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Quasi-Static Tensile Deformation Measurements of Select Model Poly(urethane urea) (PUU) Elastomers

by Alex J. Hsieh and Paul Moy

ARL-TR-6806 **February 2014**

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14. ABSTRACT

The molecular influence on quasi-static mechanical properties of select model 4,4'-dicyclohexylmethane diisocyanate-diethyltoluenediamine-poly(tetramethylene oxide)-based poly(urethane urea) (PUU) elastomers is investigated. Increasing the hard segment (HS) content gives rise to PUUs with higher stiffness, higher flow stress, as well as greater strain hardening upon tensile deformation. Furthermore, PUUs with similar HS contents but varying in the molecular weight (MW) of poly(tetramethylene oxide) reveal a significant difference in the mechanical deformation response, particularly the ultimate tensile strength, in addition to earlier reported observations that dynamic strain-rate sensitivity of these PUUs was strongly dependent upon the MW of poly(tetramethylene oxide). These results highlight that a proper choice of PUUs with optimized tensile strength in addition to the desired dynamic strain-rate hardening characteristics is required for use in the design of a multilayer matrix composite.

15. SUBJECT TERMS

poly(urethane urea) elastomers, tensile strength, dynamic strain-rate hardening

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1. Introduction

High-performance elastomers capable of deformation-induced glass transition have shown great potential in providing enhanced ballistic protection and shockwave mitigation capabilities (*1*–*4*). However, challenges towards a rational design of responsive hierarchical elastomeric materials reside in a better understanding of key physical events occurring on various temporal and spatial scales. Recent work via solid-state Nuclear Magnetic Resonance (ssNMR) spectroscopy has been utilized to probe the molecular dynamics associated with tunable microstructure of select model 4,4’-dicyclohexylmethane diisocyanate-diethyltoluenediamine-poly(tetramethylene oxide)-based poly(urethane urea) (PUU) elastomers. It is noteworthy that ssNMR measurements enable the discern and differentiation of segmental dynamics on the atomistic scale, where PUU was found to contain four different regions of segmental movement, including the rigid-hard segment (HS), mobile-HS, rigid-soft segment (SS), and mobile-SS regions (*5*). The dynamics in the rigid-SS fraction was at least an order of magnitude slower than that in mobile-SS for all PUUs (*5*). For a variety of SS molecular weights (MWs), the dynamics and relative portions of rigid versus mobile fractions among HS were substantially similar, while those for the SS were largely different (*5*). Greater phase-mixing between the HS and SS substantially lowered the SS mobility, facilitating SS to undergo glass transition at high-strain rates, thus can be key to enhancing dynamic mechanical strengthening (*5*).

In addition to the strain-rate sensitivity previously reported (*6*–*9*), these PUU elastomers also exhibited a variation in the mode of failure. It was noted that ductile mode of failure was observed in most of the select model PUU elastomers upon impact against a 0.22-cal fragment simulating projectile (FSP), where the size of perforation was much smaller than the diameter of the FSP (*10*). This is significantly different from a plug-type of failure typically observed in ductile polycarbonate. In the case of PUUs, change in the mode of failure from ductile to brittle also occurred in some compositions—such as PUU 431-1K and PUU 211-650 (see table 1 below for the PUU nomenclature) (*10*)—though the brittle mode of failure occurred in PUU 211-650 appeared to be very much different from the failure observed in PUU 431-1K. It is noteworthy that PUU 211-650 was reported to exhibit greater dynamic strain-rate hardening characteristics.

In practice, both the dynamic strain-rate hardening characteristics and the ultimate tensile strength properties are critical for use in the design of PUU elastomers in the form of a multilayer matrix composite to achieve multi-functionalities. This unique design concept was conceived under the U.S. Army Research Laboratory (ARL) Director’s Research Initiative (DRI), FY11-WMR-029, entitled “Hierarchical Elastomers with Tunable Microstructures: Molecular Modeling from Robust Mechanical Strengthening to Multi-Functionalities” (*9*). An ARL patent application entitled, “A Multi-Layer Matrix Composite Having Improved Energy

Absorption, Dissipation and Shock Wave Mitigation Capabilities" was also recently filed (S/N 14/022,837) (*11*). In this work, tensile deformation measurements of select model PUU elastomers are carried out. The goal is to determine and differentiate the tensile true stress versus true strain response in order for the mechanical properties optimization of select PUU elastomers, and additionally providing support towards feasibility demonstration and validation of a multilayer matrix composite design concept.

2. Experimental

2.1 Materials

Select model PUU elastomers composed of 4,4'-dicyclohexylmethane diisocyanate (HMDI), diethyltoluenediamine (DETA), and poly(tetramethylene oxide) (PTMO), with three different MW of the PTMO SS, 650, 1000 (1K) and 2000 (2K) g/mol, were chosen for this study. The PUU elastomers were prepared via a two-step, prepolymer synthesis method where details can be found elsewhere (*6*). In the sample nomenclature, the numerals "xyz" refer to the molar ratio of HMDI:DETA:PTMO, and the succeeding "650", "1K", and "2K" refer to the MW of PTMO as 650, 1000, and 2000 g/mol, respectively.

The calculation of HS content is undertaken as follows (*12*):

$$\%HS_u = \frac{100(R-1)(M_{di}+M_{da})}{\left(M_g + R(M_{di}) + (R-1)(M_{da})\right)} \tag{1}$$

where R is the molar ratio of the diisocyanate to PTMO, and M_{di}, M_{da} and M_g are the number average molecular weights of the diisocyanate (HMDI), diamine (DETA), and PTMO, respectively. Table 1 lists the composition along with the weight-percent (wt.%) of HS values for the select PUUs.

Table 1. Composition and the calculated values of hard segment content of select model PUUs.

	Molar Ratio HMDI: DETA: PTMO	**MW of PTMO (gm/mol)**	**HS (wt.%)**
PUU 211-2K	2:1:1	2000	16
PUU 211-1K	2:1:1	1000	26
PUU 532-1K	5:3:2	1000	34
PUU 431-1K	4:3:1	1000	51
PUU 211-650	2:1:1	650	33

2.2 Quasi-Static Mechanical Characterization

Tensile experiments were conducted on an Instron[*] model 4505 electromechanical testing machine at ambient temperature. A constant displacement rate was achieved with a crosshead speed of 10 mm/minute (min). To ensure the PUU sample does not slip during testing, wedge-style action grips were used. In addition, a relatively smooth grip surface face assists in preventing damage on the thin PUU material. The axial deformation measurements were acquired by digital image correlation (DIC) method (*13–15*). DIC is a noncontact, optical technique that employs digital cameras to record subsequent images of the surface of the test sample during loading. In each case, a random speckle pattern has been applied to the PUU surface. The basic concept of DIC is the conversion of pixel displacement by tracking the digital images at gray-level scale of a speckle pattern on the surface of the deforming body. Through postprocessing of the digital images with the correlation software, the full-field axial displacement and strains are acquired for each corresponding force values. DIC provides some key advantages over other methods (i.e., clip-on extensometer or strain gages), such as noncontact, less intrusive sample preparation, and most importantly the strain measurements obtained directly from the sample gage length.

3. Results and Discussion

3.1 Molecular Influence on Dynamic Strain-Rate Hardening

As stated above, high-performance elastomers capable of deformation-induced glass transition have shown great potential in providing enhanced ballistic protection and shockwave mitigation capabilities. In the FY11-WMR-029 DRI, it has been demonstrated that the propensity towards the formation of a three-dimensional (3-D) interconnected hydrogen bonded network in PUU elastomers—as well as the corresponding segmental mobility of SS—are key to the dynamic response over a broad range of the temporal scales, ms – μs – ns (*9, 16*). The segmental mobility is calculated based on broadband dielectric analysis and typically reflects the most probable dynamics associated with the respective PUU, which is often used to interpret the dynamic material response. As the SS MW decreases, the segmental dynamics changed drastically among select model PUU ealstomers, as shown in figure 1. For PUU 211-650 at 298 K, there appeared to be a strong relaxation at approximately 8 Hz along with a second loss maximum at approximately 4600 Hz; the former was hypothesized to be corresponding to the most phase-mixed microstructure regions, whereas for PUU 211-1K, a strong relaxation at approximately 21,166 Hz was observed (*11, 16*).

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[*] Instron is a registered trademark of Illinois Tool Works Inc.

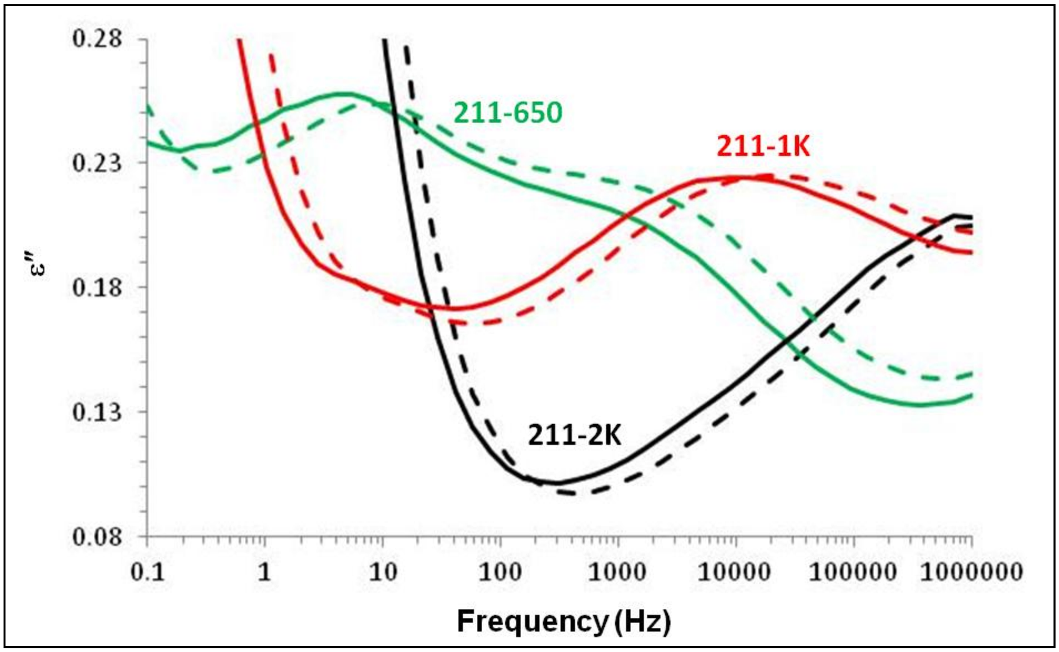

Figure 1. Influence of SS MW on dielectric loss spectra obtained for PUU 211-650 (green), PUU 211-1K (red), and PUU 211-2K (black) at 293 K (solid) and 298 K (dashed), respectively (*11, 16*).

It is expected that deformation-induced glass transition can occur in the case when the imposed strain-rate reaches—and is greater than—the segmental mobility of a given PUU (*4, 9, 11, 16*). Thus, these dielectric loss data indicated that for PUU 211-650 the dynamics-induced glass transition can occur at a frequency nearly three and five orders of magnitude sooner than that for PUU 211-1K and PUU 211-2K, respectively (*11, 16*). In fact, PUU 211-650 was noted to become glassy upon split Hopkinson pressure bar (SHPB) impact in contrast to PUU 211-1K and PUU 211-2K, where the segmental mobility of 211–650 is approximately 50 s^{-1} lower than the strain rate in the range of 1000–2500 s^{-1} experienced under SHPB (*16*).

3.2 Tensile Deformation Measurements

In addition to the dynamic strain-rate hardening characteristics, the molecular influence on the ultimate tensile strength properties is also important, particularly when considering the choice of PUU elastomers in the form of a multilayer matrix composite design.

Figures 2–4 display good reproducibility of the true stress – true strain data obtained for PUU 211-1K, PUU 532-1K, and PUU 211-650, respectively. For the PUU 1K series, increasing the HS content results in an increase in both stiffness and flow stress values for PUU 532-1K versus PUU 211-1K, so as a clear difference in the inception of strain hardening as highlighted in figure 5. With respect to the influence of the MW of PTMO, PUU 211-650 having higher HS content than PUU 211-1K also exhibits higher stiffness and flow stress values than the latter. It is noteworthy that PUU 532-1K having similar HS contents as PUU 211-650 reveals much greater tensile strength, despite that PUU 211-650 was shown to be much more dynamic strain-rate sensitive than PUU 532-1K (*8*, *11*, *16*). These tensile true stress–true strain measurements clearly demonstrated that the choice of layers configuration, including those in the outmost layer facing the threat as well as the spall-shield layer, is important for a multilayer matrix composite design as shown in a schematic in figure 6 (*11*).

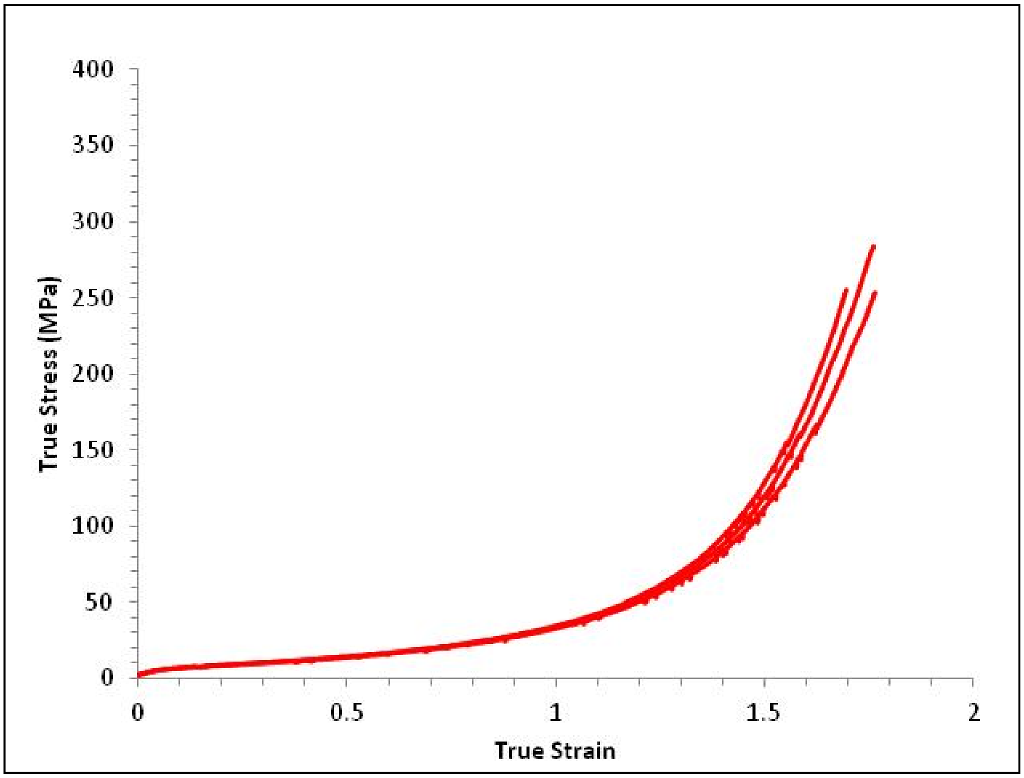

Figure 2. Tensile true stress vs. true strain data obtained for PUU 211-1K showing good reproducibility.

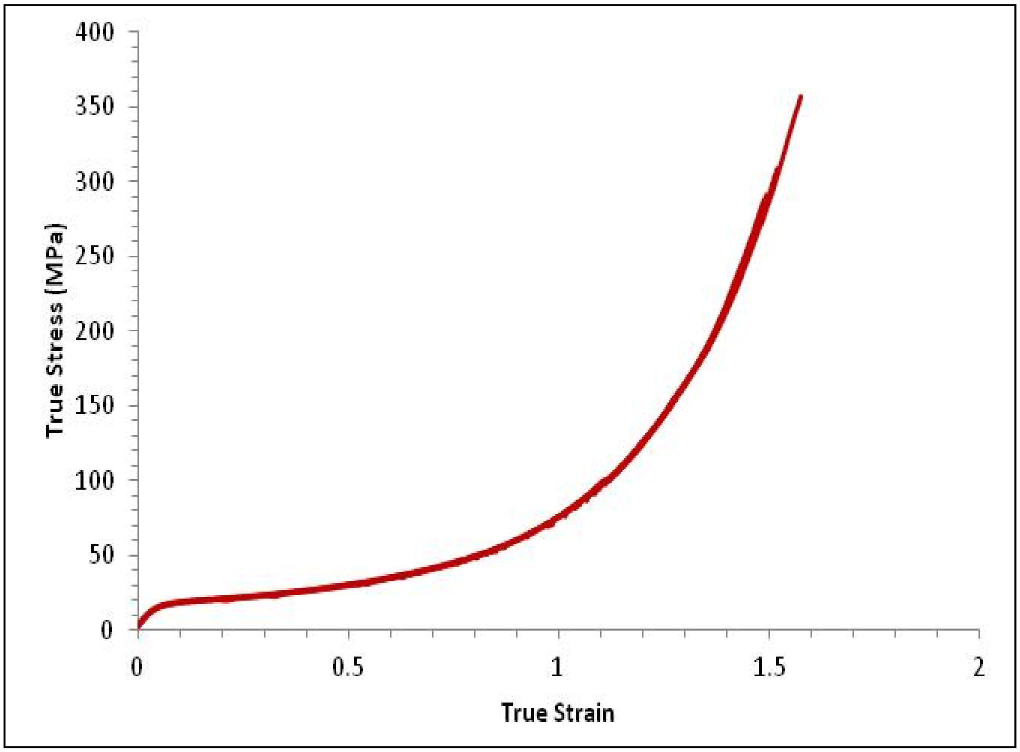

Figure 3. Tensile true stress vs. true strain data obtained for PUU 532-1K showing good reproducibility.

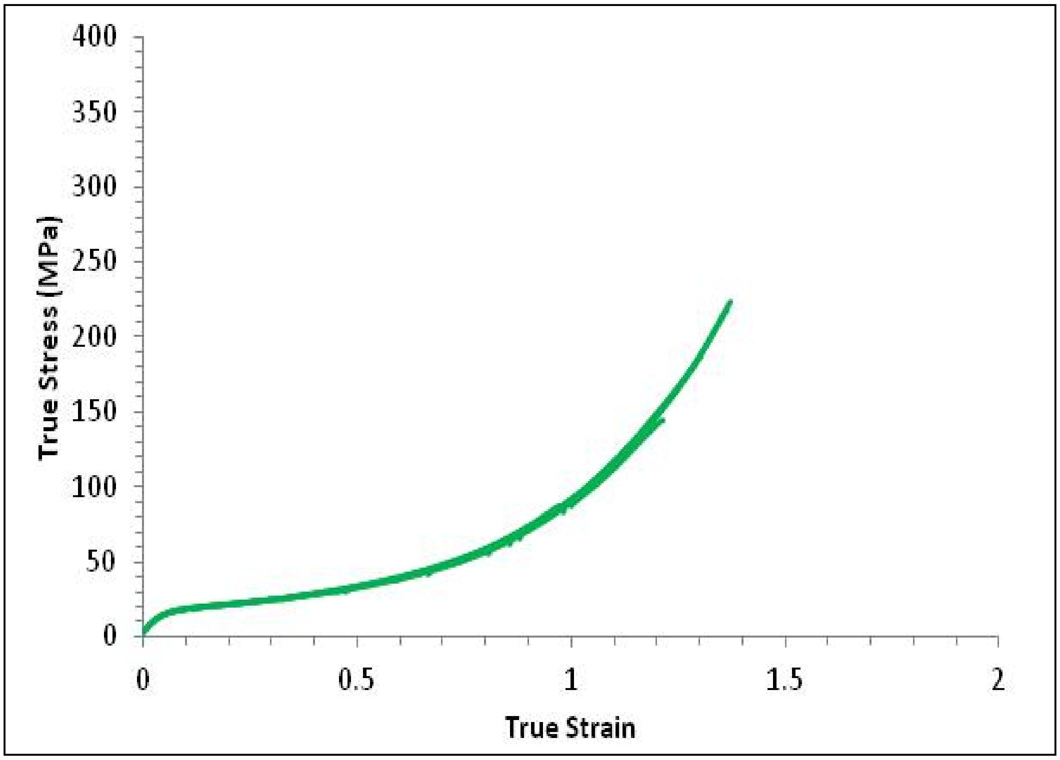

Figure 4. Tensile true stress vs. true strain data obtained for PUU 211-650 showing good reproducibility.

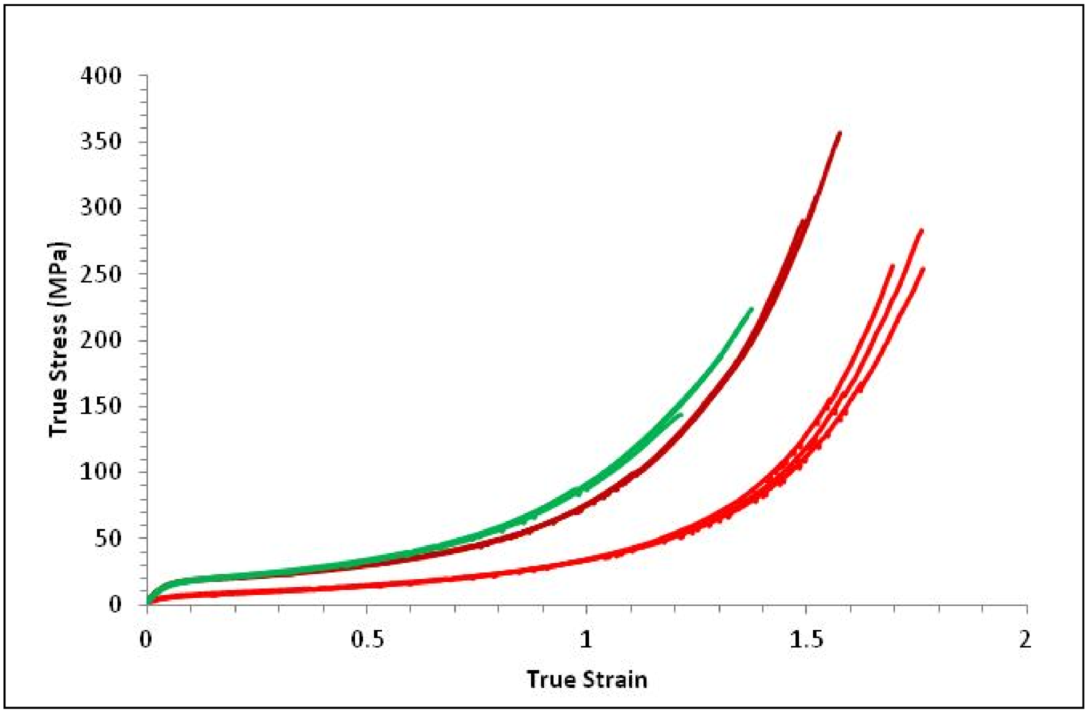

Figure 5. Comparison of true stress vs. true strain data obtained for PUU 211-1K (red), PUU 532-1K (dark-red), and 211-650 (green).

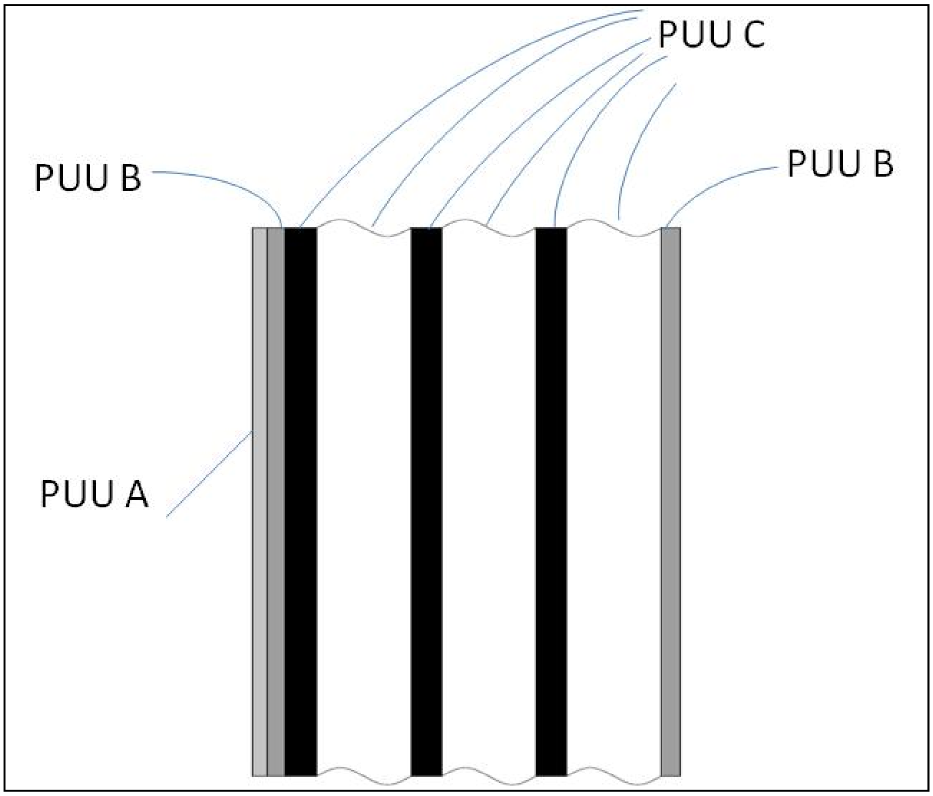

Figure 6. A schematic of a representative matrix composite (*11*); the white sections represent repetitive layers of PUU C.

4. Conclusions

Tensile deformation measurements were performed on select model PUU elastomers, where DIC was utilized to enhance the determination of the real-time local strain profiles during elongation. PUUs exhibit higher stiffness and flow stress values, as well as greater strain hardening as the HS content increases. Both PUU 532-1K and PUU 211-650 despite having similar HS contents reveal a significant difference in the mechanical deformation response. PUU 211-650 is much more dynamic strain-rate sensitive, yet PUU 532-1K exhibits better tensile strength. These results clearly indicate that a better understanding of the molecular influence on the overall mechanical deformation response is important, including both tensile strength and dynamic strain-rate hardening characteristics, for use in the design of a novel multilayer matrix composite having improved energy aborption, dissipation and shock wave mitigation capabilities.

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6. List of Symbols, Abbreviations, and Acronyms

3-D	three-dimensional
ARL	U.S. Army Research Laboratory
DETA	diethyltoluenediamine
DIC	digital image correlation
DRI	Director’s Research Initiative
FSP	fragment simulating projectile
HMDI	4,4’-dicyclohexylmethane diisocyanate
HS	hard segment
min	minute
MW	molecular weight
PTMO	poly(tetramethylene oxide)
PUU	poly(urethane urea)
SHPB	split Hopkinson pressure bar
SS	soft segment
ssNMR	solid-state Nuclear Magnetic Resonance

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