Abstract: In order to improve the compatibility between lignin fillers and polyurethane matrix, two different chemical strategies were used to modify the lignin macromolecules. Modified lignin was incorporated into vegetable oil-based polyurethanes to produce composites with high bio-content. Lignin modified with octadecyl isocyanate (lignin urethane) was found to be more compatible with the polyurethane matrix than lignin modified with butyric anhydride. The effect of lignin urethane loading on the thermo-mechanical properties, thermal resistance, and dielectric properties were investigated. High lignin content (up to 30 wt. %) increased the Young's modulus and lowered the onset of thermal degradation. Incorporation of lignin urethane did not change the glass transition temperature of the polyurethane composites significantly, but it increased the dielectric constant compared to neat polyurethane. This work provides an effective way of using lignin as a low-cost bio-renewable resource in the polyurethane industry.
High bio-content polyurethane composites with urethane modified lignin as filler

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Abstract

In order to improve the compatibility between lignin fillers and polyurethane matrix, two different chemical strategies were used to modify the lignin macromolecules. Modified lignin was incorporated into vegetable oil-based polyurethanes to produce composites with high bio-content. Lignin modified with octadecyl isocyanante (lignin urethane) was found to be more compatible with the polyurethane matrix than lignin modified with butyric anhydride. The effect of lignin urethane loading on the thermo-mechanical properties, thermal resistance, and dielectric properties were investigated. High lignin content (up to 30 wt. \%) increased the Young’s modulus and lowered the onset of thermal degradation. Incorporation of lignin urethane did not change the glass transition temperature of the polyurethane composites significantly, but it increased the dielectric constant compared to neat polyurethane. This work provides an effective way of using lignin as a low-cost bio-renewable resource in the polyurethane industry.

Keywords

Lignin; Polyurethane; Renewable resource
1. Introduction

Polyurethanes (PUs), typically synthesized through addition polymerization of polyisocyanates and polyols, are among the most versatile polymeric materials and have been widely used as foams, coatings, and sealants [1]. Currently, most of the polyisocyanates and polyols for PU production are derived from petroleum. Increasing concerns about the unsustainability of chemicals from petroleum resources and environmental problems caused by fossil fuels, have led to considerable efforts to develop materials based on renewable resources, such as natural oils, starch, cellulose, and lignin [2, 3]. For example, vegetable oil based PUs were successfully developed and their structure-property relationships have been extensively investigated [4, 5].

Lignin, second only to cellulose in abundance, is composed of three different types of phenylpropane units that form a rigid, three dimensional network [6]. More than one million tons of lignin and its derivatives are produced annually as byproducts of the paper and pulping industry, and traditionally most are burned as a low cost fuel [7, 8]. An attractive application of lignin is as an economical starting material to replace petroleum feedstock for various polymer products. Because lignin contains a large amount of hydroxyl groups (phenolic and aliphatic), one of the most widely studied strategies is to use lignin as a starting material for renewable polyols in polyurethane synthesis. This strategy has resulted in thermoplastics PU films from polybutadiene diisocyanate and lignin modified by formaldehyde [9], as well as strong thermoset PU films from a three-component system of Alcell® lignin, polyethylene glycol and polymeric methyl-diisocyanate [10]. Lignins from organosolv pretreatment and kraft pulping have been evaluated to replace petroleum-based polyols in the production of rigid PU foams [11]. Water-soluble lignosulfonate from sulfite pulping was used to prepare rigid polyurethane foam with glass transition temperatures ranging from 80 ºC to 140 ºC [12]. Modified kraft lignin
doped with multiwall carbon nanotubes was used to prepare nano-composites for sensor applications [13]. In the applications listed above, hydroxyl groups in the lignin were used as reaction sites. However, the structure and functionality of lignin fluctuate depending on its source and processing conditions (humidity, temperature and UV exposure) [14], which in turn influence the properties of the final PU to a large degree. Also, these structure and functionality variations may lead to heterogeneous final products, which is not acceptable for the current commercial polymers that require high-purity starting materials with significant and reproducible reactivity.

Incorporating lignin into PU matrices as non-covalent filler may be a more effective and economically viable approach [15]. Unfortunately, the large number of aromatic and aliphatic hydroxyl groups in lignin makes it highly polar, and therefore insoluble in non-polar thermosetting resins. Therefore, the chemical modification of lignin is necessary to synthesize well distributed composites.

In this research, two different chemical modifications of lignin are investigated to improve the interfacial interaction between a bio-based PU and the lignin filler. The chemical structure of the modified lignin are characterized by FTIR, elemental analysis and GPC. The modified lignins are incorporated into vegetable oil based-polyurethane to prepare composites with different filler loadings. Finally, the effect of filler loading on the mechanical, dynamic-mechanical, and dielectric properties, and the thermal resistance of the composites are investigated and discussed.

2. Materials and Methods

2.1 Materials
Epoxidized soybean oil was purchased from Scientific Polymer Inc., New York, NY. Methyl ethyl ketone (MEK), n-hexane, and ethyl ether were purchased from Fisher Scientific Company (Fair Lawn, NJ). Castor oil, sodium hydroxide, hydrochloric acid, butyric anhydride, isophorone diisocyanate (IPDI), and octadecyl isocyanate were obtained from Sigma-Aldrich (Milwaukee, WI). Lignin (Protobind 2400) in dry powder form was supplied by ALM Private Limited, India. The catalyst for the lignin-anhydride reaction was 1-methyl imidazole (1MI) obtained from Sigma-Aldrich (Milwaukee, WI). Dibutyltin dilaurate (DBTDL), used as the catalyst for hydroxyl group-isocyanate reactions, was purchased from Sigma-Aldrich (Milwaukee, WI). All materials were used as received without further purification.

2.2 Synthesis of vegetable oils based polyols

A soy-castor oil based polyol (SCP) was prepared according to a method developed by Zhang [5]. Here, the castor oil was saponified into castor oil fatty acid by sodium hydroxide and hydrochloric acid at 80 °C. Then, the castor oil fatty acid was used to ring open epoxidized soybean oil at 170 °C to obtain a light reddish/yellow, viscous liquid. The ratio of carboxyl acid groups to epoxy groups was 0.5:1. The OH number, acid number, number and weight average molecular weight, and polydispersity index of the SCP are shown in Table 1.

Table 1 The properties of SCP

<table>
<thead>
<tr>
<th></th>
<th>OH number (mg KOH/g)</th>
<th>Acid number (mg KOH/g)</th>
<th>Number /weight average molecular weight</th>
<th>Polydispersity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCP</td>
<td>148</td>
<td>3.7</td>
<td>2611/3442</td>
<td>1.32</td>
</tr>
</tbody>
</table>

2.3 Synthesis of lignin butyrate
Under vigorous stirring, 100 g lignin, 200 g butyric anhydride, and 1 wt. % catalyst 1-MI were added in a flask. The reaction mixture was heated to 50 °C and reacted overnight. Then, 200 ml ethyl ether was added to reduce the viscosity. The mixture was precipitated with 200ml n-hexane. Finally, the mixture was filtered and washed with n-hexane for at least three times. Lignin butyrate was obtained by drying in a vacuum oven overnight at 60 °C. The preparation of lignin butyrate is shown in Fig. 1(a).

2.4 Synthesis of lignin urethane

Under vigorous stirring, 100 g lignin, 150 g octadecyl isocyanate, 1 wt. % DBTDL, and 200ml MEK were added in a flask. The reaction mixture was heated to 80 °C and reacted for 24 h. After the reaction mixture had cooled down to room temperature, 200ml n-hexane was charged into the mixture under vigorous stirring. Finally, the mixture was filtered, washed with n-hexane for at least three times, and dried in a vacuum oven overnight. The preparation of lignin urethane is shown in Fig. 1 (b).

2.5 Preparation of PUs composites

Soy-castor oil based polyol and IPDI were mixed in a flask and stirred vigorously. The ratio of OH groups to NCO groups was 1:1.1. Then, 0.5 wt. % DBTDL was added as catalyst. The mixture was heated to 70 °C and held at this temperature for 1 h. Then, modified lignin at different loadings levels was added to the reaction mixture and the reaction continued for another 1 h. Finally, the mixture was poured into a Teflon mold and post-cured in an oven at 80 °C overnight. Specimens of the PU composites were cut into specific dimensions for thermal, mechanical and dielectric testing.

2.6 Characterizations
The FTIR spectra of lignin and modified lignin were recorded on a Nicolet 460 FTIR spectrometer (Madison, WI). The molecular weight distributions of lignin and modified lignin were determined using a THF-eluted GPC equipped with a refractive index detector. Elemental analysis results (%C, %H, %N) were obtained using a PE 2100 Series II combustion analyzer (Perkin Elmer Inc., Waltham, MA).

The distribution of butyrate lignin and urethane lignin in the polyurethane matrix were investigated by scanning electron microscopy (SEM, FEI Quanta 250 FEG) coupled with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments Aztec). The samples were sectioned by blades and examined by elemental mapping methods. Each map was generated by accumulating 40 scans with each scan collecting for 15 seconds at 5000× magnification at 10 kV with an output count rate of 12 kcps.

Dynamic mechanical analysis (DMA) of the PU films was conducted with a TA Instruments (New Castle, DE) model Q800 dynamic mechanical analyzer using a film-tension mode at 1 Hz. The samples were rectangular with 0.5 mm thickness, and 8 mm width. The samples were cooled and held isothermally for 3 min at -80 °C, then they were heated to 140 °C at a rate of 5 °C/min.

A TA Instrument model Q50 thermogravimetric analyzer (TGA) was used to measure mass as a function of temperature of the initially 7 mg samples. The samples were heated from room temperature to 800 °C at a rate of 20 °C/min in air.

The mechanical properties of standard dog-bone shape samples were tested using an Instron universal testing machine (model 4502) with a crosshead speed of 50 mm/min. At least four samples were tested for each experimental condition to obtain average property values.
The dielectric properties of both composites and neat PU were characterized using a Novocontrol dielectric spectrometer (Novocontrol Technologies, Hundsangen, Germany) with a frequency range from 1 Hz to 1 MHz at room temperature.

3. Results and discussion

3.1 Characterization of lignin butyrate and lignin urethane

The FTIR spectra of lignin, lignin urethane, and lignin butyrate are shown in Fig. 1 (c) where the important peaks have been assigned. Compared to the spectrum of unmodified lignin, in the spectra of lignin urethane and lignin butyrate the alcohol bands (3300-3700 cm\(^{-1}\)) were reduced in size, while the methyl and methylene C-H bands (2880-2966 cm\(^{-1}\)) increased, indicating that
Fig. 1 The preparation of lignin butyrate (a) and lignin urethane (b), and FTIR spectra of lignin, lignin urethane, and lignin butyrate (c).

the hydroxyl groups were consumed during butyration and the formation of urethane linkages. Direct evidence of the successful modification of lignin is the appearance of peaks at 1737 cm\(^{-1}\) corresponding to C=O ester, and the appearance of peaks at 1216 cm\(^{-1}\) corresponding to urethane linkages [16]. Elemental analysis was used to determine the composition of the modified lignins, see Table 2. Butyration increased the percentage of carbon in lignin butyrate. After modification
by octadecyl isocyanate, both the percentage of carbon and nitrogen in lignin urethane increased because of the formation of urethane groups.

Table 2 Elemental analysis of lignin, lignin butyrate and lignin urethane

<table>
<thead>
<tr>
<th></th>
<th>Lignin</th>
<th>Lignin butyrate</th>
<th>Lignin urethane</th>
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<tbody>
<tr>
<td>C (wt. %)</td>
<td>61.8</td>
<td>64.6</td>
<td>72.6</td>
</tr>
<tr>
<td>H (wt. %)</td>
<td>6.4</td>
<td>6.2</td>
<td>11.2</td>
</tr>
<tr>
<td>N (wt. %)</td>
<td>0.6</td>
<td>0.7</td>
<td>3.6</td>
</tr>
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</table>

3.2 Characterization of polyurethane composites

Fig. 2 Polyurethane composites with different loadings of modified lignin (a) photo of dog-bone samples: the top row is the composites with the lignin urethane (LU) and the bottom is the composites with the lignin butyrate (LB). (b) SEM microstructure of polyurethane/lignin urethane composites, (c) SEM microstructure of polyurethane/lignin butyrate composites (d) map of oxygen element of polyurethane/lignin butyrate composites.
Fig. 2 (a) shows samples of PU composites with different loadings of lignin urethane and lignin butyrate. All samples with lignin urethane exhibited homogenous morphologies, and with increasing lignin urethane loading, the samples became darker. The samples with lignin butyrate exhibited numerous agglomerations. The distribution of lignin butyrate and lignin urethane in the PU matrix were also investigated by SEM as shown in Fig. 2 (b) and Fig. 2 (c). The lignin butyrate agglomerated in the PU matrix, leading to the heterogeneity of oxygen content as shown in Fig. 2 (d) (A light area indicates a higher element concentration than a dark area). The urethane lignin disperses homogenously in the matrix. The homogenous distribution of lignin urethane in the PU matrix was attributed to the entanglement effect caused by the long, dangling octadecyl urethane chains and to hydrogen bonding between N-H from octadecyl urethane with C=O from the PU chain [17]. It was concluded that lignin urethane was more compatible with the PU matrix. Therefore, subsequent investigations focused on the effect of lignin urethane on the properties of the composites.

Table 3 Tensile test of polyurethane/lignin urethane composites

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ from DMA (°C)</th>
<th>$T_5$ (°C)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-0% LU</td>
<td>40.7</td>
<td>310.0</td>
<td>14.5±0.6</td>
<td>96.4±7.5</td>
<td>60.7±1.5</td>
</tr>
<tr>
<td>PU-5% LU</td>
<td>36.7</td>
<td>304.5</td>
<td>12.4±0.3</td>
<td>114.2±2.5</td>
<td>34.8±0.7</td>
</tr>
<tr>
<td>PU-10% LU</td>
<td>36.9</td>
<td>306.4</td>
<td>12.6±0.3</td>
<td>115.9±5.0</td>
<td>35.6±1.6</td>
</tr>
<tr>
<td>PU-20% LU</td>
<td>37.8</td>
<td>294.2</td>
<td>12.5±0.4</td>
<td>101.3±4.3</td>
<td>44.9±4.4</td>
</tr>
<tr>
<td>PU-30% LU</td>
<td>38.2</td>
<td>281.5</td>
<td>13.3±0.5</td>
<td>87.6±5.7</td>
<td>80.3±1.1</td>
</tr>
</tbody>
</table>
Fig. 3 shows the storage modulus and tan δ of polyurethane composites with different levels of lignin urethane. The glass transition temperature ($T_g$) was determined from tan δ peaks. All samples exhibited one tan δ peak, confirming the homogeneous nature of the composites. With increasing lignin urethane loading, the $T_g$ of the PU composites increased slightly (see Table 3). However, the $T_g$ of the neat PU was higher than those of the composites. It was concluded that the filler did not significantly affect $T_g$. At low temperatures, all samples behaved like solids with high storage moduli of $10^3$ MPa. As the temperature exceeded $T_g$, the storage moduli decreased rapidly because of the dramatic increase in molecular motion and then reached a plateau. With increasing loading levels of lignin urethane, the storage moduli of PU composites increased. The
storage moduli of the PU composites were typically lower than that of neat PU; however, in certain temperature ranges the composites deviated from this pattern. This negative effect of lignin on the storage modulus of PU composites will be discussed later. In the temperature range from 45-100 °C, PU composites with 20 wt. % lignin urethane exhibited higher moduli than neat PU; composites with 30 wt. % lignin urethane also had higher moduli in the temperature range from 35–120 °C. This behavior was attributed to the fact that in the cross-linked polymer network, lignin occupied a certain portion of the free volume and developed positive interfacial interactions with the polymer matrix through effective hydrogen bonding.

![Fig. 4 TGA curves of polyurethane composites with different loadings of lignin urethane.](image_url)

The influence of lignin urethane on the thermal stability of polyurethane was studied by TGA. Fig. 4 shows the weight loss curves in air for polyurethane/lignin urethane composites. Polyurethane/lignin urethane composites underwent thermal degradation in two main stages: The initial degradation stage in the 200-340 °C temperature range corresponding to the
decomposition of unstable urethane bond and cleavage of α- and β-aryl-alkyl-ether linkages of lignin, leading to primary amines, phenols, olefins and carbon dioxide [15]. Table 3 shows the 5% degradation ($T_5$) temperature for PU composites with 0 %, 5 %, 10 %, 20 %, and 30 % lignin urethane, respectively. The degradation stage above 340 °C was attributed to the chain scission of the vegetable oils, and the further thermo-oxidation of residual mass. With increasing loading of lignin urethane, the PU composites lost more weight in the first stage because of the increasing number of urethane groups and the unstable ether linkages introduced by the lignin urethane. The incorporation of lignin improved thermal resistance of polyurethane/lignin urethane composites in the second degradation temperature range, presumably because the increased number of aromatic groups and benzene rings introduced by the lignin urethane enhanced the thermal stabilities to some degree [18].

Fig. 5 Stress/strain curves of polyurethane composites with different loadings of lignin urethane. The results of the tensile tests of PU composites with different lignin urethane loadings are shown in Fig. 5 and Table 3. The results indicate that the incorporation of lignin urethane slightly
decreased the tensile strength of the PU composites. Two reasons were associated with this decrease in the tensile strength: (1) lignin urethane decreases the crosslink density of the matrix material because of the plasticized effect of lignin urethane [19]. (2) PU network near lignin urethane may be disrupted compared with the bulk matrix, and thus lowered the matrix integrity [20]. With 5% lignin urethane content, the Young’s modulus of PU composites was lower than that of neat PU. With increasing loading of lignin urethane, the Young’s moduli of the PU composites increased and the elongation at break decreased, indicating that the composites became stiffer. At 30% lignin urethane content, the Young’s modulus of PU composites was higher than the neat PU. Entanglement of the long urethane dangling chains with the PU matrix may have caused this improvement. On the other hand, the hydrogen bonding effect between -N-H from octadecyl urethane and -C=O in PU chains may have also caused an increase in Young’s modulus. Huang et al. reported that an increase in hydrogen bonding index resulted in improved phase mixing, which in turn increased modulus and decreased maximum elongation [17].

![Fig. 6 Frequency dependence of the permittivity (a), and dielectric loss factor (b) in the polyurethane composites and neat polyurethane.](image)

The dielectric properties of PU composites with different lignin urethane loading levels were studied. As seen in Fig. 6 (a), both neat PU and its composites exhibited a similar frequency-
dependent permittivity over a frequency range from 1 to $10^6$ Hz. However, it is interesting to note that the incorporated lignin systematically increased the relative permittivity ($\varepsilon'$) of the composites, which may be attributed to the higher $\varepsilon'$ of lignin, caused by the dipole orientation and the polarization of the functional groups in lignin molecules. Fig. 6 (b) shows that the dielectric loss factor of PU composites slightly increased with incorporation of lignin fillers. Although no major difference was observed in loss factor within higher frequency range ($10^3$-$10^6$ Hz) at any given loadings, the presence of higher content of lignin resulted in the reduction of dielectric loss factor at lower frequencies. This phenomenon was attributed to the higher dielectric dispersion caused by the lagging behavior of dipoles in the higher frequency field oscillations. It is notable that the polyol used in this study was 100% bio-based and with lignin loading up to 30%, the bio-content of neat PU and PU/lignin composites reached approx. 76 % and 83 %, respectively.

4. Conclusion

Two kinds of chemical pathways were used to modify lignin to improve the compatibility of lignin fillers and polyurethane matrix. The incorporation of lignin urethane as a bio-filler had a complex effect on the tensile properties of the obtained composites. High lignin contents up to 30 wt. % improved the composite’s Young’s moduli. Incorporation of lignin urethane decreased thermal degradation of polyurethanes composites at low temperatures, but increased their thermal degradation at high temperatures. Incorporation of lignin urethane did not change the $T_g$ of PU composites significantly, but it greatly improved their dielectric properties.

References

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Highlights

- Two kinds of chemical pathways are used to modify lignin
- Lignin modified with octadecyl isocyanate is compatible with polyurethane matrix.
- High lignin contents up to 30 wt. % improves the composite’s Young’s moduli.
- Incorporation of lignin greatly improves dielectric properties of polyurethane.