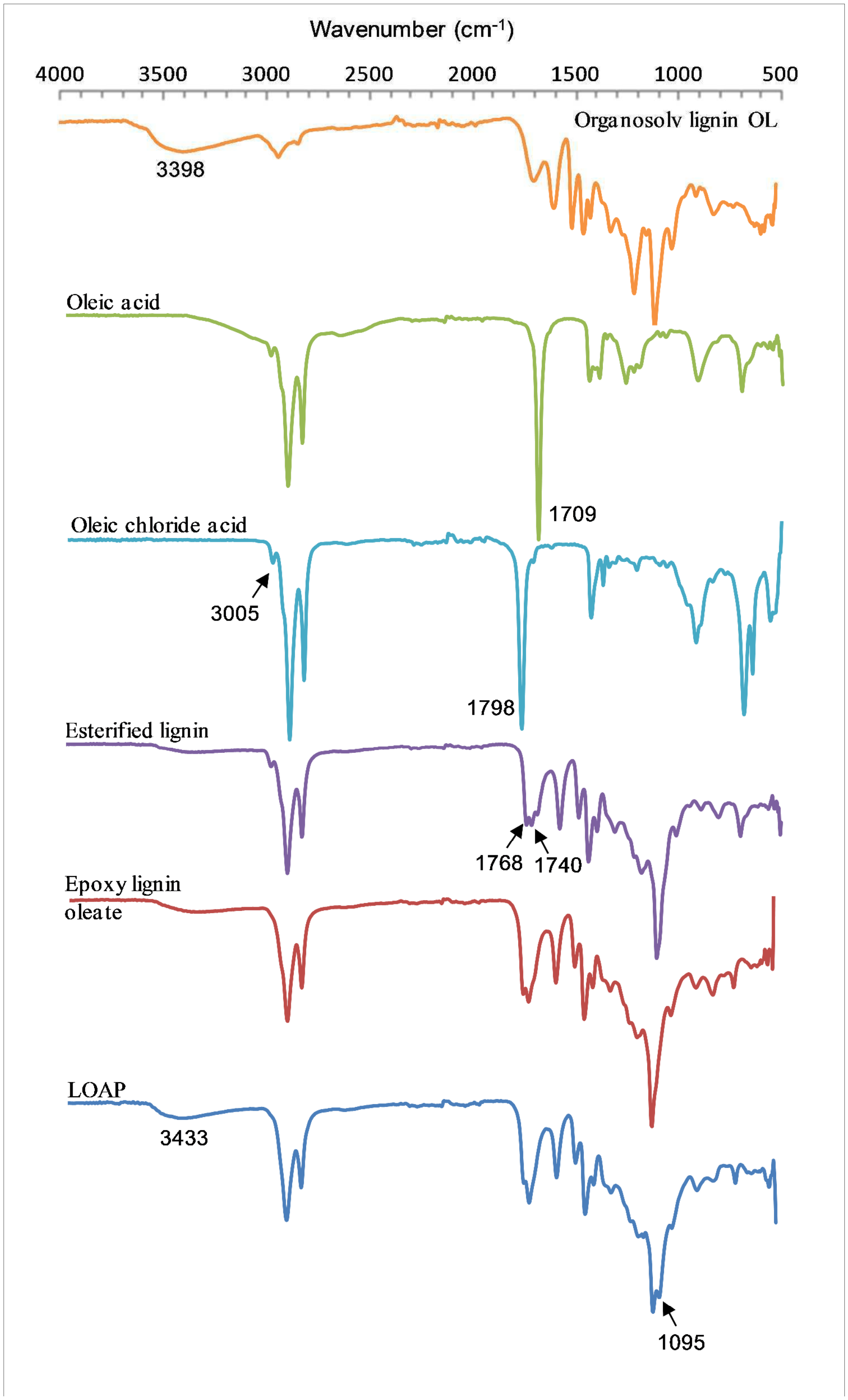


Figure 4. FTIR spectra of intermediates based on lignin and oleic acid.

The esterification of lignin with OC gave EL as the main product along with oleic acid as remaining product from the corresponding synthesis. EL was characterized by FT-IR and ^{1}H NMR. Esterification reaction resulted in a drastic reduction of the OH absorption band along with the appearance of the ester bands at 1761 and 1737 cm^{-1}, corresponding to the esterification of aliphatic and phenolic hydroxyl groups, respectively. ^{1}H NMR spectrum of EL is presented in Figure 5. The appearance of peaks at 3.60 ppm confirms the formation of ester protons whereas a peak at 2.34 ppm assigned to CH_2 to which carboxylic group is attached is still remaining and assigned to the presence of oleic acid in the final product. The amount of oleic acid chain present in this mixture was estimated by NMR integration at 80% of fatty acid grafted onto lignin whereas 20% are free chains. EL is a very viscous product where residual free oleic acid chains are partially imbedded due to a challenging incomplete extraction of the oleic acid in excess.

In the third step, EL was treated with peracetic acid to obtain epoxy lignin oleate (ELO). FTIR spectrum of intermediate ELO shows the absence of a band at 3005 cm^{-1} which was linked to the C=C-H group. The corresponding molecular structure was also confirmed by ^{1}H NMR with the appearance of a new peak at 2.89 ppm due to the epoxy ring protons and the disappearance of the vinylic protons at 5.32 ppm. The fourth and last step of the reaction pathway consists in the ring-opening of epoxide using methanol in the presence of acid catalyst (PTSA) to obtain a mixture of two regioisomers (4/4'- LOAP) containing secondary hydroxyl groups. Further onward, only one isomer structure will be used for the simplicity of the reaction scheme (see Figure 3). FT-IR spectrum of the resulting macropolyol shows the appearance of a band at 3432 cm^{-1} due to the hydroxyl groups and another band at 1097 cm^{-1} attributed to ether bond. Moreover, the appearance of three new significant peaks at 2.99, 3.41 and 3.49 ppm in ^{1}H NMR spectrum confirmed the ring-opening of the epoxides. These peaks are attributed to CH to which methoxy groups is attached, methoxy protons and CH to which hydroxyl groups is attached, respectively. The resulting macropolyol was then characterized by pH metric titration; the hydroxyl value was estimated at 60 mg KOH.g^{-1} of sample. This value is in the range of hydroxyl value for bio-based polyester polyols usually used for PU synthesis (between 30 and 200 mg KOH.g^{-1})[27, 34].

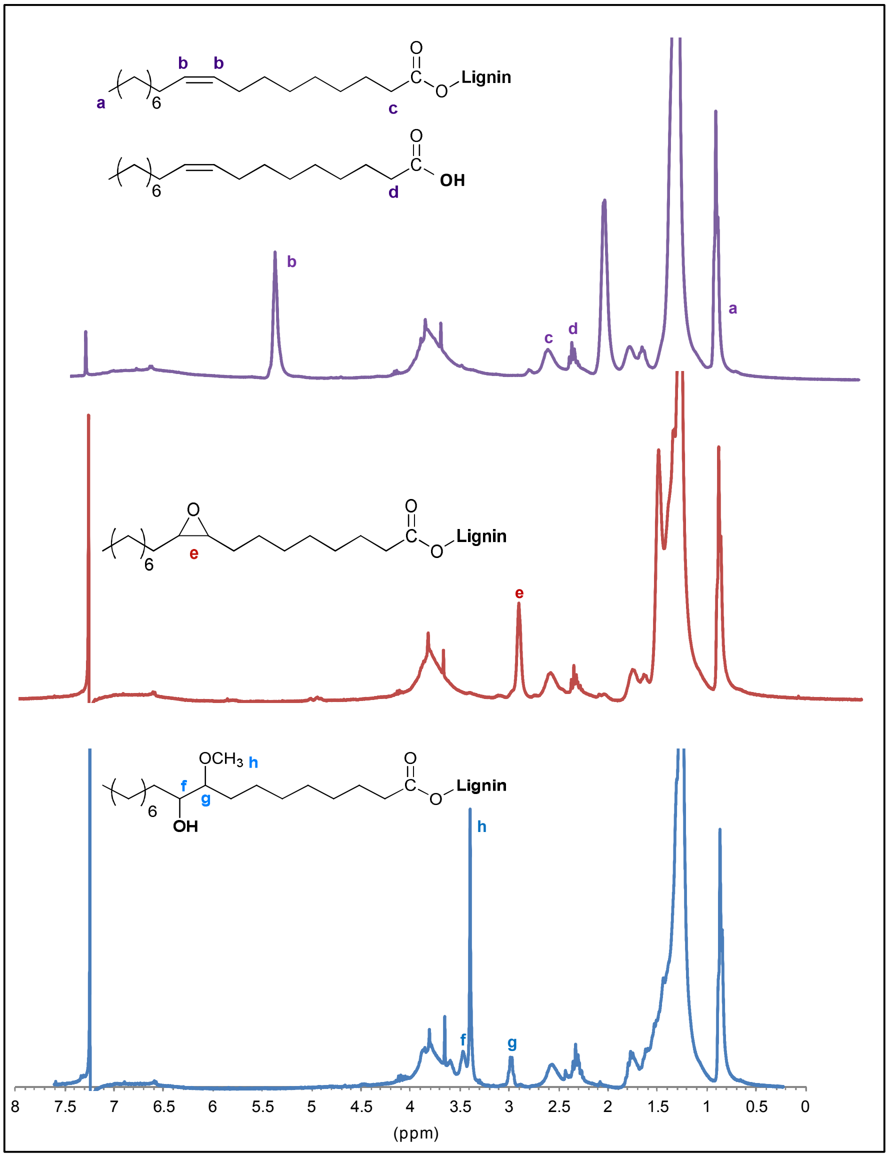


Figure 5. ^{1}H NMR spectra of intermediates based on lignin and oleic acid.

3.3 Synthesis and characterization of PUs

The reaction between LOAP and isocyanate was followed, analysed and confirmed by FT-IR analyses. The isocyanate absorption band is assigned at approximately 2270 cm^{-1} and the absence of this absorbance can be used to monitor and check the isocyanate group conversion during the polymerization reaction. In this study, the absorbance corresponding to the NH stretching region, assigned at approximately 3300 cm^{-1} was used to follow and confirm the reaction between isocyanate and hydroxyls groups but also to qualitatively evaluate the effect of the NCO:OH molar ratio. Figure 6 shows the FT-IR spectra of PU samples synthesized with P_{425} at five different NCO:OH ratios. The signal attributed to OH stretching band at around 3500 cm^{-1} tends to decrease with increasing NCO:OH ratios whereas the NH stretching band becomes more intense. The conversion rate can be controlled and followed through the formation of urethane functions and the disappearance of the hydroxyl groups from macropolyol.

Concerning the properties of the synthesized PUs, thermal and mechanical behaviours should reflect the corresponding structural chemical organization, e.g., the cross linking efficiency (related to the evolution of the NCO:OH molar ratio) and the chain prepolymer length in the flexible domain of the PU architecture. These statements will be investigated in the following sections.

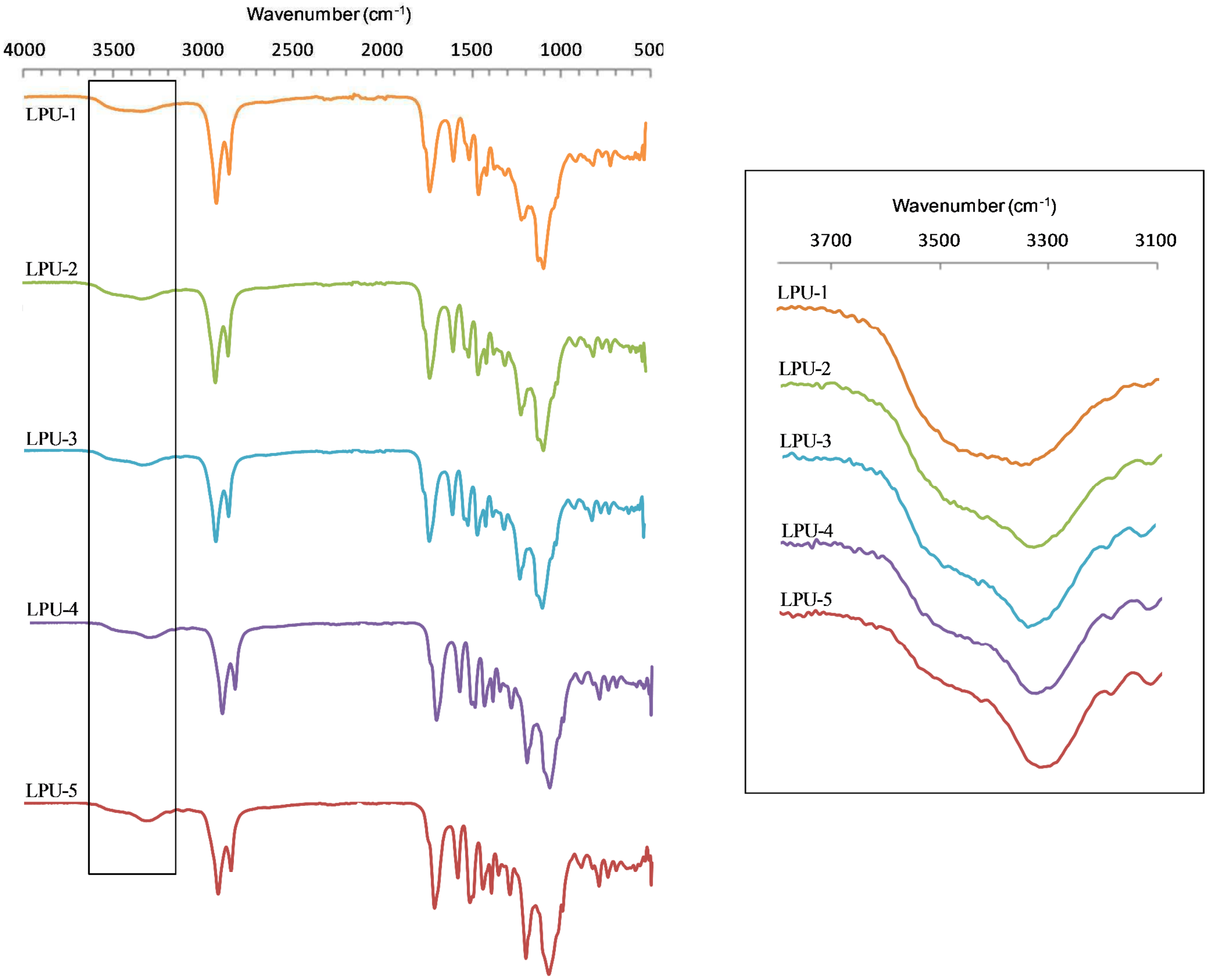


Figure 6. FTIR spectra of PUs synthesized with P_{425} and different NCO:OH molar ratios.

3.4 Effect of the NCO:OH molar ratio

Polyaddition reactions between LOAP and P_{425}, P_{1000} or P_{2000} were carried out at 70°C in anhydrous THF in the presence of DBTDL. The NCO:OH molar ratio was regulated based on the hydroxyl value and isocyanate index of the macropolyol and prepolymers respectively (Table 3).

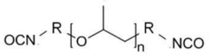
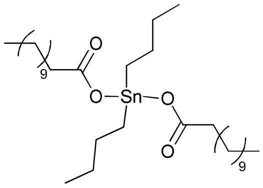
Designation	Description	Structural formula	I_{OH} (mg KOH.g^{-1})	% NCO	Functionality	T_g (°C)
LOAP	Polyol		60	-	-	-24
P_{425}	Isocyanate prepolymer		-	7.9	2	-11
P_{1000}			-	4.7	2	-30
P_{2000}			-	3.7	2	-48
DBTDL	Catalyst		-	-	-	-

Table 3. Chemicals and materials used in the PU synthesis with their corresponding properties.

In comparison with linear TPU resulting from the reaction between diols and diisocyanates molecules, we may obtain a highly branched and three-dimensional polyurethane network derived from the lignin macropolyols[35] (as suggested in Figure 7). In these systems, lignin should act as a crosslinking point, covalently bonded with more or less flexible PPG-based chains.

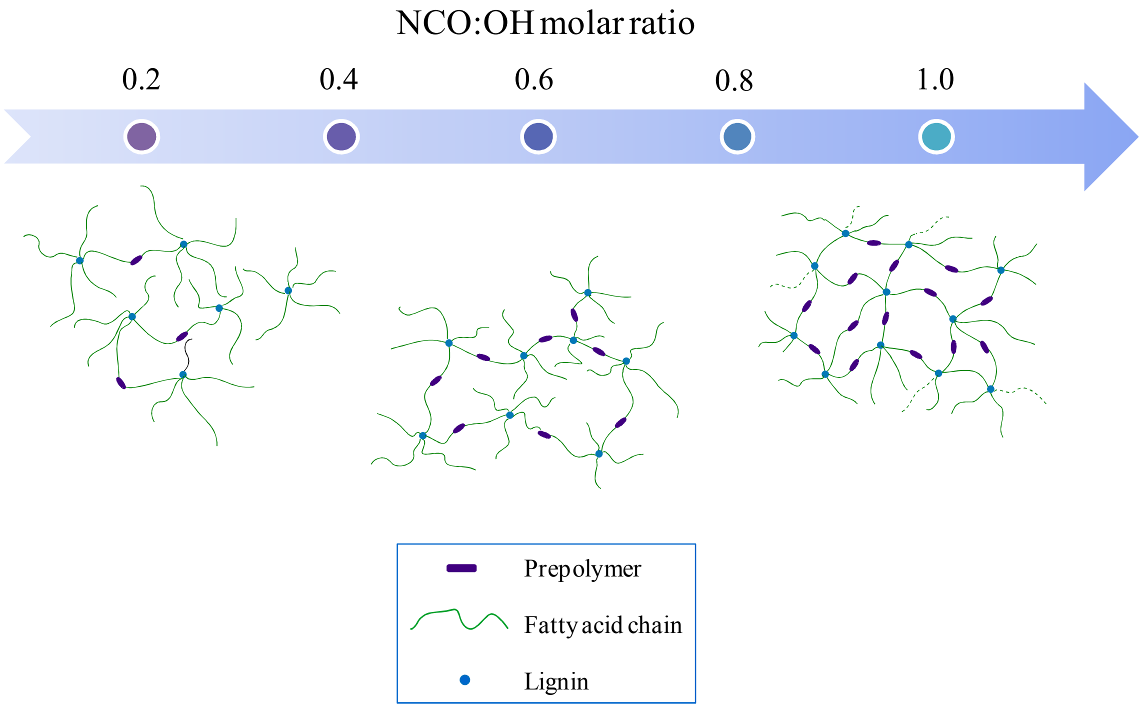


Figure 7. Schematic representation of PU networks with different NCO:OH molar ratios.

Table 4 showed T_g data for synthesized PUs. Neither melting nor crystallization transition temperatures were observed by DSC, indicating the amorphous nature of these PUs.

DMTA experiments were carried out in order to obtain further information on the morphology of these PUs. Figure 8 shows storage modulus as function of temperature for PUs films based on different NCO:OH molar ratio, in a large temperature range from -100 to 140°C. With increasing temperature, all polymer materials showed a similar trend. In details, E' presents no variations in the glassy plateau from -100°C to around -50°C and show for some samples a very broad transition before reaching the rubbery state, or decreasing for the others until the limit of the measurement. All the samples with high NCO:OH molar ratio demonstrated a rubbery plateau confirming their high cross-linking density[36, 37] while those with low NCO:OH molar ratio display a decrease of storage modulus. The resulting data are summarized in Table 4. As expected, for polymers presenting a rubbery plateau, the cross-linking density increases with the NCO:OH molar ratio[30], which confirm that a modulation of the properties of these PU systems is possible.

As widely reported in literature on lignin and/or fatty acid based polymers and their corresponding morphological behaviours[26, 28, 38, 39]; we should expect a phase separation on the segmented PU materials between soft and hard segments. Transition temperatures of both types of segments were determined by DSC and DMTA experiments.

The T_g of the prepolymers (i.e P_{425}, P_{1000} and P_{2000}) measured by DSC (Table 3) were in the range of -48 to -10°C. These values were in good correlation with the first transition observed in DSC for PUs (Table 4). This T_g can be attributed to the relative chain's motion of PPG soft segments into the PU architecture. It is also worth to mention, that the T_g of soft segment in PU material is related to the NCO:OH molar ratio, i.e the presence of crosslinking points.

A second transition (T_α) was observed at higher temperature by DMTA from the peak maximum in tan δ. This transition was also observed and then confirmed by DRA (Supplementary Information) which exhibit a relaxation temperature (maximum tan δ) in the same range than by DMTA. This second type of transition temperatures were above ambient temperature from 30 to 54°C. This relaxation temperature can be attributed to the transition linked to the hard segments motion, mainly composed by lignin-based crosslinking points and urethane bonds. Moreover, modulated DSC experiment carried out on crude organosolv lignin showed a T_g at 76°C (Table 1). This glass transition can be associated to the relaxation temperature obtained from DMTA experiments with PU samples. In addition this transition becomes closer of the T_g of crude lignin as the lignin content increases in the PU.

These different results may indicate phase separation behaviour of PU samples, which is in good correlation with those reported in literature. While the T_g attributed to the soft segments is below the ambient temperature, the T_g of hard domains is above. In summary, these synthesized PUs might be at least partially described as amorphous segmented polyurethane with phase separation. Soft phase is composed by PPG polymer while lignin and urea groups form hard segment. This microphase separation is also responsible for the elastomeric properties of these polyurethanes as shown by ambient stress-strain curves [28]. Table 5 presents main mechanical properties under uniaxial tensile tests including tensile strength, Young Modulus and elongation at break, obtained from the corresponding stress-strain curves. At ambient temperature, these materials present rubbery behaviour with a high elongation at break from 170 to 360 % and corresponding quite low modulus, from 0.2 to 2.8 MPa. The maximum strength significantly increased with the NCO:OH molar ratio. These results can be explained by the increasing of cross-linking points between isocyanate and hydroxyl groups causing the formation of a PU with strong bonds, thus giving a more rigid material. The highest value is obtained for PU synthesized with P_{425} and with the highest NCO:OH molar ratio (i.e., NCO:OH = 1.0) and reached 9.6 MPa.

Samples	Isocyanate prepolymer	NCO:OH molar ratio	DSC	DMTA	
			T_g (°C)	T_α (°C)	ν_e (mol.m^{-3})
LPU-1	P_{425}	0.2	-7	53	-
LPU-2		0.4	-7	49	20.6
LPU-3		0.6	-10	42	35.2
LPU-4		0.8	-7	42	75.6
LPU-5		1.0	-6	41	28.5
LPU-6	P_{1000}	0.2	-27	51	-
LPU-7		0.4	-19	44	10.1
LPU-8		0.6	-24	31	30.8
LPU-9		0.8	-19	29	43.0
LPU-10		1.0	-15	22	14.6
LPU-11	P_{2000}	0.2	-36	51	-
LPU-12		0.4	-39	50	1.8
LPU-13		0.6	-42	38	8.2
LPU-14		0.8	-41	34	12.2
LPU-15		1.0	-42	30	44.8

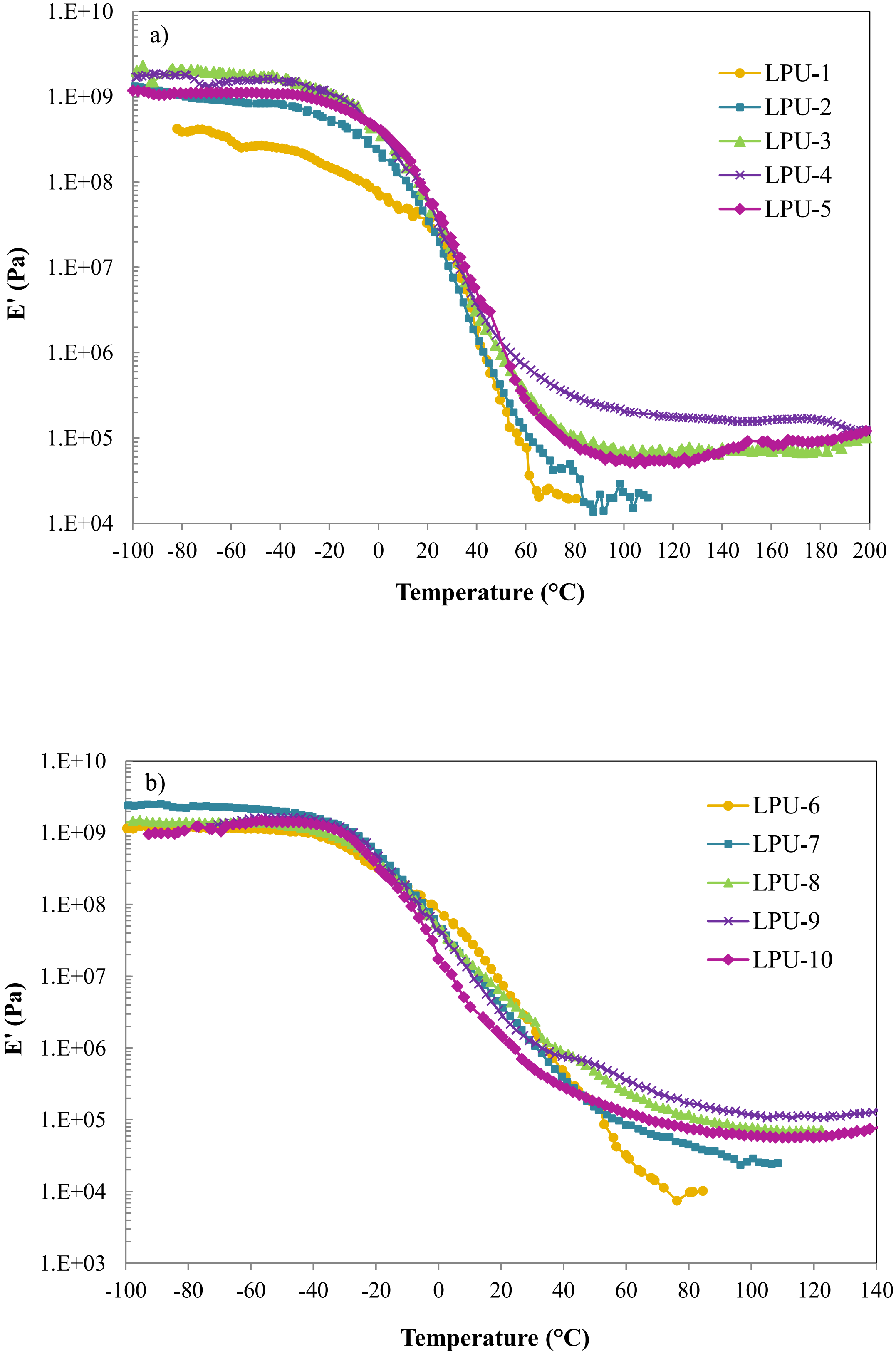
Table 4. Dynamical mechanical and thermal properties for the synthesized polyurethanes.

3.5 Effect of the prepolymer molar mass

The stress-strain curves of all the polymer materials show no decrease in the stress evolution vs. strain, until the rupture occurred. This typical mechanical behaviour can be compared to those of lightly crosslinked amorphous rubbers. The values of elongation-at-break display a very interesting trend which was linked to the evolution of the molar masses (M_n = 425, 1000 or 2000 g.mol^{-1}) of the prepolymers, P_{425}, P_{1000} and P_{2000}, respectively. The increasing of PPG molecular weight results in the increasing of elongation at break for all PUs series. In addition, longer soft segments are more able to respond to tensile deformations leading to higher elongations at break. Contrary to NCO:OH molar ratio, the isocyanate prepolymer chain length seems to impact the mechanical properties of PUs. As explained before, since the isocyanate prepolymers are incorporated into the PU network, the stretching distance between the macropolyol (LOAP) and isocyanate groups is modified by variation of the molecular weight of PPG. PPG chains provide flexibility to the resulting PUs and act as soft segment in the macromolecular architecture where lignin macropolyol acts as a cross linking point. The increasing of ν_e is linked to the decreasing of prepolymer molecular weight. PPG with low molecular weight bring stiffness and stability at high temperature (large rubbery plateau) whereas PPG with higher molecular weight bring flexibility at room temperature. However, it is relevant to notice that LPU 11 to 13 flow up to 80-100°C.

Samples	**Isocyanate prepolymer**	**NCO:OH molar ratio**	**Traction**		
			σ Maximum strength (MPa)	ε Elongation at break (%)	E Young's Modulus, (MPa)
LPU-1	P_{425}	0.2	2.7 ± 0.1	173 ± 22	1.6 ± 0.1
LPU-2		0.4	4.7 ± 0.7	235 ± 62	2.5 ± 0.2
LPU-3		0.6	6.6 ± 0.8	255 ± 34	2.3 ± 0.3
LPU-4		0.8	6.1 ± 0.2	201 ± 2	2.0 ± 0.2
LPU-5		1.0	9.6 ± 0.8	181 ± 10	2.8 ± 0.2
LPU-6	P_{1000}	0.2	3.2 ± 0.1	235 ± 22	0.8 ± 0.1
LPU-7		0.4	3.5 ± 0.2	240 ± 22	0.7 ± 0.1
LPU-8		0.6	4.1 ± 0.5	205 ± 15	0.7 ± 0.1
LPU-9		0.8	5.2 ± 1.0	202 ± 21	0.9 ± 0.0
LPU-10		1.0	-	-	-
LPU-11	P_{2000}	0.2	1.7 ± 0.1	317 ± 12	0.5 ± 0.0
LPU-12		0.4	1.5 ± 0.2	360 ± 6	0.2 ± 0.0
LPU-13		0.6	1.4 ± 0.1	230 ± 35	0.2 ± 0.0
LPU-14		0.8	1.5 ± 0.2	237 ± 6	0.2 ± 0.0
LPU-15		1.0	-	-	-

Table 5. Mechanical properties from uniaxial tensile tests of different synthesized PUs at ambient temperature with a crosshead speed of 20 mm.min^{-1}


a)
1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
E' (Pa)
-100 -80 -60 -40 -20 0 20 40 60 80 100 120 140 160 180 200
Temperature (°C)
LPU-1
LPU-2
LPU-3
LPU-4
LPU-5
b)
1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
E' (Pa)
-100 -80 -60 -40 -20 0 20 40 60 80 100 120 140
Temperature (°C)
LPU-6
LPU-7
LPU-8
LPU-9
LPU-10

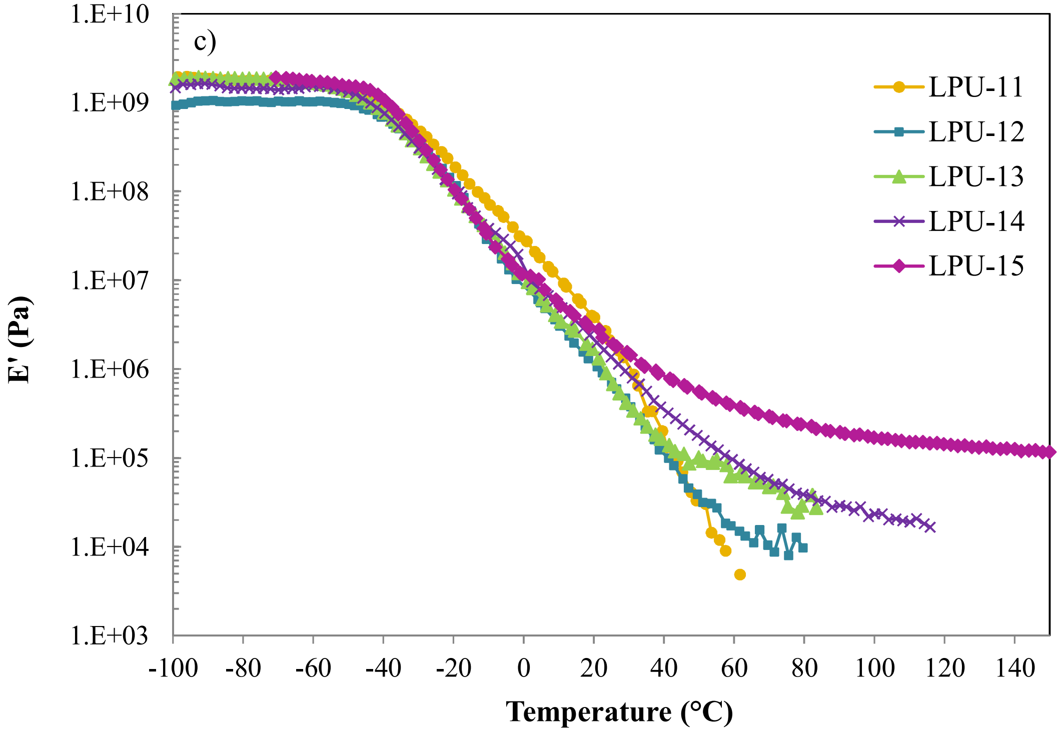
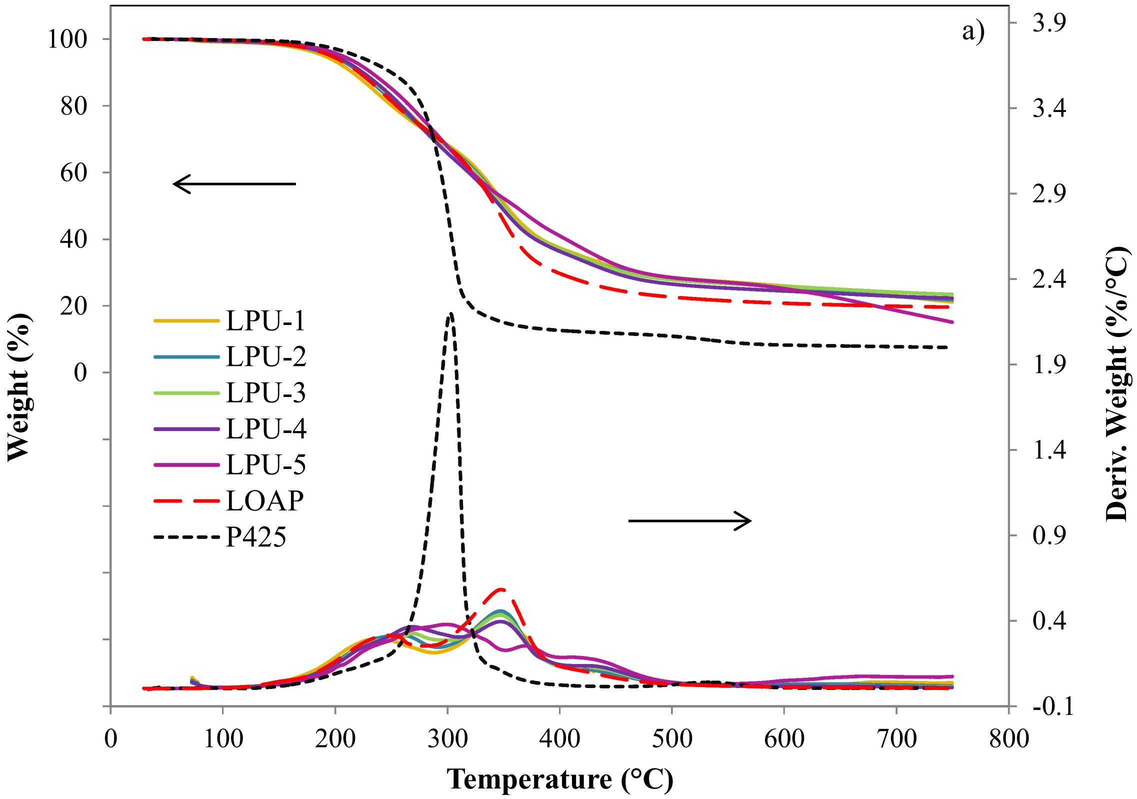


Figure 8. DMTA curves of the PUs (a : E' of PU based on P_{425} systems ; b : E' of PU based on P_{1000} systems; c : E' of PU based on P_{2000} systems)

3.6 Thermogravimetric analysis

Segmented LPUs are mainly composed by two different structural block based on LOAP and isocyanate prepolymer, respectively. Their relative compositions affect their thermal degradation. Usually, PUs thermal decomposition is a multi-stage process with e.g., the decomposition of urethane bonds and the degradation of the soft segments[40]. Figure 9 (a, b and c) displays the TGA and DTGA curves of PU samples under nitrogen atmosphere at 10°C.min^{-1}. It can be observed that all of the PU materials show quite similar a two-step degradation behavior. First degradation step occurs between 200°C and 300°C (T_{1max}) and concerns decomposition of hard segments attributed to LOAP component. On the other hand the second step is attributed to soft segments decomposition[34] with T_{2max} is between 350-400°C. In fact, the degradation of isocyanate prepolymer (P_{425}, P_{1000} and P_{2000}) is based on urethane bonds decomposition which begins at 240°C and reaches a maximum rate at 302-359°C depending on molar mass of PPG used. While LPU based on P_{2000} and P_{1000} show a clear two-step degradation mechanism, LPU-1 to 5, show a broader degradation with no distinctive peak on DTGA curves similar to LOAP behavior. However this LPU series shows the best thermal resistance compared to the others. This might be due to the high content of LOAP into the LPU matrix (from 89 to 63 % w/w). Figure 9 also shows a char residue at 750°C for all LPUs materials. This high char residue (almost 20% of weight) is due to the high thermal resistance of lignin due to the large number of ether linkages and aromatic groups in its chemical structure[41].



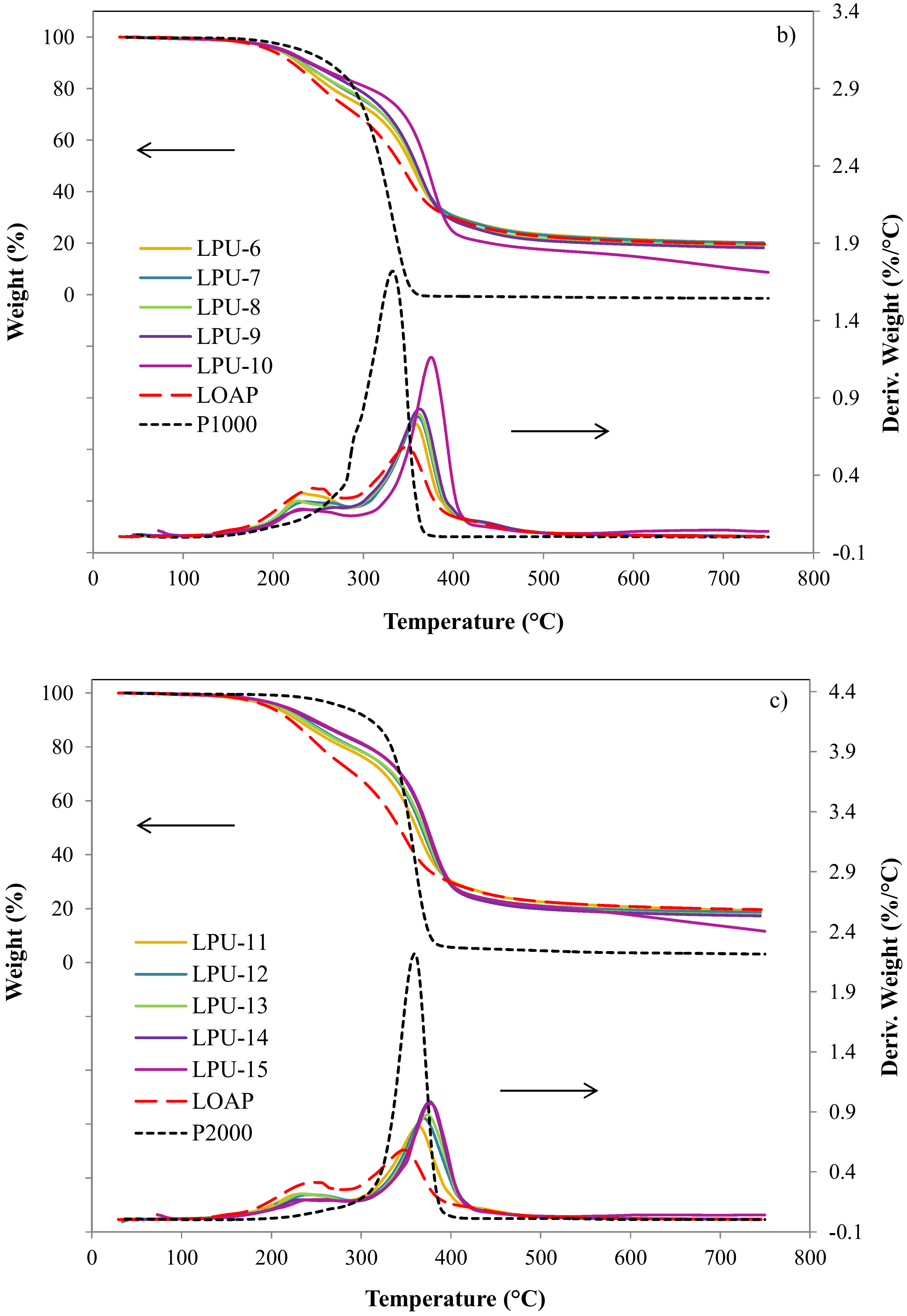


Figure 9. TGA/DTGA curves for PUs based on LOAP and isocyanate prepolymers (P_{425}, P_{1000} and P_{2000}).

a) LPU-1 to 5 and their respective components (LOAP and P_{425}).
b) LPU-6 to 10 and their respective components (LOAP and P_{1000}).
c) LPU-11 to 15 and their respective components (LOAP and P_{2000}).

4. Conclusion

The reaction conditions of lignin esterification and fatty acid modification were investigated leading to the synthesis of a new original macropolyol based both on lignin and fatty acid. This macropolyol was then characterized and subsequently used as an efficient building block for the synthesis of PU architectures. The macromolecular structure of the resulting PUs were designed in series by varying the NCO:OH molar ratio and the molecular weight of PPG soft segments. The thermal, mechanical and rheological properties of the corresponding LPUs were investigated by DSC, TGA, DMA and uniaxial tensile tests.

For high NCO:OH molar ratio, LPUs exhibit a temperature independent rubbery plateau (indicated by dynamic mechanical thermal analysis) and a clear phase separation based on DSC and DMA results. It has been concluded that soft segments were composed by PPG polymer chains and hard domains were mainly based on lignin crosslinking points. Each domain was characterized through their characteristic temperatures, which are below and above ambient temperature for soft and hard segments, respectively.

The increases in the molecular weight of PPG soft segment resulted in greater soft segment mobility and a lower glass transition temperature. In term of thermal stability of LPU samples, lignin confers to material a high thermal resistance compared to isocyanate prepolymer.

From this study, it can be concluded that a new type of macropolyol based on lignin can be used as a building block to design a new PU architectures with advanced properties. Such organized macromolecular systems with a high biobased content (up to 89%), might be foreseen to widen the scope of materials used for certain durable applications (e.g. in building and automotive industries). Hence, this work highlighted new possibilities for the valorization of crude lignin in comparison with its currently known applications. It is now worth considering the use of this industrial by-product for a larger range of green applications without competition with food.

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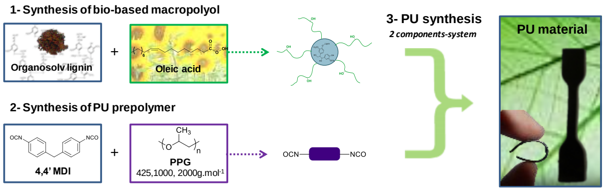

Short Text:

Macropolyols were successfully elaborated through combining two different biomolecules from biomass i.e., lignin (extract from lignocellulose) and oleic acid (from vegetable), without catalyst and solvent. Then, new performing and highly biobased Polyurethanes with controlled architectures have been synthesized and analysed.