



**Molecular Design of Novel Poly(urethane-urea) Hybrids as
Helmet Pads for Ballistic and Blast Trauma Mitigation**

by Alex J. Hsieh, Joshua A. Orlicki, and Rick L. Beyer

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14. ABSTRACT Polyurethane (PU) and poly(urethane urea) (PUU) based foams are currently being used as helmet pad materials. The U.S. Army still has a critical need for more efficient foam pad materials and designs that will provide warfighters with improved survivability against blast-induced traumatic brain injuries. Recent work has shown that tailoring the microphase-separated morphology is critical in controlling the high strain-rate mechanical deformation of bulk PU and PUU elastomers. In this work we focused on molecular influence and have successfully synthesized select model PU and PUU elastomers incorporating triptycene moieties. Adding triptycene-1,4 hydroquinone resulted in a 9 °C increase in the soft segment glass transition temperature compared to hydroquinone-containing PU. The 1,4-diaminotriptycene modified PUUs revealed improved tensile modulus and flow stress, which correlated well with the rubbery plateau modulus data determined from dynamic mechanical analysis and with the interdomain-correlation data from the small-angle X-ray scattering measurements.					
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Acknowledgments

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1. Objective

The goal of this research was to explore the role of molecular mechanisms on the mechanical strengthening of polyurethane (PU) and poly(urethane-urea) (PUU) elastomers to further the design and development of advanced helmet pads for ballistic and blast trauma mitigation.

2. Background and Approach

The current Advanced Combat Helmet (ACH) system incorporates stiffened carbon-fiber-based composite layers on the front surface and has provided the desired ballistic performance. However, there is still a critical need to drastically mitigate traumatic brain injury among surviving Soldiers wounded during the current combat operations in Iraq and Afghanistan. Microcellular foams have been evaluated as part of a materials system for their potential to attenuate the peak pressure and impulse of a blast wave in air for blast energy absorption. The current ACH helmet also includes a combination of microcellular foam materials in the design. In practice, the material property of foams depends on at least two parameters: the geometry of microcellular structure and the properties of the foam materials of which they are composed (1).

Microphase-separated PU and PUU elastomers exhibit versatile mechanical properties and have drawn great interest for use in a wide variety of engineering and structural applications, including as potential protection against projectile impacts and blast loading impacts. In general, both PU and PUU consist of long-chain polyols and diisocyanates to form the soft segments, while short-chain diols and diamines are used as chain extenders to react with diisocyanates to form the hard segments of PU and PUU, respectively. During the polymerization of PUU, the urethane linkage is formed from the diisocyanate-polyol reaction, while the urea linkage is formed from the diisocyanate-diamine reaction. Microphase separation as a result of thermodynamic incompatibility between the soft and hard segments gives rise to a wide range of useful physical and mechanical properties (2). The type and molecular weight of polyols for soft segments, and the choice of diisocyanates and chain extenders used in the synthesis of hard segments, significantly affect the morphology and bulk properties of both segmented PU and PUU.

Despite the microcellular structure dependence of foam properties, we envision that the molecular aspect of PUs and PUUs can also play an important role in the dynamic mechanical deformation of foam materials. In this Director's Research Initiative (DRI), our intent is to elucidate molecular mechanisms that are critical to enabling mechanical strengthening in

microphase-separated elastomers. First, we evaluate the film properties of PUs and PUUs simply for the ease of processing and structure-property characterization, as well as to minimize the microcellular parameters.

This report summarizes the experimental findings from a systematic study undertaken to design and synthesize a series of select model PU and PUU elastomers to determine the composition influence on microstructure, viscoelastic relaxation, and mechanical deformation. In particular, we use results obtained through characterization techniques, including small-angle X-ray scattering (SAXS) and dynamic mechanical analysis (DMA), to correlate with and analyze the stress-strain data of triptycene-modified PUUs.

3. Experimental

We evaluated the influence of triptycene moieties (figure 1) in select model PU and PUU compounds. One included addition of 1,4-diaminotriptycene onto the synthesis of PUUs, while triptycene-1,4 hydroquinone was added in the second set to synthesize triptycene-modified PUs. The preparation of both PU and PUU materials was important, as the inter-chain hydrogen bonding is quite different in urethane and urea systems. The cohesive strength of the bidentate H-bonding interaction in urea is reportedly stronger than the monodentate interaction in urethane. In this way, we ensured maintaining the proper extent of bidentate interaction while adding the triptycene moieties in PUUs. Other reactants used for synthesis of PUs and PUUs were Terathane[®] polyether glycol (PTMO), 4,4'-methylenebis (phenyl isocyanate) (MDI), 4,4'-dicyclohexylmethane diisocyanate (HMDI), hydroquinone, diaminobenzene, diethyl toluene diamine (DETA), and catalyst dibutyltin dilaurate. Anhydrous dimethylacetamide (DMAc) was used as a reaction solvent and for the casting of film samples. All chemicals were used as received.

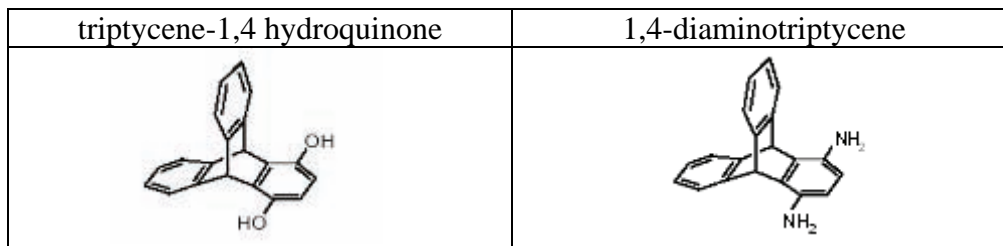


Figure 1. Chemical structures of triptycene-1,4 hydroquinone and 1,4-diaminotriptycene.

We prepared the PU and PUU compounds following a two-step, pre-polymer synthesis method. The procedure used for synthesis of PUs was as follows. PTMO of 2000 g/mol molecular weight was prepared in a 300 mL flask with 2 drops of dibutyltin dilaurate and ~40 mL DMAc. The flask was then sealed and sparged with nitrogen for 1 h in an oil bath at approximately 80 °C. The hard segment was added first and given time to react with the soft segment before

the chain extender, either hydroquinone or triptycene-1,4 hydroquinone, was added. In this case, the MDI was added directly after the sparging and the chain extender was added 4–5 h later. The flask was then brought to ~100 °C and left in the oil bath for approximately 30 h. After that time, the polymer was precipitated into a flask containing a 2:3 mixture of ethanol and de-ionized water. Any visible solid precipitate was collected and dissolved in tetrahydrofuran (THF), while the remaining solution was filtered for remaining precipitate. Once collected, we dried the participate under a slow flow of nitrogen gas, and then heated it in a 100 °C vacuum oven to remove as much solvent as possible. Figure 2 shows the polymerization reactions that follow the Scheme 2 path. A select amount of polymerized PU was heated and dissolved in DMAc. These solutions were then cast on Rain-X treated glass slides and left to dry overnight, followed by a drying in the oven to facilitate removal of the solvent.

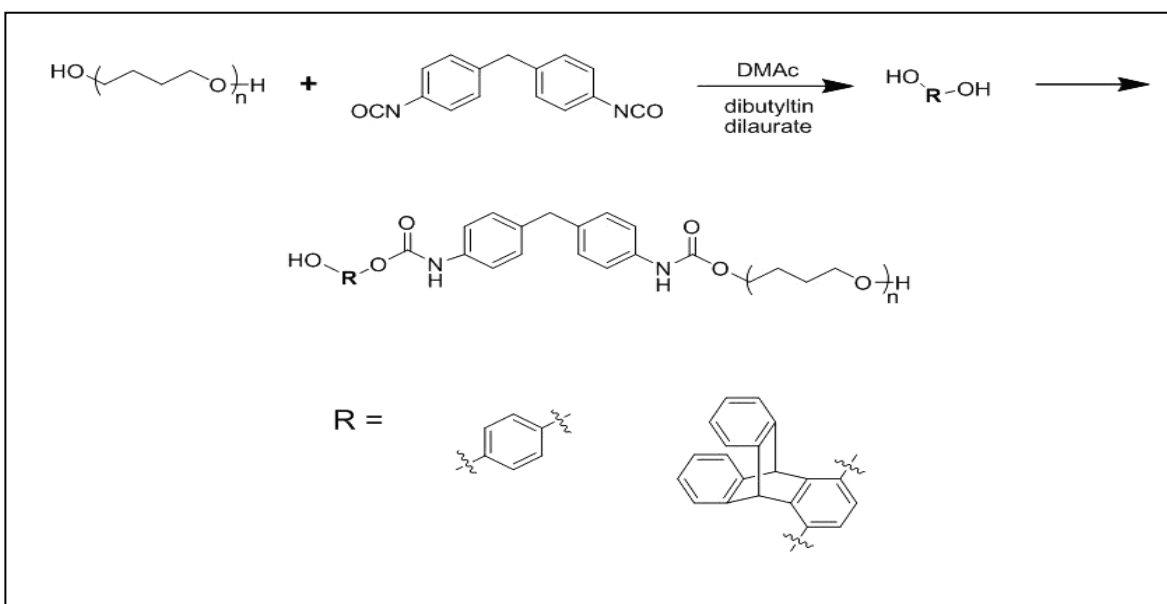


Figure 2. Synthesis reaction of PTMO and MDI to form pre-polymer followed by addition of chain extender dihydroxyl of either hydroquinone or triptycene-1,4 hydroquinone.

In parallel, an in-situ polymerization/cast method was used for preparing the PUU films. First, to prepare the pre-polymer, the diisocyanate was weighed and heated to 65 °C in a dried round-bottom flask in a nitrogen environment. Separately, the PTMO was accurately weighed and mixed thoroughly with catalyst in another container and the mixture was then held at 45–50 °C. The PTMO/catalyst mixture was then added to the diisocyanate and blended with the help of a mechanical overhead stirrer, during which an exothermic reaction occurred. After the exotherm subsided, the mixture was heated in an external oil bath and held at 130–135 °C for several hours. The reaction mixture was then cooled and allowed to stand overnight at room temperature. Next, the pre-polymer was mixed with anhydrous DMAc and heated to 65 °C. The chain extender was then added in one portion and the mixture was heated at 65 °C for approximately

1 h. The choice of chain extenders for PUUs included diaminobenzene, DETA, and 1,4-diaminotriptycene. The solution, which at this point was fully reacted, was poured onto a level glass slide in an oven and heated to 80 °C for approximately 3 h to evaporate the DMAc.

4. Results

4.1 Influence of Triptycene-1,4 Hydroquinone in PUs

We used the set of model PU compounds we prepared to investigate the molecular influence on glass transition temperature and viscoelastic relaxation. We synthesized these PUs from MDI, PTMO of molecular weight 2000 with a chain extender of either hydroquinone or triptycene-1,4 hydroquinone.

Figure 3 is a sample graph of single-frequency temperature ramp data obtained from the DMA measurements of the triptycene 1,4-hydroquinone modified PU. The soft segment glass transition temperature, T_g , determined from the loss modulus data was about -46 °C, higher than -55 °C for the hydroquinone-PU. Additionally, we compared the dependence of T_g with respect to the frequency. Figure 4 is a plot of multi-frequency loss modulus data obtained for the triptycene 1,4-hydroquinone modified PU. The increase in frequency resulted in the loss modulus curves shifting to the right causing an increase in the glass transition temperature. Similarly, one can further deduce the evolving shape of the storage modulus curve with increasing frequency to create a master curve by following the Williams Landel Ferry (WLF) equation:

$$\log[a_T] = C_1(T - T_{ref}) / (C_2 + T - T_{ref}) \quad (1)$$

where a_T is the melt viscosity at T_{ref} , C_1 and C_2 are constants that define the temperature shift according to frequency, and T_{ref} is defined as T_g in these experiments. At T_g , C_1 and C_2 are universally accepted to be 17.4 and 51.6, respectively, for all polymers (3). Using the time-temperature superposition principle, data were shifted between temperatures along the frequency axis to align with the curve of the reference temperature (in this case, the glass transition temperature). Preliminary master curves for samples hydroquinone-PU and triptycene-1,4 hydroquinone are shown in figure 5. The values of apparent activation energy calculated for the glassy-rubbery transition are 353.3 and 289.3 kJ/mol for the hydroquinone-PU and triptycene-1,4 hydroquinone, respectively (4).

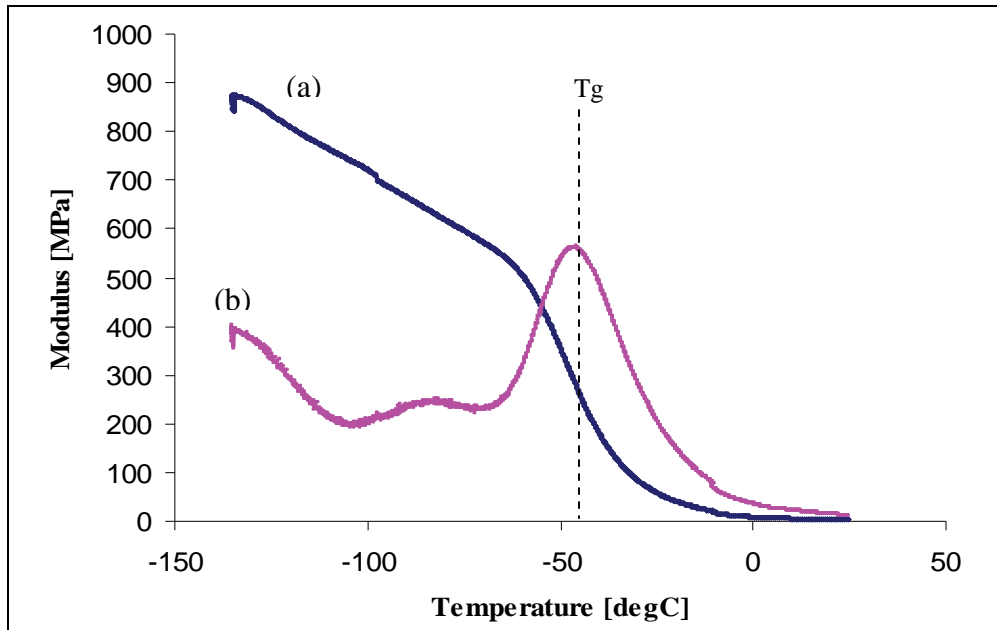


Figure 3. Sample DMA temperature sweep data for triptycene 1,4-hydroquinone modified PU; (a) storage modulus and (b) loss modulus data.

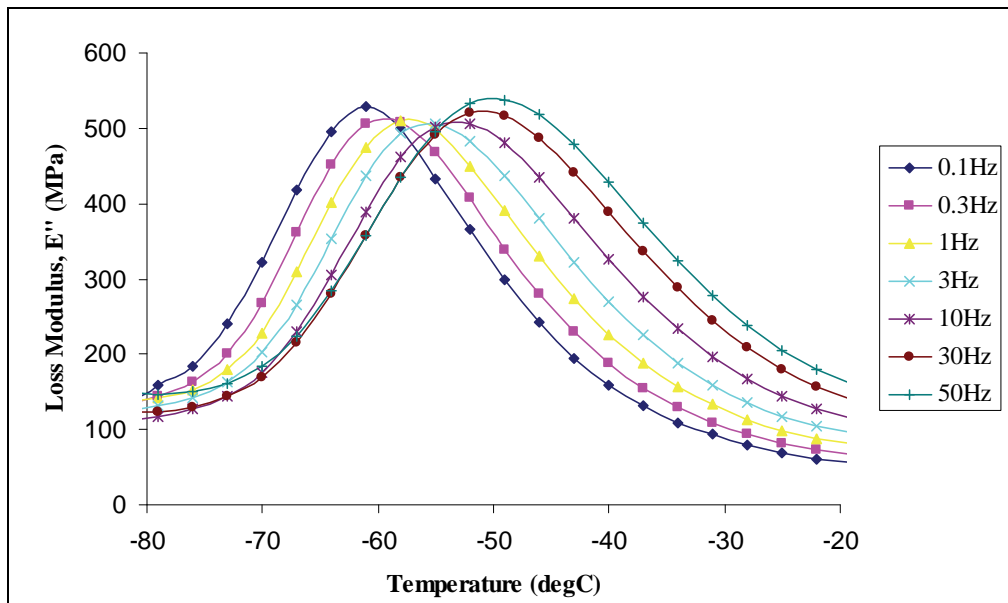


Figure 4. Sample multi-frequency oscillation data obtained for triptycene 1,4-hydroquinone modified PU.

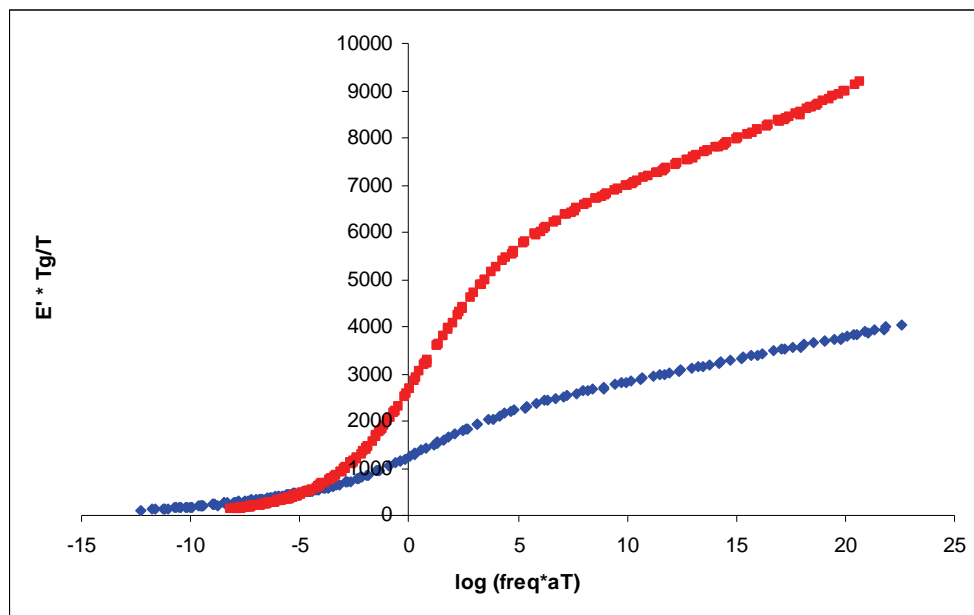


Figure 5. Preliminary master curves for hydroquinone-PU (blue) and triptycene 1,4-hydroquinone modified PU (red), created from DMA data.

4.2 Influence of 1,4-Diaminotriptycene on Mechanical Properties of PUUs

To better assess the influence of the triptycene moiety on the mechanical properties of PUUs, we first compared the influence of 1,4-diaminotriptycene as a chain extender versus *p*-diaminobenzene in select PUUs consisting of HMDI and PTMO of 2000 g/mol molecular weight. The choice of diaminobenzene was simply based on the similarity in chemical structure to 1,4-diaminotriptycene. Both are aromatic amines and possess *para*-substitution of the diamines, except there is a larger inherent free volume associated with 1,4-diaminotriptycene.

Figure 6 shows the results of storage modulus data obtained from DMA. The diaminobenzene-PUU, once above the glass transition temperature, exhibits a drastic decline in the modulus (a drop of about two orders of magnitude) until the rubbery plateau is eventually reached. Incorporation of 1,4-diaminotriptycene appears to result in much higher rubbery plateau modulus than in diaminobenzene-PUU. These results correlate well with improved mechanical properties obtained from the tensile measurements. Figure 7 compares the true stress-true strain data. The 1,4-diaminotriptycene-PUU shows much higher values of modulus and flow stress than the corresponding diaminobenzene-PUU.

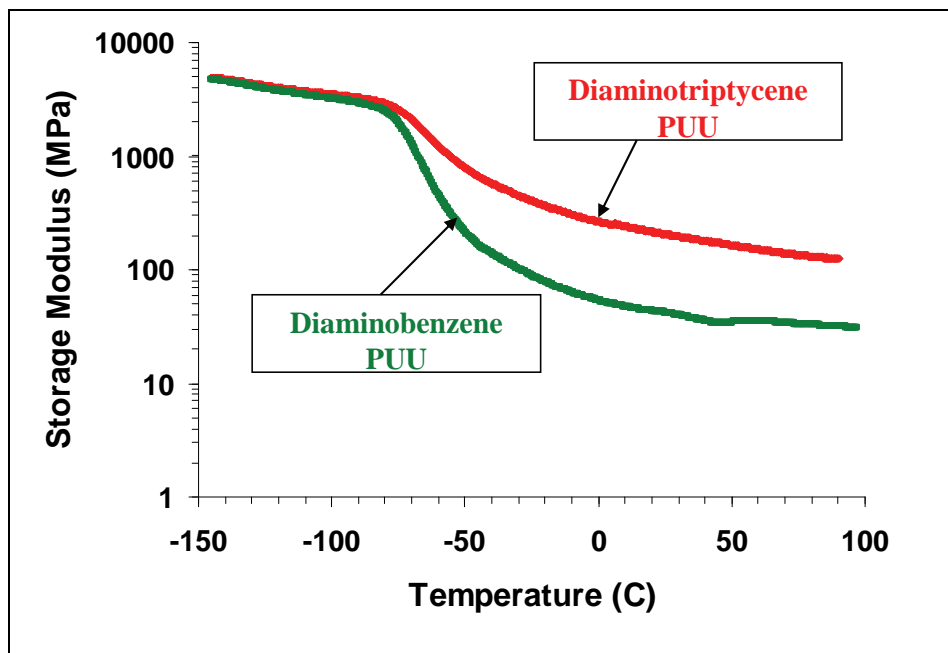


Figure 6. DMA storage modulus data for diaminotriptycene-PUU (red) and diaminobenzene-PUU (green).

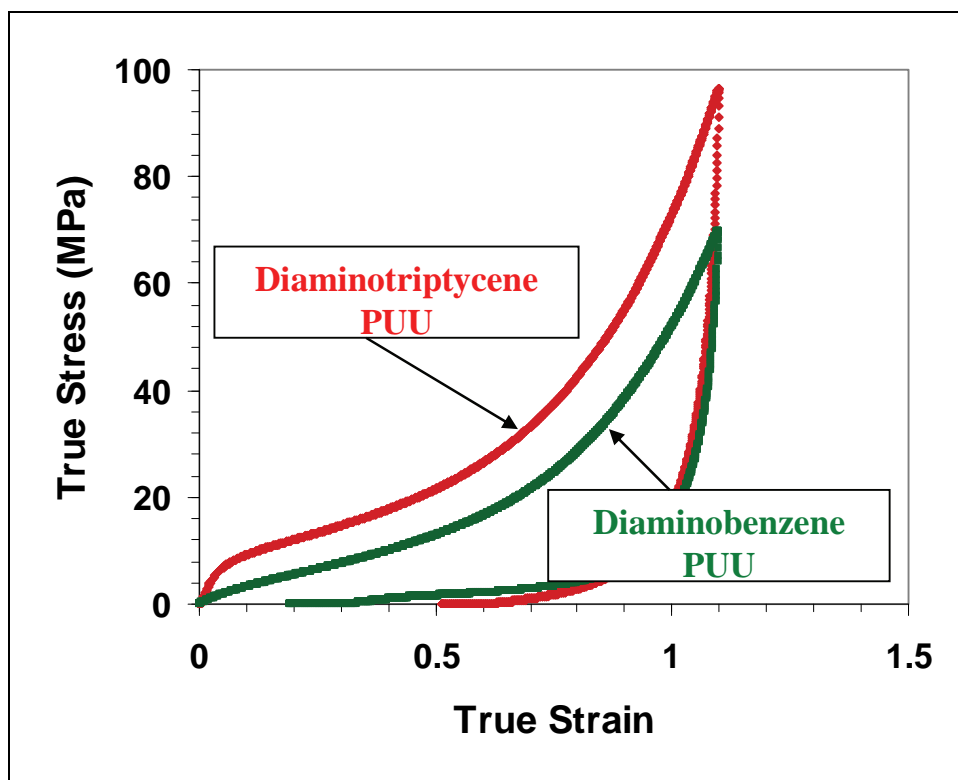


Figure 7. True stress-true strain data under uniaxial tension for 1,4-diaminotriptycene-PUU (red) and diaminobenzene-PUU (green).

In the second set of model PUU compounds, we compared 1,4-diaminotriptycene versus DETA used as chain extender. The diamine groups in DETA are *meta*-substituted, as compared to a *para*-arrangement in 1,4-diaminotriptycene. Three PUUs consisting of HMDI, and PTMO of molecular weight of 2000 g/mol, with varying composition of chain extenders (100% diaminotriptycene, 50/50 diaminotriptycene and DETA, and 100% DETA) were synthesized for evaluation. Figure 8 displays the results obtained from the SAXS measurements. The intensity of the scattering peak drastically increases with incorporation of diaminotriptycene, suggesting that there is an appreciable increase in the inter-domain correlation. This can be partly attributed to the presence of diamine groups in *para*-configuration favoring a better packing of hard segments in 1,4-diaminotriptycene-containing PUUs, and correspondingly leading to an increase in the scattering contrast between the hard domains and the soft segment regions.

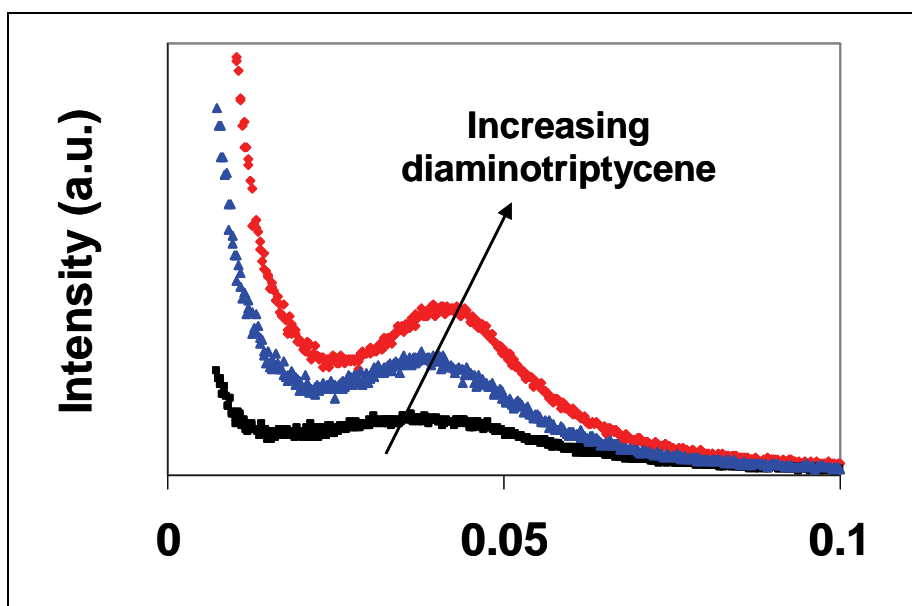


Figure 8. SAXS data for 100% 1,4-diaminotriptycene-PUU (red), 50:50 1,4-diaminotriptycene/DETA-PUU (blue), and 100% DETA-PUU (black).

Figure 9 reveals a strong composition dependence of rubbery plateau modulus values among these model PUUs. The 100% 1,4-diaminotriptycene-PUU exhibits much higher values of rubbery plateau modulus than the corresponding 100% DETA-containing PUU. Increasing the 1,4-diaminotriptycene content also yields PUUs with much improved tensile properties including both modulus and flow stress, as shown in figure 10. Furthermore, strain hardening is much more prominent in 100% 1,4-diaminotriptycene-PUU than in the 100% DETA-PUU. These results reveal an excellent correlation between the mechanical properties and microstructures with respect to 1,4-diaminotriptycene incorporation in these select PUUs.

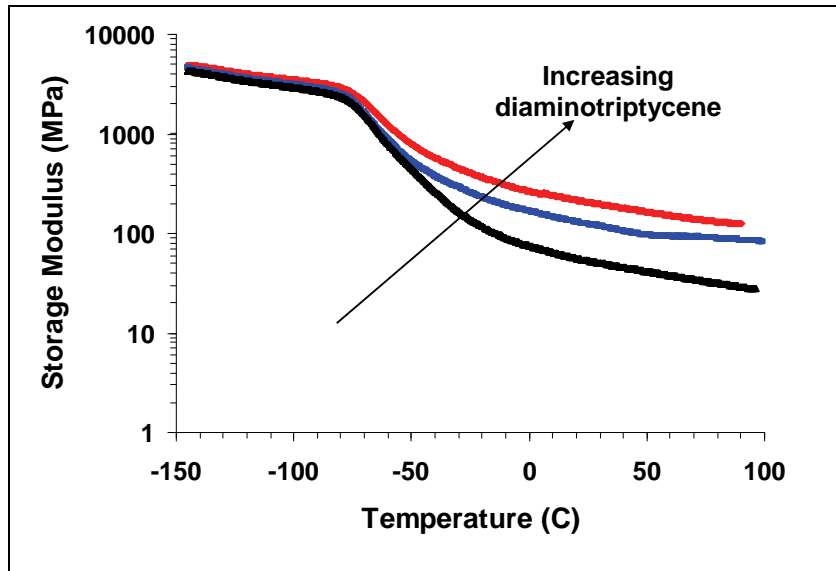


Figure 9. DMA storage moduli curves for 100% diaminotriptycene-PUU (red), 50:50 diaminotriptycene/DETA-PUU (blue), and 100% DETA-PUU (black).

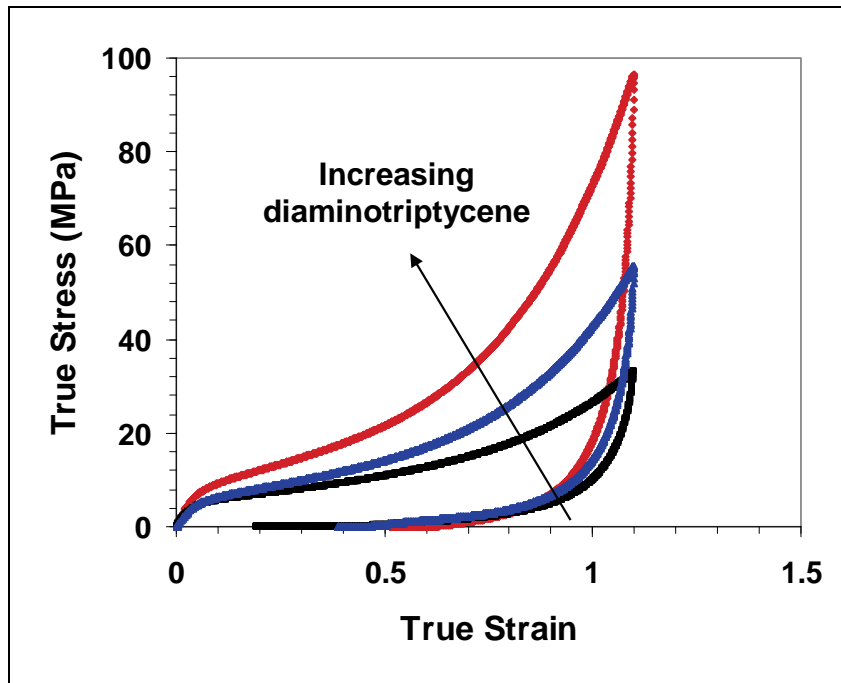


Figure 10. Tensile true stress – true strain data for 100% diaminotriptycene-PUU (red), 50:50 diaminotriptycene/DETA-PUU (blue), and 100% DETA-PUU (black).

5. Discussion

The material response of typical polymer foam is characterized by three different regimes in the stress-strain curve, including an initial linear-elastic bending followed by a long plateau where elastic buckling of the cell walls takes place and most of the energy absorption occurs. The plateau region is followed by the foam densification, whereby the stress increases sharply with further strain as a result of the total collapse of the skeleton walls (5, 6). For any microcellular material to be effectively to attenuate a blast wave, it is important that foam with proper plateau stress can endure most energy absorption without cellular walls densification (6).

Figure 11 is a plot of compressive stress-strain curves obtained from an earlier work for a select set of model PUU materials synthesized using DETA as a chain extender (7). Results clearly indicated that the flow stress can be increased from rubbery to leathery by simply increasing the hard segment content of PUUs. In this DRI, we demonstrate a route to further mechanical strengthening of PUUs through incorporation with 1,4-diaminotriptycene.

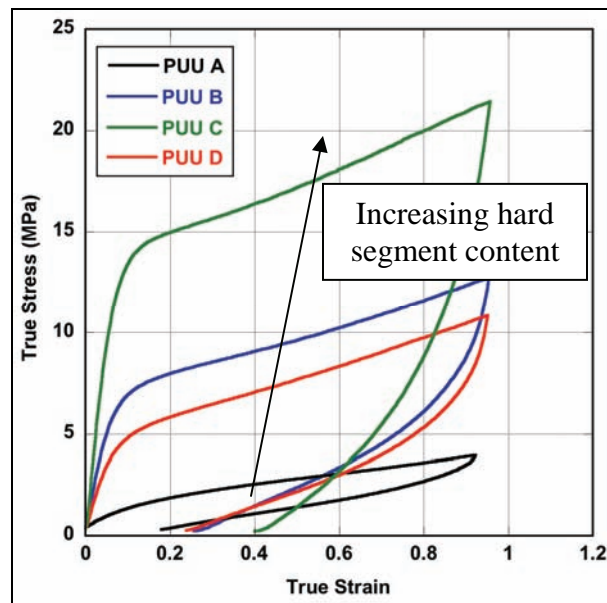


Figure 11. Stress-strain curves of a select set of model PUU materials under uniaxial compression (7).

6. Conclusions

In this study, we demonstrated the successful design and synthesis of PU and PUU materials incorporating triptycene moieties. Adding triptycene-1,4 hydroquinone resulted in a 9 °C increase in the soft segment glass transition temperature compared to hydroquinone-containing PU. The triptycene-1,4 hydroquinone modified PU also revealed a lower apparent activation energy, suggesting that it is more strain-rate sensitive than the corresponding hydroquinone-PU.

In PUUs, the incorporation of 1,4-diaminotriptycene yielded higher modulus and flow stress when used instead of DETA as a chain extender. The composition dependence of mechanical strengthening correlated well with the rubbery plateau modulus data from DMA, as well as with the interdomain-correlation data from SAXS.

These experimental findings strongly suggest that molecular influence can play an important role in the viscoelastic relaxation and mechanical deformation of PU and PUU materials. Future work will include the synthesis of triptycene-modified PU and PUU foams in order to first validate the influence of microstructure on the overall mechanical properties, which will be further exploited to enable the design of microcellular PU and PUU foam materials with the desired ballistic and blast trauma mitigation.

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List of Symbols, Abbreviations, and Acronyms

ACH	Advanced Combat Helmet
DETA	diethyl toluene diamine
DMA	dynamic mechanical analysis
DMAc	dimethylacetamide
DRI	Director's Research Initiative
HMDI	4,4'-dicyclohexylmethane diisocyanate
MDI	4,4'-methylenebis (phenyl isocyanate)
PTMO	Terathane [®] polyether glycol
PU	polyurethane
PUU	poly(urethane-urea)
SAXS	small-angle X-ray scattering
THF	tetrahydrofuran
WLF	Williams Landel Ferry

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