



Exploring the application potential of incompletely soluble organosolv lignin as a macromonomer for polyurethane synthesis



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ABSTRACT

A new type of organosolv wheat straw lignin, so-called Biolignin™, was studied. It is obtained according to the biomass processing in water diluted organic acid media and is not completely soluble in conventional organic solvents traditionally applied for polyurethanes (PU) synthesis. The fractionation of the lignin by sequential extraction with dichloromethane, methanol and a mixture of both solvents was performed. The total yield of the separated soluble fractions was 40%. The separated fractions were characterized, and preliminary kinetic investigations were used to reveal the reactivity of fractions obtained towards 4,4'-methylene diphenylene diisocyanate (MDI) in dioxane media. PU films were synthesized by casting the three component systems: lignin fraction – polyethylene glycol with a molecular weight of 400 g mol⁻¹ – polymeric methyl diisocyanate prepolymerized in tetrahydrofuran solution at a constant NCO/OH ratio of 1.05. The content of lignin in PU compositions was varied in a range of 5–40%. The PU films were characterized in terms of crosslink density, tensile properties, glass transition temperature and thermal stability. The obtained results show that the isolated fractions of Biolignin™ act as a crosslinking macromonomer in the PU network. Depending on the lignin fraction type and its content in the composition, the tensile properties of PU films with a high elastic state at room temperature or the tensile properties of glassy cross-linked films were obtained. Evidence for the activity of lignin fractions as antioxidants of PU compositions and charcoal formation promoters in the case of the high temperature treatment of PU in air was obtained.

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1. Introduction

Lignin is a unique polyphenolic renewable raw material available as a by-product of the existing chemical processing of plant biomass that has an excellent capability for producing a value-added polymeric material, characterized by competitive mechanical and thermal properties, and chemical stability (Belgacem and Gandini, 2008; Hu, 2002). Nowadays, the annual industrial output of lignin is about 50 million tons, which are used primarily for energy production by combustion. Only a small amount (1–2%) is used for manufacture of a wide range of value-added products (Lora and Glasser, 2002). However, this approach disagrees with the main principle of the modern biorefinery conception – achievement of the most profitable usage of all components of the lignocellulosic complex.

All known technical lignins, irrespective of how they have been obtained and from what plant sources, are amorphous het-

erogenic aromatic polymers with glass transition in a range of 70–170 °C, containing a significant amount of functional groups and reactive sites, namely, phenolic, aliphatic, carboxylic OH groups, substituted aromatic sites and C=C bonds (Belgacem and Gandini, 2008). These chemical feasibilities allow considering lignin as a prospective building block for different polymeric compositions: phenol- and urea-formaldehyde resins, polyester resins, epoxy resins, polyurethanes etc. (Hu, 2002). In the broad spectrum of modern industrially produced polymers, PU are considered as a most versatile materials (Ionescu, 2005). Free aliphatic and phenolic OH groups are the most important functional groups opening up considerable opportunities for lignins' application as an aromatic polyol building block, capable of forming a number of covalent bonds with isocyanates in PU compositions. Although different technical lignins (kraft lignin, liginosulfonates, some organosolv lignins) have been successfully tested for obtaining PU materials on a laboratory scale (Belgacem and Gandini, 2008; Hu, 2002; Hatakeyama et al., 2004), lignin-containing PU materials have not yet been manufactured on an industrial scale. The main difficulties in working out market-oriented lignin-containing polymeric composite materials are as follows: heterogeneity of technical lignins,

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variation in the functional groups' content, their types and proportion in lignins, as well as the difference in molecular mass distribution (MMD) of the lignin fragments formed during the biomass processing, the structure of lignin-forming phenyl propane units, links between them, the solubility in organic solvents that varies in a wide range and restricted accessibility of reactive sites towards isocyanate due to their steric hindrance (Gosselink et al., 2010; Kelley et al., 1989; Lora and Glasser, 2002; Mahmood et al., 2016).

Various pretreatments are used to decrease the above-mentioned disadvantages of lignin and to enhance the efficiency of technical lignins' application as a macromonomer capable of taking part in the formation of polymeric structures that have to improve the target properties of polymeric materials. These methods are based on the depolymerization of the lignin matrix via the cleavage of ether linkages into more uniform oligomeric or reduced molecular weight products with enhanced accessibility of functional groups in reactions with isocyanates (Mahmood et al., 2016). Acid-, base- and metal-catalyzed as well as ionic liquids-assisted, and sub- and supercritical fluids-assisted depolymerizations of lignins have been investigated (Wang et al., 2013). The produced depolymerized lignins were successfully utilized as bio-polyols replacing up to 50% of commercial polyols for the preparation of rigid PU foams (Mahmood et al., 2016). Oxypropylation of technical lignins at ambient pressure in the presence of alkali catalysts is recognized as another approach to overcome the molecular and functional heterogeneity of lignins, and obtain lignopolyols for the formation of rigid PU foams that meet the requirements of commercial standards (Arshanitsa et al., 2015; Cateto et al., 2009; Li and Ragauskas, 2012). In this case, the degradation of the lignin core is accompanied by the attachment of oxypropyl units towards the OH groups of lignins, thus converting the acidic groups (phenolic, carboxylic) into aliphatic ones with higher reactivity towards isocyanate. Undoubtedly, the above mentioned processes are challenging due to the severity of reaction conditions (220–300 °C, and a pressure of 5–30 bar) (Mahmood et al., 2016; Arshanitsa et al., 2015). The fractionation of technical lignins by organic solvents extraction at atmospheric pressure and room or refluxing temperature could be a prospective opportunity, increasing the efficiency of lignin application as a macromonomer for PU materials' fabrication. Fractionation of different unmodified commercial kraft and organosolv (ethanol – water) lignins by diethyl ether, *n*-propanol, methanol and the dichloromethane/methanol mix allows obtaining of lignin samples with a lower molecular weight (MW), more uniform by MMD, completely soluble in organic solvents commonly used in PU chemistry and suitable to fulfill successfully the role of macromonomers in PU material synthesis (Gosselink et al., 2010; Kelley et al., 1989; Li and McDonald, 2014; Morck et al., 1986; Vanderlaan and Thring, 1998; Yoshida et al., 1987a). Fractionation is not an exclusive technique for obtaining a more uniform raw material for further processing but is used as an approach to elucidate the mechanism of the process, to gain new knowledge about the integral impact of different lignin characteristics on the properties of PU materials and, finally, to reveal a new application potential of non-modified lignins. Such an approach permits obtaining of PU elastomers with predictable thermal and mechanical properties, which can be varied in a wide range depending on the lignin fractions' MW, their content in PU and the type of the used soft segment (Yoshida et al., 1987b; Yoshida et al., 1990; Reiman et al., 1990). PU composites that have a potential for application in the field of high performance coatings and adhesives are obtained also on the basis of the methyltetrahydrofuran soluble fraction of kraft lignin Indulin AT and toluene diisocyanate-trimethylolpropane adduct (Griffini et al., 2015).

Today, the production of bioethanol as an alternative to fossil gasoline can be performed by acid and enzymatic hydrolysis of var-

ious pretreated plant biomasses. Therefore, various processes are currently under development. This leads to a new type of technical lignins, the properties of which are strongly dependent on the biomass origin and the pretreatment technology (Zhao et al., 2009). This is a challenge for the synthesis of novel lignin-containing polyols for application in different PU materials.

In this work, the object of investigation was a novel organosolv lignin of wheat straw, Biolignin™, obtained as a product of the technology developed by Compagnie Industrielle de la Matière Végétale (CIMV, France). This technology allows separating all the three main plant polymeric biomass components – cellulose, hemicellulose and lignin – without their significant degradation using a mix of water diluted acetic and formic acids and represents the first biomass refinery technology (Delmas et al., 2011).

The objective of the present study was to evaluate the suitability of application of the novel wheat straw lignin, Biolignin™, as a hydroxyl-containing macromonomer for PU films' synthesis. The poor solubility in organic media and the high polydispersity eliminate the use of Biolignin™ as a macromonomer in a lignopolyurethane (LPU) system. To avoid this disadvantage, Biolignin™ was fractionated by sequential extraction using solvents of different polarity and their mixture. Each fraction was characterized in terms of the composition, MMD, functionality and reactivity with MDI. The effects of the incorporation of each fraction on the structure, and tensile and thermal characteristics of model LPU systems on the basis of polyether diol and aromatic polyisocyanate were studied and discussed. The valorization of the fractionated novel lignin as an antioxidant and a charcoal formation promoter in PU systems was discussed.

2. Materials and methods

2.1. Lignin sample

Biolignin™ (further "lignin") was extracted from wheat straw using a mixture of acetic acid/formic acid/water at the CIMV pilot plant (Pomacle, France). Klason lignin ($89.0 \pm 1.0\%$) was determined according to TAPPI T222 standard. Ash content ($1.0 \pm 0.1\%$) was measured according to LVS EN 14775, 2010. Before fractionation, lignin was washed with deionized water up to pH 4.4, then air dried up to a moisture content of 5% and ground using a disintegrator DESI-11 (DESINTEGRAATOR Tootmise OU). The particle size of the ground lignin was ≤ 0.1 mm.

The chemicals used for analyses, including solvents, were of analytical grade (Sigma–Aldrich, Karl Rotch GmbH) with the exception of dioxane and tetrahydrofuran, which were extra-dry (Fluka).

2.2. Solvent fractionation

Lignin was fractionated by successive extraction with a dichloromethane, methanol, and methanol/dichloromethane mixture (7:3 v/v), differing by their polarity. The fractions obtained were abbreviated as DCM-F, MET-F and MET/DCM-F, respectively. The choice of solvents was conditioned by their proven efficiency for fractionation by molar mass and purification of different wood and grass lignins, targeted for application in binder compositions (Gosselink et al., 2010). Lignin (20 g) was suspended in 100 mL of the respective solvent and continuously stirred using a laboratory shaker at room temperature for 6 h. The undissolved material was filtered off and resuspended for a second identical extraction. The fractions from both steps were combined. The collected dissolved material was filtered over a glass filter (pore size 40–100 μm) and vacuum dried. The yields of the fractions were shown in percentage on oven dry ash-free non-extracted lignin. Three replicates of each fractionation were made.

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