Non-isocyanate Polyurethanes for Adhesives and Sealants

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Introduction

Thermoplastic polyurethanes (TPUs) and foams are in many ways commodity products due to their high level of incorporation into daily life.[1–7] A multitude of applications are employed for these materials including furniture, biomedical devices, clothing, shoes, cushions, equipment, as well as building, refrigerator, and freezer insulation.[2,8–10] PU foams are unique because they provide low density solutions to insulation and structural support, as well as soft, compressible solutions for improved ergonomics. Density, hardness, and cell-type/size determine the range of applications accessible for each PU foam.[2] Unfortunately for these staple materials, growing concerns over the toxicity of isocyanates plague the PU foam industry.[11] Recent research in the area of isocyanate-free (or non-isocyanate, NI) PUs illuminates potential routes towards sustainability.[12,13,22–26,14–21] Isocyanates typically produce CO_2 through a decarboxylation reaction with water, resulting in foaming. The removal of isocyanates results in the need for new in-situ blowing processes. There are a number of methods in the literature to circumvent isocyanate-based foaming; these include sodium bicarbonate with heat,[1,3] di-tert-butyl dicarbonate with heat,[1,3] poly(methylhydrogenosiloxane),[21] and physical blowing agents (chlorofluorocarbons, hydrofluorocarbons, hydrocarbons, supercritical fluids (N_2 and CO_2)).[1,3,27–29]

Carbonyldiimidazole (CDI) provides a unique opportunity in PU synthesis due to its high reactivity towards alcohols and amines. CDI typically finds application in coupling reactions and small molecule synthesis.[30–38] In the late 1980s, and more recently, CDI's reaction between monomeric diols became of interest in forming polycarbonates without the use of phosgene.[39–44] Rannard et al. used CDI to synthesize dendritic and hyperbranched PUs with highly selective control.[45,46] They found that using CDI to generate BCI macromonomers enabled step-growth polymerization with diamines at elevated temperatures.

This investigation provides the first example of PU foam generation in the absence of isocyanates or additional blowing agents. Instead, thermal decomposition of the BCI moiety releases CO_2 that blows the rapidly crosslinking PU into a foam structure. This process not only eliminates the need for isocyanates, catalysts, and solvents, but also uses a sustainable blowing process that poses no environmental concerns. The resulting foams range from closed- to open-cell in structure and have a broad range in thermal properties.

Experimental

A small molecule diol reacts with CDI to produce bis-carbonylimidazolide (BCI) monomers. The BCI monomers then react with diamines and triamines to produce TPUs and PU foams, respectively. The reaction proceeds at elevated temperatures to circumvent the need for solvent or catalyst. The elevated temperatures coincidentally produce CO_2 allowing for foam generation.

Results and Discussion

Dynamic mechanical analysis (DMA) offered a thermomechanical approach to the determination of T_g's for polyurethane films (Figure 1 and Table 1). Small rectangular bars cut from the melt pressed, thin films enabled DMA testing. The T_g's for the BBCI-based polyurethanes followed the same trends as the DSC results (Table 1). Low-temperature storage moduli values were above 2000 MPa for all samples. Room temperature moduli values differed greatly (~2 orders of magnitude) between the homo- and co-polymers due to the influence of PPG segment present in both of the copolymers. The PPG plasticized the systems and decreased the T_g by > 60 °C.

Table 1. Tabulated TGA, DSC, and DMA data for the TPU samples.

Sample Description	$T_{d,5\%}$ (°C)	DSC T_g (°C)	DMA T_g (°C)
BBCI-DAO	298	13	34
BBCI-DAO-70%PPGda	277	-57	-43
BBCI-HMDA-70%PPGda	281	-53	-41

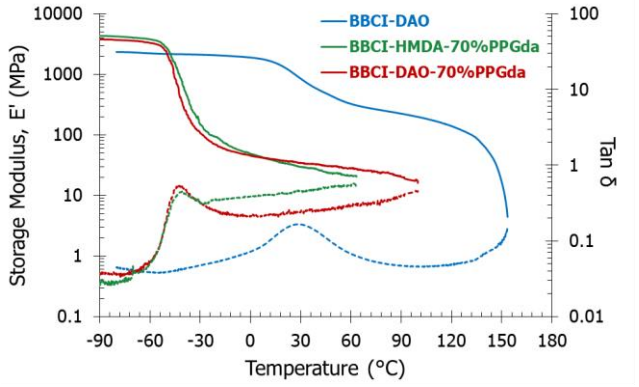

Figure 1. DMA provided T_g's and enabled the comparison of moduli values and flow/yield temperatures for each TPU.

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Thermomechanical analysis (TMA) provided the glass transition temperatures for the PU foams, and the data points were plotted (Figure 2). A clear trend of higher aromatic amine content leading to higher T_g existed for each system. The CHDMBCI-TADE:T-403 series exhibited T_g's ranging from 30 °C to 111 °C, while the BBCI-TADE:T-403 series ranged from 3 °C to 88 °C (Figure 4). Scanning electron microscopy (SEM) provides morphological characterization of the PU foams (Figure 3). The foams have a closed-cell or partially open-cell structure indicating a lack of porosity and better insulating properties than open cells, which are more frequently used in vibrational damping applications. Cell structures appear to be on the order of ~500 µm.

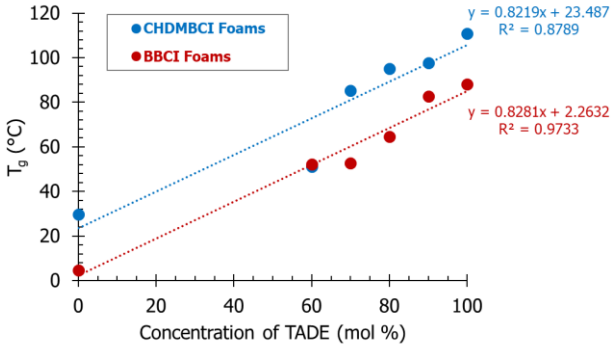

Figure 2. TMA showed an increase in T_g with an increase in the concentration of TADE in PU foams.

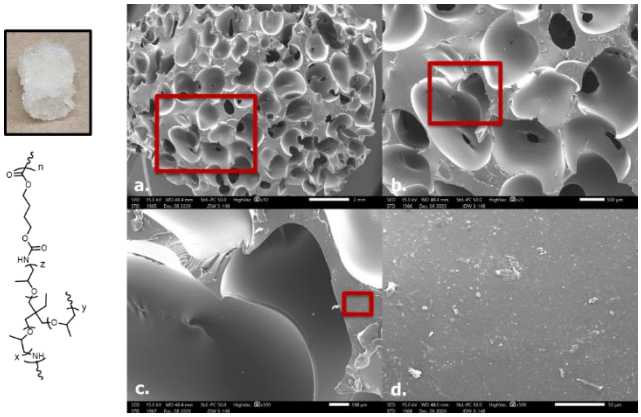

Figure 3. SEM of butanediol-based NIPU foam.

Conclusions

We established a novel methodology towards isocyanate-free foaming of polyurethane systems. This process utilized a thermal degradation mechanism of bis-carbonylimidazolide monomers in order to generate CO_2 as the blowing agent for PU foams. We synthesized two series of foams with varied concentrations of aromatic amines (di- and triamines) in concert with a PPG triamine for higher conversion. The increase in MDA or TADE incorporation yielded foams with higher T_g's and more rigid structures. SEM indicated that the process described herein provided closed-cell foams. Small molecule byproducts were easily removed through a solvent extraction; however, further work is investigating promising pathways to completely negate the concern of monomeric byproducts. This process permitted the production of flexible to rigid PU foams with a wide range of T_g's utilizing a green and sustainable method.

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