Lignin Effect to Synthesis of the Hybrid Polyurethane

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Abstract. Lignin which is hydrophobic due to presence of carbonyl; carboxyl; hydroxyl and phenol functional group, can be used as compatibilizing agent through grafting a hydrophobic part such as polyurethanes. Lignin-based biopolyurethane (bioPU), was synthesized by two stages of reaction viz., polyurethane preparation through reacting 4,4'- Methylenebis (CyclohexylIsocyanate) (HMDI) and polyethylene glycol (PEG, molar mass of 4000 g/mol); bio-PU preparation through grafting lignin onto the polyurethane. The ratio of diisocyanate to polyol and lignin addition were varied in 1: 4, 1:1 and 0.25 g, 0.5 g, 1 g, respectively. Products were investigated by observing FESEM (Field Emmision Scanning Electron Microscope), 1H NMR (Nuclear Magnetic Resonance) and FTIR (Fourier Transform Infra-Red Spectroscopy). The FESEM result shows that lignin based bioPU with isocyanate/polyol ratio 1:4 and 1 g lignin addition is more homogenous than isocyanate/polyol ratio 1:1 and 0.25 g lignin. The NMR and the FTIR spectra reveal the lignin grafed onto polyurethane product. The addition of 0.25 and 1 g lignin resulted in 0.2 and 0.6 hidrophilic/hidrophobic segment ratio, respectively. Furthermore, characterizations of the products confirmed that the lignin-based bioPU can be a promising compatibilizer.

1. Introduction
Biomass materials such as lignin and cellulose are the promising sources to face some challenges regarding material problems [1-5]. Researches about lignin has grown up significantly due to its potential and advantageous properties like numerous reactive functional groups, renewability and separable from almost of plant kingdom after cellulose [6-11]. Being different from cellulose and hemicellulose, the lignin is not able to be divided by hydrogen enzymes due to irregular network. Waste and residue which contain of lignin can cause environment problem [12]. There are some solutions such as incineration of lignin wastes to obtain energy in a production process, and only 1-2% of lignin is converted into derivative products. On the other hand, some reserches have been explored the lignin application such as for biopolymer modification, epoxy polymer, compatibilizer and polyurethane [1,3,11,13-14].

Lignin is a highly branched polymer with a variety of functional group, where hydroxyl group as hydrophilic part and hydrocarbons and benzene ring as hydrophobic part. Therefore it has possibility to enhance compatibility between hydrophilic and hydrophobic material in a composite. Previous research showed that the addition of lignin/polypropylene (PP) can increase mechanical properties of coffee ground reinforced polyactic acid (PLA) composite. Moreover, the fact that lignin contains a more hydrophilic than hydrophobic part, leading to more compatible to hydrophilic materials. The other side, becuase of hydroxy group abundances, this material has a chance to be modified by grafting onto a polyurethane in order to enhance its hydrophobicity. Furthermore, it gives a possibility
to replace polyols in PU production, either play the role of “hard segment” or can become a chain
extender [4,8,14-17].

Shuai Li, et.al. has reported that modification of lignin by creating new chemical active sites with
carboxymethylation produced carboxymethylated lignin (CML) for highly-stable oil-in-water fuel
emulsions [18]. Rigid PU foam derived from lignosulfonate and lignin molecules act as hard segment
has been studied by Hatakeyama, et.al. [19]. Surface tension of lignin from black liquor has been
characterized by Rojas and friends and it showed the potency of lignin as polymeric surfactant and
emulsion stabilizer [15]. Furthermore, Xue, et.al. has made lignin based PU were prepared by replacing
polyol with lignin from 10 to 50% (molar percentage) and reinforced with 0.5 and 5 wt% content of
cellulose nanocrystals (CNC) [17]. These reports indicated that lignin is a potential biomass for some
versatile application and can be produced as compatibilizer with chemical modification of hydroxyl
groups by urethanization. It will be important to study the level of hydrophilic-hydrophobic of
modified lignin for compatibilizer application.

The aim of this study was to investigate the lignin composition effect to enhance hydrophobicity of
lignin through evaluating a ratio of hydrophilic to hydrophobic part of the hybrid lignin polyurethanes.
The products were characterised by measuring FTIR and H-NMR to investigate chemical structure of
the products, and FE-SEM to observe morphology of the products.

2. Experimental

2.1 Materials

Raw material Lignin from TCI, 4,4-Methylenebis (cyclohexylisocyanate) (HMDI), Polyethylene
glycol (PEG) Mw 4000, and DibutylinDilaurate catalyst (DD) obtained from SigmaAldrich.

2.2 Lignin-based Polyurethane Preparations

The first stage. Prepolymer was made by reacting 15.0 g PEG-4000 and variations on isocyanate, in the
20 mL dimethylformamide (DMF) and 2 drops of dibutyltindilaurate catalyst (DD) in the reactor
schlenk tube with inert nitrogen gas in temperature 80°C under stirring for 60 minutes.

The second stage. Lignin was dissolved in 5 mL of DMF with some variations and continue stirring
for 2 minutes. Samples was terminated by adding water to react with isocyanate as the end-group.

Material compositions for all experiments are showed in Table 1.

| Sample code | HMDI (mol) | PEG-400 (mol) | Lignin (g) |
|-------------|------------|---------------|------------|
| 1425        | 0.01       | 0.0025        | 0.25       |
| 1450        | 0.01       | 0.0025        | 0.50       |
| 14100       | 0.01       | 0.0025        | 1.00       |
| 1225        | 0.005      | 0.0025        | 0.25       |
| 1250        | 0.005      | 0.0025        | 0.50       |

2.3 Characterizations

The sample was characterized by using 1H Nuclear Magnetic Resonance (NMR) and Fourier
Transform Infra-Red Spectroscopy (FT-IR Spectroscopy) to confirm the structure of molecules and
reactions and Field Emission Scanning Electron Microscopy (FESEM) was used to know the
morphology of the sample. The polar and nonpolar ratio also can be calculated by the Equation I.

\[
p_{np} = \frac{\text{Total integration of spectrum } (H-a)}{3 \text{ atoms } H} \times \frac{\text{Total integration of spectrum } (H-e)}{4 \text{ atoms } H}
\]

3. Results and Discussions

3.1 Synthesis of hybrid lignin-based polyurethane

Hybrid lignin-based polyurethanes in this experiment were synthesized by exotermically reacting the
hydroxyl at lignin with an isocyanate group at the ends of polyl-based polyurethane (pre-
polyurethane) in the last synthesis stage [16]. In the first step, the pre-polymerization of polyurethane causes some of the isocyanates unreacted yet due to the excess amount of diisocyanates compared to the polyol. Those unreacted isocyanates were then reacted with lignin to obtain the lignin-grafted polyurethane. Presence of urethane group in chemical structure of the products was proved by analyzing NMR spectra which is confirmed by FTIR spectra. In detail the chemical structure analysis is given in Figure 2 and 3.

![Figure 1. FT-IR spectra of lignin](image1)

![Figure 2. NMR spectra of 1425 sample](image2)

![Figure 3. The FT-IR spectra of the products](image3)

FT-IR and NMR analysis confirms a two-step reaction process. Fig. 1 shows the spectra of lignin and Fig. 3 shows the absence of FT-IR absorption band in 2250 cm\(^{-1}\) confirms that there is no cyanate group any more in the product chemical structure. Meanwhile wide absorbance band in the range of 3000 cm\(^{-1}\), which belongs to cyanate group has been diminished as well. New absorbance band present in the 3420 cm\(^{-1}\), which belongs to either group of secondary amine and/or OH in the carboxylic acid functional group. Further analysis showed that specific band belongs to secondary
amine. The formation of this band confirms the existence of urethane group. Discussion above concludes that the method to synthesize the lignin-based polyurethane, was working well within the experimental

3.2 Morphology of hybrid lignin based polyurethane

The Field-Emission Scanning Electron Micrograph in Fig. 4 shows morphology of sample 14100 with lignin phase, which is good dispersion and distribution. The arrows indicate that the lignin phase segregations are not present. This leads to an indication of the high miscibility between lignin and pre-polyurethane phase during polyurethanization.

![Figure 4. FE-SEM sample of the 14100 at 1000x (a) and 2000x (b) magnification](image)

Meanwhile on the 1425 sample, the lignin-modified polyurethane has a fiber-like phase with agglomerated lignin small particles. Existence of the microsegregation in the micrograph indicated that the availability of the two different phases is present as shown in Fig. 5.

![Figure 5. FE-SEM sample of the 1425 product at 500x magnification](image)

3.3 Hydrophobicity of hybrid lignin-based polyurethane

One of the expected output in this research is to understand the compatibility of the polyurethane product through theoretically analyzing from the ratio of hydrophilic to hydrophobic phase. The hydrophobic phase is reflected by the number of the polyurethane phase indicated by chemical shift of outer PEG-4000 on 4.00 to 4.70. The hydrophilic phase is reflected by the lignin phase, as indicated on chemical shift of lignin on 7.80 to 8.2. By calculating the number of functional group, we can determine the relative number of H-aromatic lignin to the total H number which representing the hydrophilic functional group as well as the relative number of outer H of PEG to the total H number in the product which representing the hydrophobic functional group. By comparing the relative number of
each functional group, we can calculate the ratio of lignin to the PEG. From the data above, we can conclude that the 1250 has a hydrophilic to hydrophobic ratio of 1:5, whilst the 1450 is 4:10, and 14100 is 6.3:10. The data from Fig. 2 indicates that the higher the lignin content, the higher the ratio of hydrophilic content. The NMR spectra confirm that the product has been reacted with lignin. The existence of lignin spectra at chemical shift 7.8567 to 8.1897 confirms the reaction of polyurethane with lignin. Therefore, based on the absorbance of FTIR at 2250 and 3240 cm which indicated above, we can conclude that isocyanate and polyol has been reacted successfully. The NMR spectra peak at 1250, 1450, and 14100 indicated that the polyurethane has been reacted with lignin.

4. Conclusions
All polyurethanes samples composed of PEG, HMDI, and lignin has been reacted. From the FT-IR spectra which then supported by the NMR, the samples has reacted from the lignin. Meanwhile from the theoretical compatibility that is calculated from the ratio of the hydrophilic to hydrophobic functional group, we know that the addition of 0.25 gram of lignin makes the ratio between hydrophilic to hydrophobic phases of 1:5. Meanwhile the addition of 1 gram lignin makes the ratio to 6.25:10. The FE-SEM spectra indicates that phase segregation is present in the product, which makes it highly probable as a compatibility agent for polyblend purposes.

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