



## A simple methodology for improving the performance and sustainability of rigid polyurethane foam by incorporating industrial lignin



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### ABSTRACT

Lignin, an inexpensive renewable biopolymer that offers both aliphatic and aromatic hydroxyl (–OH) functional groups, is a potential raw material for the polyurethane industry. Contemporary approaches for incorporating lignin in rigid polyurethane foam (RPUF) involve mechanical mixing of microscale lignin powder under ambient conditions or at high loading levels, resulting in the RPUF with inferior compressive mechanical and thermal conductivity properties compared to petrochemical-based controls. Herein, we demonstrate a significant improvement in the dispersion of an industrial grade kraft lignin in a polyol mixture (96% sucrose/glycerine initiated polyether polyol and 4% glycerol) by dispersing at high-temperature (120 °C, 12 h) resulting in RPUF with enhanced performance. Through this methodology, the polyol/lignin dispersion with 5 wt.% lignin has afforded a simultaneous improvement in thermal insulation (by 5%) and compressive strength (by 4%) of RPUF compared to the control and such a property profile, to the best of our knowledge, has not yet been achieved in lignin substituted RPUF systems.

### 1. Introduction

Lignin, a renewable aromatic biopolymer, is produced at least ~50 million tons annually as a by-product from the refining of biomass. Regardless of its renewability and abundance and availability, only about 1–2% is used in value-added applications. (Arshanitsa et al., 2014; Gandini, 2008; Lora and Glasser, 2002) Possessing a considerable amount of both aliphatic and aromatic hydroxyl (OH) groups per molecule, lignin is a potential alternative to petrochemical polyols in the polyurethane industry. (Arshanitsa et al., 2014; Cateto, 2008; Oribayo et al., 2017; Thielemans and Wool, 2005; Xue et al., 2014). However, it is a complex macromolecule having a high average molecular weight, and inherent steric hindrance in its structure which limits the accessibility of its hydroxyl functional groups. (Obaid et al., 2016) The full potential of lignin can only be exploited in urethane systems if these functional groups are made accessible for reacting with isocyanates which can maximise the potential improvement in physical, thermal and mechanical properties of the final product. Rigid polyurethane foam (RPUF) is widely used in a range of applications, including the

building industry and domestic refrigeration, because of its superior thermal insulation properties, excellent strength to weight ratio, self-adhesive properties and good dimensional stability. (Bernardini et al., 2015; Lim et al., 2008; Mahmood et al., 2016) Currently the polyols used in the production of RPUF are largely derived from petrochemical sources. These resources, however, are finite and subject to global economic cycles. Therefore, there is an increasing interest in alternative renewable feedstocks for polyols, ideally without increasing cost or compromising performance. (Briones et al., 2011)

One approach of exploiting the potential of lignin in RPUF is replacing petrochemical polyols with oxypropylated lignin polyols. (Cateto et al., 2014; Cateto et al., 2009; Li and Ragauskas, 2012; Nadji et al., 2005) While this chemical derivatisation approach improves the mechanical properties of the RPUF, it also increases the cost of the final RPUF compared to its counterpart based on petrochemical polyols alone. The direct use of inexpensive industrial lignin types with minimal chemical modifications or use of large amounts of organic solvents is preferred from an economic and environmental point of view. The use of kraft lignin, an inexpensive by-product of the

**Abbreviations:** RPUF, rigid polyurethane foam; RP-series, room temperature processed polyol dispersions; HP-series, high-temperature processed polyol dispersions; RF-series, foams from polyol/lignin dispersions prepared at room temperature; HF-series, foams from polyol/lignin dispersions prepared at high temperature; pMDI, polymeric methylene diphenyl diisocyanate

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mainstream pulp and paper industry, has up until now been associated with significant limitations due to its high molecular weight and highly complex molecular architecture. To date, the direct incorporation of lignin under ambient mixing (and at high loadings up to 64 wt.%) in the petrochemical polyol component has resulted in RPUF with inferior mechanical properties compared to RPUF based solely on petrochemical polyols. (Luo et al., 2013b; Pan and Saddler, 2013; Xue et al., 2014) This is not surprising given that the presence of micro-scale fillers (Kuranska and Prociak, 2012; Xue et al., 2014) and a lack of homogeneity of the polyol blend (Duval and Lawoko, 2014) is known to be detrimental to achieving consistent mechanical properties in RPUF. The incorporation of lignin into petrochemical polyols would be expected to be difficult given that lignin is highly polar, while polyether polyols are of relatively low polarity (Duval and Lawoko, 2014). As acknowledged in a recent review (Mahmood et al., 2016), the most prominent drawback direct incorporation of unmodified lignin in RPUF is its poor solubility of lignin in the polyol system. Hence, the direct incorporation of lignin in polyol with enhanced dispersion and miscibility still remains a challenge. Therefore, this study looks at an alternative strategy for increasing the disaggregation, dispersion and miscibility of kraft lignin in petrochemical polyol through the use of lower loadings together with the judicious selection of other RPUF components and processing conditions. Hatakeyama et al. (Hu, 2002) have studied the use of glycols such as polyethylene glycol (PEG) and polypropylene glycol (PPG) as solubilising agents for industrial lignin, including kraft lignin and hardwood organosolv lignin, in RPUF systems. However, the choice of such materials is not ideal for RPUF as they are di-functional polyols, and as such will have a negative impact on the overall cross-link density of the resultant RPUF. In this regard, glycerol would be a better choice as a compatibiliser between the polyol and lignin given that it is a trifunctional low molecular weight polyol and already used in RPUF, either directly as a cross-linker or as an initiator for the production of polyether polyols. (Luo et al., 2013a) Further, it is readily available from a sustainable resource as a by-product of the biodiesel industry at a rate of at least 10 kg for every 1000 kg of biodiesel obtained. (Hejna et al., 2017)

In this study, while using the glycerol as compatibiliser and cross-linker, our methodology was to disperse lignin in polyether polyol at a temperature closer to the 'softening' point of kraft lignin in order to enhance the dissolution, disaggregation and dispersion. The influence of this heat-assisted dispersion method was systematically investigated by comparing the polyol/lignin dispersions, prepared through conventional mixing at room temperature and at 120 °C for 12 h, and the structure and performance of the resultant RPUF. A polyol mixture of 4% of glycerol and 96% of a commercially available polyether polyol (Voranol®RH360) was chosen for developing a model RPUF. In summary, although efforts have been made to substitute the petrochemical-based polyols with various types of unmodified industrial lignin through mechanical mixing methods (Pan and Saddler 2013; Luo et al., 2013a,b; Xue et al., 2014; Arshanitsa et al., 2014), it has been at the expense of compressive mechanical properties. To the best of our knowledge, this is the first study demonstrating improvement in compressive strength and reporting thermal insulation properties for RPUF containing unmodified industrial lignin, more specifically within the commercially acceptable specifications for the properties. This has been achieved by systematically investigating the influence of processing conditions (at a temperature close to the 'softening' point of lignin) and the dispersion of lignin (< 10%) on the functional properties of the resultant RPUF.

## 2. Experimental

### 2.1. Materials

Kraft lignin (370959) from Sigma-Aldrich is a brown powder with a specified pH and moisture content of 5.5–7.5 and 5% respectively

(specification document PRD.0.ZQ5.10000058413). The lignin powder was dried under vacuum at 80 °C overnight prior to use. It was also further characterised (Fig. S1, Table S1 and S2 in Supplementary information) and the total hydroxyl value (OH<sub>v</sub>), molecular weight (*M<sub>w</sub>*) and polydispersity index (*M<sub>w</sub>*/*M<sub>n</sub>*; PDI) were found to be 356 mg(KOH)/g, 9500 and 3.21, respectively. From this data, the nominal functionality was calculated to be around 60. The lignin was also found to have 1.5% sulphur and insignificant carboxylic acid groups consistent with other reported values. (Boeriu et al., 2014; Sameni et al., 2016) Voranol®RH360 (Dow Chemicals), a sucrose/glycerine initiated polyether polyol, with a nominal hydroxyl value of 345–375 mg (KOH)/g, water content of less than or equal to 0.1 wt.% and a functionality of 4.4, was tested for hydroxyl value prior to use and found to be slightly out of specification (340 mg (KOH)/g). Glycerol (VWR Chemicals) was also tested for hydroxyl value (1926 mg (KOH)/g) prior to use and found to be slightly higher than specification (nominally 1827 mg (KOH)/g). All other materials including surfactant (Tegostab®8460, from Evonik), catalyst dimethylcyclohexylamine (DMCHA), blowing agent hydrofluorocarbon HFCM1 (a proprietary blend of HFC245fa and HFC365mfc) and polymeric methylene diphenyl diisocyanate (pMDI) were used as received from Applied Polymers without further purification. The NCO content of the pMDI was reported at 31.5% in the Applied Polymers product data sheet. Hydrochloric acid, dimethyl formamide (DMF), and deuterated dimethyl sulphoxide (DMSO-*d*<sub>6</sub>) were used as received from Sigma-Aldrich. Pyridine and acetic anhydride were also used as received from VWR Chemicals.

### 2.2. Preparation and characterisation of polyol/lignin dispersions

Prior to making foam, the solubility behaviour of lignin in a mixture of Voranol®RH360 and glycerol was investigated. Keeping the glycerol content (4%) constant, the polyol/lignin dispersions were prepared with increasing loading of lignin from 2.5 to 10% under two different conditions. The first polyol blend series (RP<sub>0</sub> to RP<sub>10</sub> series) was prepared by mechanical mixing at room temperature for 10 min using a vortex mixer at 3000 rpm, which is similar to the process used in previous reported studies. (Pan and Saddler, 2013; Xue et al., 2014). The second polyol blend series (HP<sub>0</sub> to HP<sub>10</sub>) was prepared by mixing the lignin, glycerol and Voranol®RH360 at 120 °C for 12 h using an overhead stirrer (at 400 rpm) and a hotplate. The selection of 120 °C was chosen from the DSC thermogram of lignin which exhibited an endotherm between 80 and 120 °C in the first heating thermogram (Fig. S2 in Supplementary information). It also corresponds to the "softening temperature" reported for dry softwood kraft lignin. (Tomani et al., 2011)

After mixing, the solubility of lignin in Voranol®RH360/glycerol was determined based on the method described by Cybulska et al. (Cybulska et al., 2012) with minor modification to align with the foam-making procedure. The insoluble fraction was filtered using a 0.45 μm cellulose acetate filter paper under vacuum, washed with deionised water and dried at 70 °C (air-oven) overnight prior to weighing. The weight fraction of soluble lignin was calculated from the initial lignin weight. All of the polyol/lignin dispersions were examined using optical microscopy (OLYMPUS BX61) to investigate the dispersion quality as well as the average particle size of lignin in the polyol blends. 10 μL of each blend was clamped between microscopic slides and examined under optical microscopy. The viscosity of the lignin-polyol blends was measured using a parallel plate rheometer (AR1500 rheometer) at 25 °C within the shear rate range of 0.1–100 s<sup>-1</sup> under steady state flow mode.

The hydroxyl values (OH<sub>v</sub>) of the Voranol™ RH360, glycerol, lignin and polyol/lignin dispersions were analysed according to ASTM D4274-99 and ISO 14900:2001 through acetylation and a conventional acid-base volumetric titration (See Table S1 in Supplementary information). The nominal functionality of the lignin was calculated from the total hydroxyl value (OH<sub>v</sub>) including both aliphatic and aromatic hydroxyl

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