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ABSTRACT

Xylan is a hemicellulose, which is found abundantly in nature. In this work, a novel polyurethane was developed involving xylan and tolylene-2,4-diisocyanate (TDI). Polymer synthesis was achieved through conventional heat or microwave-assisted reaction in dimethyl sulfoxide. Because xylan has multiple OH groups on each polymer chain, the TDI/xylan molar ratio had to be adjusted to produce a soluble polymeric product. The reaction products were characterized by $^{13}$C NMR, FTIR, thermogravimetric analysis, and differential scanning calorimetry. The xylan polyurethane was shown to exhibit improved thermal stability over xylan.

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DSC; FTIR; microwave; NMR; polyurethane; TGA; toluene diisocyanate; xylan

Introduction

Carbohydrates are useful platform for the generation of polymers from agri-based sustainable and renewable resources. Indeed, many derivatives of carbohydrates have been prepared and are available as commercial products. One of the processes for derivatization is to react carbohydrates with diisocyanates to produce carbohydrate-based polyurethanes. Polyurethanes are, of course, typically formed by reacting a diisocyanate with a polyol and are industrially important in diverse materials such as foams, elastomers, bushings, adhesives, surface coatings, and synthetic fibers. The substitution of a petroleum-based polyol with a carbohydrate has the potential advantage of lowering the product cost and also making it more biodegradable. This approach has attracted a fair amount of interest and has been reviewed.

Among the many agri-based materials, xylan is of interest to the present authors. Xylan occurs in plant cell walls and is a part of hemicellulose, which is among the most abundant carbohydrates available on earth. There has been a recent surge of interest in xylan and its derivatives. Nevertheless, thus far there has been no prior publication on the preparation of polyurethanes from xylan and diisocyanate. In the literature, only two articles reported the reactions of monoisocyanates with xylan. In the first article, Vincendon reacted xylan with phenyl isocyanate and tolyl isocyanate and obtained the carbamates with good yield. In the second article, Heinze et al. included the xylan/phenyl isocyanate reaction in a review of xylan reactions.

The purpose of this work was to explore the synthesis of polyurethanes from xylan and to characterize these new polymeric materials. Synthesis was achieved with both conventional heat and microwave-assisted reactions. Consistent with an earlier work, the use of microwave facilitated
the carbohydrate–diisocyanate reactions. The structures of the resulting polyurethanes were fully characterized by NMR, FTIR, and thermal analyses.

**Experimental section**

**Materials**

The samples of xylan, tolylene-2,4-diisocyanate (TDI), dimethyl sulfoxide (DMSO), and N,N-dimethylformamide (DMF) were all acquired from Sigma-Aldrich (Milwaukee, WI, USA). The specification sheets indicated that xylan was from beechwood and contained >90% xylose residues with a few percent of 4-O-methyl-D-glucuronic acid side chain. TDI consisted primarily of 2,4 isomer and only 4% 2,6 isomer. Dimethyl sulfoxide-d$_6$ (d$_6$-DMSO) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

**Extraction of xylan from cottonseed hull**

Cottonseed hull is the outer covering of cotton seed that is primarily used as animal feed, mulch, soil conditioner, and substrate for mushroom cultivation. For the extraction of xylan from cottonseed hull, the procedure by Goksu et al. [16] was followed. Cottonseed hull (10 g) was ground and put into a beaker with 100 ml of 24% KOH and 1% of NaBH$_4$ and stirred overnight at room temperature. The solution was filtered and the supernatant mixed with 400 mL of cold ethanol with 10% acetic acid for 3 h. The solution was then centrifuged at 9,000g for 30 min. The pellet was washed twice with 80% ethanol and dried at 60°C for 24 h.

**Synthetic methods**

Although xylan is readily soluble in water, it is known not to dissolve well in organic solvents. [11,12] In the literature, there have been at least four solvent media used to dissolve xylan in an organic solvent: (1) pyridine, [12] (2) DMSO:water (90:10 by weight), at 80°C or higher temperature for 1 h or more, [9] (3) DMSO–LiCl (94:6 by weight) at 80°C for 2 h; [8] the typical ratio reported for a 5% xylan solution is xylan:LiCl:DMSO = 5.0:5.7:89.3, and (4) DMF–LiCl (90:10 by weight) at 120°C for 2 h; [10] a typical ratio reported for a 6% xylan solution is xylan:LiCl:DMF = 6.0:8.5:85.5. Indeed, when we first tried to dissolve beechwood xylan in DMF, only about 88% xylan dissolved. We switched to DMSO and found the xylan solubility to depend on temperature. For our purpose, we found beechwood xylan to dissolve in DMSO at 170°C with the application of microwave energy; however, xylan from cottonseed hull was only partly soluble under the same conditions. In view of the previous work on DMSO/LiCl, [9,10] we first dissolved xylan (0.25 g) and LiCl (typically 0.475 g, but variable) in 5 g of water and then dried the water. DMSO (4.75 g) was then added and heated at 120°C for 2 h. This procedure seemed to work with xylan from both beechwood and cottonseed hull.

Conventional thermal reaction was performed on a heating block (Reacti-therm™ from Thermo Fisher, Pittsburgh, PA, USA) with feedback control of temperature. The reaction was started by adding TDI (at 0.15–0.66 g) to the xylan/DMSO solution and heating the mixture with stirring at 145°C for a fixed length of time (usually 20–30 min). Care was taken to vent the reaction vessel, or else the carbon dioxide produced from the reaction of TDI with water in DMSO could drastically increase the pressure in a sealed reaction vessel. The product was recovered by washing once with water, thrice with ethanol, and dried at 60°C in a vacuum oven overnight.

Microwave-assisted synthesis was conducted on a microwave reactor (Biotage® Initiator Microwave Synthesis Systems, Biotage AB, Uppsala, Sweden). A typical procedure entailed the addition of TDI, xylan/DMSO solution, and a stir bar into a 10–20-mL Biotage vial. The Biotage reactor was programmed for 30-s pre-stirring and then heating to 145°C in 3 min. The resulting polyurethane was transferred into a beaker containing ethanol, stirred for 30 min, and then filtered. It was then
washed once with water, thrice with ethanol, filtered after each wash, and then dried at 60°C overnight in a vacuum oven.

All xylan polyurethane products were tested for solubility in hot DMSO. Typically, 0.1 g of product was stirred with 4 mL of DMSO in a vial placed in a Reacti-therm™ heating block at 100°C for 60 min. The vial was then checked to see if a clear solution was obtained (for soluble sample) or if any insoluble particulates were observed.

**Characterization of products**

The NMR analysis was conducted on a Bruker DRX 400 spectrometer (Karlsruhe, Germany). The xylan polyurethanes were dissolved in d6-DMSO, and 13C NMR spectra were obtained at ambient temperature. The 13C shift reference was tetramethylsilane (at 0 ppm).

The FTIR spectra were obtained on the solid samples on a Thermo Nicolet Nexus 470 FTIR system (Thermo Fisher Scientific, Madison, WI, USA) coupled with the Smart Orbit accessory in a scanning range of 650–4,000 cm⁻¹ for 32 scans at a spectral resolution of 4 cm⁻¹.

Thermogravimetric analysis (TGA) was performed on a TA instrument Q500 TGA (TA Instruments, New Castle, DE, USA). Each sample (~5 mg) was weighed into a tared, open platinum TGA pan. The sample was loaded onto the TGA and then heated at a rate of 10°C min⁻¹ up to 800°C under a nitrogen atmosphere. Samples were analyzed in duplicate to confirm the results.

Differential scanning calorimetry (DSC) experiments were performed using a TA Instrument Q2000 MDSC (New Castle, DE, USA). Each sample (~5 mg) was weighed into a standard (non-hermetic) aluminum DSC pan and sealed. The sample was loaded into the DSC cell under nitrogen, with an empty sample pan as the reference. The sample was equilibrated to 20°C and then analyzed at a heating rate of 10°C min⁻¹ up to 400°C. Samples were analyzed in duplicate to confirm the results.

**Results and discussion**

A preliminary study of xylan–TDI reaction was first conducted in DMF at 135–145°C, but the reaction gave inconsistent results because of the partial solubility of xylan in DMF. For beechwood xylan, a microwave-assisted procedure was found that enabled beechwood xylan to be dissolved rapidly in DMSO at 170°C. The addition of LiCl to xylan improved the solubility of beechwood xylan. Reactions were first performed with xylan and phenyl isocyanate at 145°C for 30 min (Table 1). Urethane formation seemed to occur readily. The 13C NMR spectrum of sample P3 is shown in Figure 1. Spectral assignments were made on the basis of previous work[12] and 13C shift calculations.[17,18] Note that the xylan peaks stay relatively unchanged despite being reacted with isocyanates.

Xylan/TDI reaction was then conducted in DMSO at the same reaction conditions (145°C for 30 min). Since xylan has multiple OH groups on each polymer chain and TDI has two isocyanates per molecule, the TDI/xylan molar ratio needed to be carefully adjusted to produce a soluble polymeric product. It was quickly learnt that a TDI/xylan molar ratio above 0.35 tended to produce some insoluble products (samples C1–C7, Table 2). The 13C NMR spectrum of sample C7 is shown in Figure 2. Spectral assignments were achieved by comparison with phenyl isocyanates adduct (Figure 1), the NMR data of related compounds,[14,15] and 13C shift calculations[17,18]. Note that the peaks corresponding to positions 1, 3, and 5 on the toluene moiety are broad, because of the shift sensitivity to the bonding situations at the urethane linkage. Note also that there are extra peaks at

| Table 1. Polyurethane formation involving xylan and phenyl isocyanate (PI) through conventional heating at 145°C in DMSO solvent. |
|---|---|---|---|---|---|
| Sample | Xylan | PI/xylan mol ratio | Heat mode | Time (min) | Obsd phenyl/xyl ratio (NMR) | Solubility in DMSO |
| P1 | Beechwood | 0.11 | Conventional | 30 | 0.02 | Soluble |
| P2 | Beechwood | 0.21 | Conventional | 30 | 0.10 | Soluble |
| P3 | Beechwood | 0.45 | Conventional | 30 | 0.35 | Soluble |
147, 116, 107, and 104 ppm due to toluene 2,4-diamine, which originated from the reaction of TDI with the water present in DMSO and xylan:

\[
O
\]

\[
R-N=\text{C}=\text{O} + \text{H}_2\text{O} \rightarrow \text{R-}\text{NH-C-OH} \rightarrow \text{RNH}_2 + \text{CO}_2
\]

In view of our earlier positive experience with microwave-assisted methodology,\cite{14,15} we attempted the xylan/TDI reaction with a microwave reactor. The results for microwave reaction on four samples of beechwood xylan and TDI in DMSO at 145°C for 3 min are shown as samples M1–M4 in Table 3. The samples looked similar to their counterparts in the conventional heat. Thus, microwave appears to be an alternative heating method that can decrease the reaction time considerably for this reaction.

Since the reaction with beechwood xylan was successful, we also performed the TDI reaction on xylan from cottonseed hull. The addition of TDI initiated the reaction. The results for conventional heat are shown as sample C8 in Table 2 and for microwave heat are shown as sample M5 in Table 3.
The FTIR spectra of the unreacted xylan and xylan polyurethane sample C7 are shown in Figure 3. The IR peak assignments of xylan were previously reported.\textsuperscript{[19–21]} As noted by Marchessault and Liang,\textsuperscript{[21]} most of the features of the xylan spectrum are similar to those of cellulose, except for

<table>
<thead>
<tr>
<th>Sample</th>
<th>Xylan</th>
<th>TDI/xylan mol ratio</th>
<th>Heat mode</th>
<th>Time (min)</th>
<th>Obsd tol/xyl ratio (NMR)</th>
<th>Solubility in DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Beechwood</td>
<td>0.11</td>
<td>Microwave</td>
<td>3</td>
<td>0.06</td>
<td>Soluble</td>
</tr>
<tr>
<td>M2</td>
<td>Beechwood</td>
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<td>Microwave</td>
<td>3</td>
<td>0.10</td>
<td>Soluble</td>
</tr>
<tr>
<td>M3</td>
<td>Beechwood</td>
<td>0.36</td>
<td>Microwave</td>
<td>3</td>
<td>0.14</td>
<td>Partly insoluble</td>
</tr>
<tr>
<td>M4</td>
<td>Beechwood</td>
<td>0.46</td>
<td>Microwave</td>
<td>3</td>
<td>0.25</td>
<td>Partly insoluble</td>
</tr>
<tr>
<td>M5</td>
<td>Cottonseed hull</td>
<td>0.34</td>
<td>Microwave</td>
<td>3</td>
<td>0.24</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

The FTIR spectra of the unreacted xylan and xylan polyurethane sample C7 are shown in Figure 3. The IR peak assignments of xylan were previously reported.\textsuperscript{[19–21]} As noted by Marchessault and Liang,\textsuperscript{[21]} most of the features of the xylan spectrum are similar to those of cellulose, except for

Figure 2. $^{13}$C NMR spectrum of xylan–TDI adduct C7. T, toluene moiety; X, xylan moiety; A, toluene 2,4-diamine; E, ethanol; D, d$_6$-DMSO. The subscripts correspond to the carbon numbers on T, A, and X.

Table 3. Polyurethane formation involving xylan and different levels of TDI through microwave heating at 145°C in DMSO solvent.

Figure 3. FTIR spectra of unreacted xylan (lower plot) and xylan–TDI adduct, sample C7 (upper plot).
the peaks attributed to 4-O-methyl-D-glucuronic acid side chain (with its C=O asymmetric stretching frequency at 1,610 cm\(^{-1}\) and symmetric at 1,414 cm\(^{-1}\)), a less well-resolved OH stretching region at \(\sim\)3,400 cm\(^{-1}\) and a more intense peak at 897 cm\(^{-1}\). For the xylan polyurethane spectrum, urethane bands are found at 1,726 cm\(^{-1}\) (free C=O of urethane), 1,704 cm\(^{-1}\) (hydrogen-bonded C=O of urethane), and 1,530 cm\(^{-1}\) (N–H of urethane); the band at 1,600 cm\(^{-1}\) corresponds to aromatic C–H of TDI.\(^{[15]}\)

The TGA curves for both unreacted xylan and xylan polyurethane sample C7 are shown in Figure 4. There is some weight loss at \(\sim\)100°C mostly due to the evaporation of adsorbed water. For xylan, the large weight loss at about 200–300°C is known to be caused by the degradation of xylan; heating beyond 300°C promotes further degradation and increasing formation of breakdown products.\(^{[22,23]}\)

For xylan polyurethane, an increase in the TGA decomposition temperature is observed; the major weight loss starts at about 240°C (Figure 4). This increased thermal stability is likely caused by the
increased molecular weight in the xylan polyurethane and the thermally more stable urethane bond. It is known that thermal degradation for polyurethane resins starts at about 300°C. Thus, one benefit of the derivatization of xylan with TDI is the increased thermal stability.

The DSC data (Figure 5) indicate that xylan begins to decompose at around 200°C, whereas xylan polyurethane begins to decompose at about 240°C, consistent with the TGA data. The broad valley between room temperature and ca. 170°C is due to the evaporation of moisture from the samples.

The fact that xylan is sustainable, biodegradable, and environmentally friendly should be an advantage over synthetic polyols in polyurethane formulations. Thus, the xylan–TDI polyurethane may find applications as a bioplastic, similar to starch polyurethanes. Some possible applications of starch polyurethanes have been given in two review articles including packaging materials, foams, composites, and biomedical materials. Xylan polyurethanes may perhaps be considered for these applications as well.

**Conclusion**

Polyurethanes from xylan and TDI were synthesized with DMSO solvent at 145°C. Microwave heating was found to be useful both for dissolving xylan in DMSO and for expediting the xylan–TDI reaction. Several polymers with specific diisocyanate/xylan weight ratios were obtained. Characterization was conducted with NMR, FTIR, TGA, and DSC. TGA and DSC data indicated that the xylan polyurethane exhibits increased thermal stability over xylan.

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