Influence of Glass Transition Temperature on Mechanical and Self-Healing Behavior of Polymers Bearing Hindered Urea Bonds

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Abstract

Considerable interest has been placed on polymers which can intrinsically self-heal. Numerous studies have shown that polymer networks bearing dynamic covalent bonds exhibit the ability to self-repair. The focus of this paper is to describe the synthesis and characterization of polymer networks of varying rigidity bearing hindered urea bonds (HUB) based on 1-(tert-butyl)-1-ethylurea (TBEU). Results indicate that the partial substitution of Hexamethylene Diisocyanate (HMDI) with an aromatic diisocyanate (m-Xylylene Diisocyanate, XDI) results in a predictable increase in \( T_g \) and a corresponding increase in both modulus and tensile strength at break. Furthermore, polymers containing up to 50mol% XDI were shown to self-heal, though the efficacy decreases with increasing XDI content at constant healing conditions (60°C/12 hours).

Introduction

Conventional thermoset polymers utilize covalent bonds to form crosslinked networks. While strong and stable, they often lack the ability to self-repair owing to the irreversible nature of the covalent bond. Repairing these materials involves human intervention and the addition of material to the fracture site and surrounding area to maintain usability of the component. A variety of methods have been explored to produce self-healing thermosetting polymers. One of the more popular methods includes the presence of a healing agent, or unreacted resin, which is contained within a vascular [1] or encapsulated [2] system. When fractured, the resin system flows into the site of damage where it encounters an imbedded catalyst that initiates the reaction responsible for healing [3].

Intrinsic self-healing polymers represent an alternative self-healing strategy. This approach relies on the presence of dynamic reversible binding groups that are capable of re-establishing themselves once broken. These dynamic groups can be based on either non-covalent [4, 5, 6] or covalent interactions [7, 8, 9, 10]. When incorporated into polymers these reversible binding groups have been shown to impart repeatable self-healing ability, environmental adaptation, and shape memory effects [11, 12].

A hindered urea bond [7] (HUB) is a dynamic covalent bond that has recently been shown to exhibit good self-healing properties when incorporated into soft elastomeric networks, even in the absence of a catalyst [13]. The dynamic nature of the HUB is afforded by incorporating a bulky substituent on the amine nitrogen, thus weakening the resulting covalent bond. Tuning this bond to behave in a stable manner is key and can be described using rate constants \( k_1 \) and \( k_2 \) which describe the forward and reverse reaction rate respectively as illustrated in Figure 1.

![Figure 1. Idealized reaction scheme showing reaction of isocyanate and amine to form a dynamic hindered urea bond (HUB).](image)

Recently, a polyurethane-urea was shown to exhibit excellent self-healing capabilities at relatively low temperatures (37°C) [7]. However, these polymer networks were soft owing to their low \( T_g \) thereby potentially limiting the number of potential applications. Understanding how tuning the \( T_g \) (and thus material properties) influences the self-healing characteristics of HUB containing polymers is the ultimate goal of this research. This knowledge would allow for the creation of polymers with a high degree of reversibility while still achieving mechanical properties acceptable for a wider array of applications. In this study, the glass transition temperature (\( T_g \)) of lightly crosslinked networks bearing 1-(tert-butyl)-1-ethylurea (TBEU) will be altered and their self-healing characteristics investigated. The \( T_g \) will be altered by varying the relative concentration of m-Xylylene Diisocyanate to Hexamethylene Diisocyanate.

Experimental

Materials. Each polyurethane-urea polymer was synthesized using as-received materials unless otherwise noted. Hexamethylene Diisocyanate (HMDI), m-Xylylene Diisocyanate (XDI), and \( N,N' \)-Di-tert-butylethylene diamine (TBEDA) were obtained from TCI Americas in a minimum of 98% purity. Dibutyltin Diacetate (DBTDA) was obtained from TCI Americas in a minimum of 95% purity. Triethanolamine (TEA) was obtained from Alfa Aesar in a minimum of 98% purity. Tetraethylene glycol (TEG) was obtained from BeanTown Chemical in 99% purity. Toluene was dried overnight over...
calcium hydride, subsequently distilled under vacuum and stored over 4Å molecular sieves.

**Synthesis.** The reactants used in this study to produce a functional polyurethane-urea polymer with self-healing capability is shown in Figure 2.

![Chemical structure of TBEU](image)

**Figure 2** Chemical structure and molar amounts of each component used in one-pot synthesis of HUB containing polyurethane-urea polymer. Isocyanate(s) and amine (1-(tert-butyl)-1-ethyldiamine) are first reacted to form a precursor molecule containing dynamic TBEU bonds and reactive isocyanate end groups. Subsequently, polyols (Tetraethylene glycol, Triethanolamine) are added to the solution where the reaction with isocyanates establishes a fully crosslinked network.

In this experiment the hindered urea bond essential to the self-healing ability of the polymer was based on the reaction between an isocyanate and an amine to form the TBEU moiety. The synthetic procedure to prepare networks was based on an approach outlined in [7] except that the proportion of an aliphatic and aromatic isocyanate (HMDI and XDI respectively) was varied in order to alter the T_g of the material. Despite the change in molecular structure of the HUBs as a result of the use of different isocyanates, the dissociation rate constant (k_1) and equilibrium constant (K_eq) of TBEU’s based on XDI (k_1=0.019 h^-1; K_eq=5.5 x 10^5 M^-1) differed only slightly from those based on HMDI (k_1=0.021 h^-1; K_eq=7.9 x 10^5 M^-1) as indicated by solution based NMR measurements [14]. In this work, sample nomenclature will reflect the relative proportion of XDI present in the formulation (e.g. a specimen containing 50mol% XDI would be labeled XDI-50). Other ingredients in the polymer formulation include TEG (used as a chain extender) and TEA (used as a cross-linker). DBTDA (molecular structure not shown) was used as a catalyst to drive the reaction between free isocyanate groups and polyols to completion. Catalyst concentration was altered between sample formulations to account for the increased reactivity of the XDI towards polyols. Dried toluene was used as a solvent to ensure solubility of all ingredients, to minimize the potential of water to react with isocyanate during synthesis, and as a means to control reaction rate.

**Synthesis of XDI-0.** Hexamethylene Diisocyanate (1.314ml, 8.20mmol) and toluene (0.5ml) were mixed in a glass vial under dry nitrogen flow and cooled to 0°C. N,N’-Di-tert-butylethylendiamine (0.589ml, 2.74mmol) was dropwise incorporated to the isocyanate solvent mixture to form the hindered urea groups. Tetraethylene glycol (1.286ml, 4.62mmol) and Triethanolamine (0.985ml, 0.69mmol) were slowly mixed into the prepolymer solution to minimize air incorporation. Dibutyltin Diacetate (0.013ml, 0.05mmol) was mixed into the solution and the polymer solution was quickly cast into dog bone and bulk material samples. The polymer was allowed to cure at room temperature under ambient conditions for twenty-four hours prior to demolding.

**Synthesis of XDI-25.** Hexamethylene Diisocyanate (0.985ml, 6.15mmol), m-Xylylene Diisocyanate (0.321ml, 2.05mmol), and toluene (0.5ml) were mixed in a glass vial under dry nitrogen flow and cooled to 0°C. N,N’-Di-tert-butylethylendiamine (0.589ml, 2.74mmol) was dropwise incorporated to the isocyanate solvent mixture to form the hindered urea groups. Tetraethylene glycol (0.797ml, 4.62mmol) and Triethanolamine (0.909ml, 0.69mmol) were slowly mixed into the prepolymer solution to minimize air incorporation. Dibutyltin Diacetate (0.010ml, 0.037ml) was mixed into the solution and the polymer solution was quickly cast into dog bone and bulk material samples. The polymer was allowed to cure at room temperature under ambient conditions for twenty-four hours prior to demolding.

**Synthesis of XDI-50.** Hexamethylene Diisocyanate (0.657ml, 4.10mmol), m-Xylylene Diisocyanate (0.643ml, 4.10mmol), and toluene (0.5ml) were mixed in a glass vial under dry nitrogen flow and cooled to 0°C. N,N’-Di-tert-butylethylendiamine (0.589ml, 2.74mmol) was dropwise incorporated to the isocyanate solvent mixture to form the hindered urea groups. Tetraethylene glycol (0.797ml, 4.62mmol) and Triethanolamine (0.909ml, 0.69mmol) were slowly mixed into the prepolymer solution to minimize air incorporation. Dibutyltin Diacetate (0.007ml, 0.025mmol) was mixed into the solution and the polymer solution was quickly cast into dog bone and bulk material samples. The polymer was allowed to cure at room temperature under ambient conditions for twenty-four hours prior to demolding.

**Synthesis of XDI-100.** M-Xylylene Diisocyanate (1.286ml, 8.10mmol), and toluene (0.5ml) were mixed in a glass vial under dry nitrogen flow and cooled to 0°C. N,N’-Di-tert-butylethylendiamine (0.589ml, 2.74mmol) was dropwise incorporated to the isocyanate solvent mixture to form the hindered urea groups. Tetraethylene glycol (0.797ml, 4.62mmol) and Triethanolamine (0.909ml, 0.69mmol) were slowly mixed into the prepolymer solution to minimize air incorporation. Dibutyltin Diacetate (0.002ml, 0.009mmol) was mixed into the solution and the polymer solution was quickly cast into dog bone and bulk material samples. The polymer was allowed to cure at room temperature under ambient conditions for twenty-four hours prior to demolding.

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**Sample preparation.** Prior to any mechanical or thermal testing, solvent was removed by drying specimens at 60°C under 25 in Hg for 24 hours. Samples were stored in a desiccator prior to testing to ensure minimal exposure to moisture.

**Characterization.** Fourier Transform Infrared Spectroscopy (FTIR) was performed on all sample batches to ensure that the material was fully cured. A representative sample from each batch was placed onto a Perkin Elmer Frontier FT-IR spectrometer to determine if any residual isocyanate remained. Sample spectrum were collected over the range 4000 cm\(^{-1}\) to 600 cm\(^{-1}\) using an attenuated total reflectance (ATR) probe (64 scans). Crosslinking of the network was confirmed by monitoring the residual isocyanate peak (2270 cm\(^{-1}\)) [15].

Thermal behavior was characterized using a TA Instruments Q100 Differential Scanning Calorimeter (DSC). Sample masses ranging from 9 – 17 mg were used in order to better elucidate the glass transition. To obtain an accurate measure of \(T_g\) samples were placed into an oven at 60°C under 25 in Hg for thirty minutes prior to testing to ensure any moisture or trace solvent was removed. Samples were equilibrated at a temperature at least 40°C below their estimated glass transition temperature and ramped at a rate of 30°C/min up to a temperature 40°C above \(T_g\). The samples were subjected to a second cycle in order to see if any changes in \(T_g\) occurred through this temperature sweep.

Tensile testing of all samples was performed on an Instron 5567 tensile tester using pneumatic jaws to fixture the sample without crushing it. Samples were loaded at a strain rate of 2.00 in/min and tested under recorded environmental temperature and humidity.

Self-healing was characterized qualitatively by aligning fractured sample faces on a flat clean surface, sliding the broken faces back together, and applying a light pressure by hand to the samples for one minute. After all testing was complete, samples were further healed by placing in an oven set at 60°C for 12 hours under dry nitrogen flow. The subsequent healing step was performed with no additionally applied stress.

**Discussion**

For the synthesis of these TBEU based polyurethane-urea polymers, substitution of aromatic isocyanate had no adverse effects on the synthesis procedure. The only significant change was that the amount of catalyst needed was varied to allow sufficient time to handle materials.

For each of the polymers synthesized, FTIR spectra showed little to no residual free isocyanate groups which would be indicated around 2270 cm\(^{-1}\). The absence of this peak in network polymers (Figure 3) along with an increase in viscosity of the polymer sample during synthesis indicated that crosslinking between polyl hydroxyl groups and isocyanate is complete.

**Figure 3.** FTIR spectra of select HUB containing polyurethane-urea samples demonstrating full crosslinking reaction had occurred. As shown the residual isocyanate peak present in the precursor molecule (XDI-100 precursor shown) was completely absent from crosslinked polymers. Note: Curves have been shifted along y-axis for clarity.

Samples tested in DSC revealed glass transition temperatures ranging from -5°C to 45°C as shown in Figure 4. This result confirms that varying the amount of XDI to HMDI alters the \(T_g\) of the resulting polymers. Sample transparency, along with the absence of any melting transition observed during DSC testing, indicates that these polymers are amorphous. Also, the fact that only one glass transition is observed suggests the presence of only one phase.

**Figure 4.** Thermal behavior of synthesized networks. Normalized DSC output of heat flow per mass of sample in test of HUB containing polyurethane-urea (2\(^{nd}\) cycle).
The tensile testing results for samples with XDI concentrations up to 50mol% are presented in Table 1. At the time of this writing the mechanical properties of XDI-100 tensile specimens has not been measured. As the glass transition temperature is increased, the elastic moduli of the samples increased accordingly. Also, breaking strain exhibits a fairly predictable negative trend with increasing aromatic content. Our control specimen (XDI-0) was synthesized using the same general synthetic technique as that described by Ying et al [7], yet our material exhibits an appreciably higher $T_g$. Mechanically this translates to a material with a higher elastic modulus, a higher breaking stress and a lower breaking strain as compared to their sample [7]. A variety of factors may contribute to this large difference in $T_g$ such as incomplete removal of solvent, differences in crosslink density and/or network architectural variations resulting from seemingly minor synthetic procedural differences.

### Table 1. Summary of thermal and mechanical behavior of TBEU-based crosslinked polyurethane-ureas with altered $T_g$. Ying et al data (6c) taken from [7].

<table>
<thead>
<tr>
<th>Batch</th>
<th>$T_g$ (°C)</th>
<th>Young’s Modulus (MPa)</th>
<th>Breaking Stress (MPa)</th>
<th>Breaking Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6c (Ying et al)</td>
<td>-52</td>
<td>1.22</td>
<td>0.93</td>
<td>426</td>
</tr>
<tr>
<td>XDI-0</td>
<td>-5</td>
<td>1.30</td>
<td>3.07</td>
<td>385</td>
</tr>
<tr>
<td>XDI-25</td>
<td>10</td>
<td>3.89</td>
<td>4.91</td>
<td>345</td>
</tr>
<tr>
<td>XDI-50</td>
<td>20</td>
<td>5.05</td>
<td>4.27</td>
<td>357</td>
</tr>
</tbody>
</table>

All samples which were mechanically assessed (XDI-0, XDI-25, and XDI-50) displayed self-healing ability after re-associating faces and healing at 60°C for 12 hours. The control specimen (XDI-0) recovered much of its original mechanical behavior following self-healing as indicated by recovery of 75% of its original breaking stress (Figure 5A). Raising $T_g$ clearly influences the self-repair ability of the material under these healing conditions. This is illustrated in Figure 5B. for the XDI-50 specimen which recovers only ~56% of its original breaking stress following healing. The XDI-25 sample (not shown) exhibited similar behavior with a tensile stress recovery ~69%.

We suspect that the decreased self-healing efficiency can be attributed to a number of causes. Firstly, as XDI concentration increases the ability to adequately deform the specimen to properly mate the two fractured surfaces decreases. This results in imperfections of the healed surface and prevents dynamic bonds from re-associating resulting in fewer bonds supporting the load when healed and tested. Furthermore, as the glass transition temperature is increased, decreased molecular mobility is anticipated to slow molecular diffusion of the chemical moieties to the fracture site.

Figure 5. Mechanical behavior of synthesized networks before and after healing at 60°C for 12 hours (typical curves shown). XDI-0; B. XDI-50.

### Conclusion

In this work, we have shown that the partial substitution of an aromatic isocyanate (XDI) for an aliphatic isocyanate (HMDI) proved to be an efficient means for increasing $T_g$ of an amorphous network polymer bearing TBEU units. Likewise, it was shown that increasing $T_g$ has a predictable influence on the polymer’s mechanical properties: Stiffness and tensile strength at break increases as $T_g$ increases.

Materials containing up to 50mol% XDI were shown to self-heal at 60°C/12hours. However, a reduction in self-healing efficiency was observed as $T_g$ is increased. It is hypothesized that this reduction in self-healing capability at 60°C is due to a reduction in intimacy between rejoined broken surfaces during healing and sluggish molecular diffusion due to an increase in polymer viscosity.

This work is part of a greater effort to understand how molecular alterations influences the reversibility of dynamic bonds. Such knowledge would enable the independent tuning of reversible bond kinetics and mechanical properties. In turn, this should allow for the
preparation of unique functional materials that meet the demands of a given application regardless of whether it is a soft material (e.g. biomaterial) or a rigid material (e.g. fiber reinforced composite matrix).

References