Polyurethane Coatings Based on Renewable White Dextrins and Isocyanate Trimers

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The polyurethane industry is strongly dependent on fossil-based polyols and polyisocyanates. Developing novel sustainable polyols from valuable biobased building blocks is a first step toward strong and durable development. The synthesis and properties of PU films based on pristine and acylated white dextrins (AVEDEX W80) as polyol and an aliphatic, low-viscosity, solvent-free trisocyanate based on hexamethylene diisocyanate (trimer—Desmodur N3300) as crosslinker is reported. After optimizing several conditions, such as the reaction time, reaction temperature, amount of solvent, isocyanate index, and amount per surface area, it is possible to obtain smooth PU films with good thermal properties.

Modern industrial developments inspired by the new concepts of sustainability and ecocompatibility require a deeper attention to renewable resources as raw materials.[1] In this respect, polymeric materials of natural origin (biopolymers),[2,3] as well as materials from renewable resources usable for the production of monomeric precursors, or semi-synthetic polymeric materials,[4,5] constitute a focal point for future development. Several new eco-friendly materials have the potential to replace conventional petroleum derived materials and monomers. Among them are natural polysaccharides.[6–10]

A naturally occurring (hyper) branched polymer is amylopectin, one component of starch.[11] Starch is the most abundant storage reserve carbohydrate in plants. It is found in many different plant organs, including seeds, fruits, tubers, and roots, where it is used as a source of energy during periods of dormancy and regrowth. Amylopectins from different sources (potatoes, maize, etc.) have different degrees of branching[12] and with this it becomes possible to study the influence of the degree of branching on the resulting properties of, for instance, coating materials.

However, the utilization of native polysaccharides as a coating material is limited since thermal decomposition takes place very easily. Moreover, their inherent moisture sensitivity leads to significant variations in their mechanical behavior with relative humidity. Thus, it is of fundamental importance to alter the used polysaccharides without modifying their biocompatible and biodegradable characteristics, in order to reach desirable physical properties.

In particular, esterified polysaccharides have a tunable range of physical properties.[13–16] For instance, modification of the starch OH groups with fatty acid esters with appropriate degree of substitution (D.S.) of about 1.5–3.0 imparts thermoplasticity and water resistance to the modified starch over the unmodified one. Modified starch–based materials are used in industry as glues, adhesives, and auxiliaries of a wide range of rheological and functional properties. It was found that the properties of polysaccharide-based plastics are strongly dependent on the degree of modification as well as on the regioselectivity of the substitution.[17–20]

In our recent work, we reported the esterification (acetylation, propionation, and esterification with longer fatty acids) of white dextrins (degraded starches) and “waxy potato” starch containing more than 95% amylopectin.[21] A very important feature of this reaction is the fact that the esterified material does not undergo a color change due to the mild reaction conditions. This can be very important for various industrial applications, such as coatings, films.

We have recently reported the PU synthesis using isophorone diisocyanate (IPDI) and two bio-based isocyanates—ethyl ester L-lysine diisocyanate (LLDI) and ethyl ester L-lysine trisocyanate (LLTI). The reaction conditions were optimized in terms of casting time and temperature, disocyanate used, amount of solvent, excess of diisocyanate.[22,23] Our previous experiments resulted in PU films with limited stability and scratch resistance. To improve this we report here the synthesis and properties of PU films based on Desmodur N3300, an aliphatic, low-viscosity, solvent-free triisocyanate based on hexamethylene diisocyanate (trimer) see Scheme 1.[24,25] Desmodur N 3300 was used as the isocyanate component in solvent casting experiments. It is a commercial isocyanate based on HDI in its trimer form and is primarily used as the hardener in two-component polyurethane coatings with a NCO content of ≈22%. PUs from Desmodur N 3300 were produced with and without tin(II) 2-ethylhexanoate as catalyst to investigate the catalytic effect.[26–28] Additional experiments with
modified carbohydrates (different D.S.) as polyol components were carried out, mechanical tests were conducted, and thermal behavior of the obtained films was studied.

The procedure/formulation to obtain good quality PU films—a uniform film and film thickness, uniform mechanical behavior over a broad temperature range, resistance to organic solvents and acids/bases—with Desmodur N 3300A (HDI) as isocyanate was optimized via different parameters like component ratio, casting time and temperature, solvent.

The polyol/isocyanate ratio is determined in two ways, one method is using the NCO content given by the supplier and calculating the amount of OH from the OH%, the other via the $M_W$ of the polyol/isocyanate. Both methods result in a weight fraction of 374 g isocyanate per 100 g polyol. See Figure 1a for results of different polyol concentrations.

The casting temperature is determined by repeating experiments with the same polyol/isocyanate ratio, amount of catalyst, etc. at different temperatures and comparing the results, for example, how uniform the film is, how wet the film still is. The same accounts for the casting time as both are not independent of each other. See Figure 1b for the results of different casting temperatures.

Another important property of the polyurethane films is their thickness. Starting with the same concentration of polyol/DMSO as in our previous work using IPDI,[22] the results are analyzed and the concentration is adjusted. The starting concentration in the case of IPDI was 122 g AVEDEX W80/L DMSO, which accounted with HDI as isocyanate in a film thickness of 0.78 mm. Adjustments lead to a final concentration in these formulations of 27 g AVEDEX W80/L (0.2 g AVEDEX W80/7.5 mL DMSO) translating to an average film thickness of 0.08 mm (Table 1).

To further enhance the reaction, tin(II) 2-ethylhexanoate was used as a catalyst. There are two possible ways of addition, the first is direct addition of the catalyst to the reaction, and the
second one is making a solution of the catalyst in the used solvent. The second approach suits these experiments better as they are conducted on a rather small scale—see Figure 2 for PU films cast with different catalyst concentrations.

With addition of catalyst the reaction time was reduced from 8 to 4 h. On the other hand, all experiments involving the tin catalyst resulted in non-uniform film. All the samples started to crack at some point during the film casting. This behavior was not only observed with HDI as isocyanate, but also with other cyanates as reported by us earlier.

Figure 3 shows that the FT-IR spectra of catalyzed PU (red) and non-catalyzed PU (blue) are almost the same, the catalyst does not change the chemical composition of the PU. The peaks of the amide I and amide II bands from the newly formed polyurethane linkages are visible at 1550 and 1650 cm\(^{-1}\), respectively. Another positive aspect of using the catalyst is an increase in glass transition temperature (\(T_g\)) of about 6–7 °C (see Table 2).

The thermal properties of the PU films are not only dependent on the amount of catalyst, but also on the amount of isocyanate added. The so-called isocyanate index represents the ratio of isocyanate to hydroxyl groups. In industry a NCO index of 1.05 is used, as with this ratio the highest observable \(T_g\) is obtained. Increasing the NCO index by 50% and 100%, respectively, reduces the \(T_g\) greatly (see Table 2), without any chemical or visible changes in the material itself—as proven by the FT-IR spectra in Figure S1, Supporting Information. The influences of the formulation on the \(T_g\) results are summarized in Table 2. Addition of a catalyst increases the \(T_g\) from 88 to 94 °C. Increasing the NCO index by 50% and 100%, respectively, decreases the \(T_g\) from 88 °C to 75 and 68 °C, respectively.

![Figure 2. PU films produced with different amount of catalyst (left—10 \(\mu\)L, left middle—20 \(\mu\)L, right middle—30 \(\mu\)L, and right—40 \(\mu\)L).](image)

![Figure 3. FT-IR spectra of catalyzed PU (red) and non-catalyzed PU (blue).](image)

To test the stability of the PU films in organic solvents, specimens of different samples were cut, dried until constant weight, and immersed in DMSO and chloroform for a defined period of time. The specimens are weighed again until constant weight and the difference in weight before and after immersion are noted. It became obvious that the samples are stable in both solvents (max. weight difference is 5%). Additionally, the concentration of material found in the washing solvents was too low to be detected.

To see the influence of the amount of solvent on the thermal properties of the PU films, samples are produced with additional 33%, 100%, and 100% + 10 \(\mu\)L tin catalyst (respectively, 133%, 200%, and 200% + catalyst). From these samples specimens are cut and studied via dynamic mechanical testing. In addition, a second batch of samples is investigated in the same way, after being dried for 3 days. Although there is not much difference in these samples chemically (see Figure 4), the materials show a slight decrease in \(T_g\) due to the additional solvent.

![Figure 4. FT-IR spectrum of PU films produced with different amounts of solvent.](image)

### Table 1. Concentration of polyol and resulting film thickness.

<table>
<thead>
<tr>
<th>Concentration [g L(^{-1})]</th>
<th>Thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>122</td>
<td>0.78</td>
</tr>
<tr>
<td>81</td>
<td>0.37</td>
</tr>
<tr>
<td>61</td>
<td>0.52</td>
</tr>
<tr>
<td>27</td>
<td>0.08</td>
</tr>
</tbody>
</table>

### Table 2. Thermal properties of synthesized PUs using pristine AVEDEX W80 as polyol.

<table>
<thead>
<tr>
<th>Polyl [g]</th>
<th>NCO [g]</th>
<th>Catalyst [(\mu)L]</th>
<th>(T_g) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.79</td>
<td>10</td>
<td>94</td>
</tr>
<tr>
<td>0.2</td>
<td>0.75</td>
<td>20</td>
<td>94</td>
</tr>
<tr>
<td>0.2</td>
<td>0.75</td>
<td>—</td>
<td>88</td>
</tr>
<tr>
<td>0.25</td>
<td>1</td>
<td>—</td>
<td>75</td>
</tr>
<tr>
<td>0.25</td>
<td>1.5</td>
<td>—</td>
<td>68</td>
</tr>
</tbody>
</table>
thermally properties change quite a bit (see Figure S2, Supporting Information) by increasing the amount of solvent used during the film casting. Again, the solvent acts as a plasticizer if not fully removed from the samples, visible in the decrease of $T_g$ going from 200% to 100% solvent.

With increasing amount of solvent during the film formation, the $T_g$ decreases from 100 to 71 °C. Increasing the amount of DMSO even further (200%) decreases the $T_g$ even further to 53 °C, attributing it to the plasticizer effect of the solvent. As already seen in the experiments above, the tin catalyst is able to increase the $T_g$ of the samples from 53 to 82 °C. With this we can clearly see that in any case the use of the tin catalyst increases the $T_g$ of the sample, especially when using much solvent.

After optimization of different reaction conditions for pristine AVEDEX W80 the conditions were also optimized for acylated AVEDEX W80 with varying D.S. The amount of isocyanate needed was calculated via the amount of free OH groups available at the acylated carbohydrate with an NCO index of 1.05. The quality of the produced PU films of acylated AVEDEX W80 with D.S. of 0.2, 0.35, 0.7, 0.9, 1.5, and 2.8, respectively, can be found in Figure 5. The produced films were not characterized further at this point.

PU films were easily prepared by pristine and acylated white dextrins (AVEDEX W80) as polyol and an aliphatic, low-viscosity, solvent-free triisocyanate based on HDI (trimer—Desmodur N3300) as crosslinker. After optimizing several conditions (reaction time, reaction temperature, amount of solvent, isocyanate index, amount per surface area) we were able to obtain smooth PU films.

It became obvious that the $T_g$ of the PU samples using pristine AVEDEX W80 is dependent on several factors. Firstly, the isocyanate index (NCO index) (the ratio of NCO to OH groups). In industry, an NCO index of 1.05 is used and with this ratio the carbohydrate-based PUs also show the highest $T_g$. Drying of the samples and thus removing residual solvent increases the $T_g$. Increasing the NCO index to 1.5 or 2.0 still resulted in a transparent film, but the thermodynamic properties suffered, visible in a reduced $T_g$, compared with samples with an NCO index of 1.05.

Using a catalyst (tin(II) 2-ethylhexanate) to speed up the reaction resulted in shorter reaction times and a higher $T_g$ of the final material compared to an uncatalyzed reaction. On the other hand, tin catalyzed samples always started to crack during the reaction and a smooth sample was never achieved.

The produced PUs show good resistance against polar organic solvents like DMSO and CHCl₃. The amount of solvent used during film casting also influences the final properties of the PU film. Since solvents act as plasticizers in these materials, the use of too much solvent should be prevented, since the material obtained in these conditions shows a greatly reduced $T_g$. This is especially the case with solvents with a high boiling point.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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