



# Molecular influence in high-strain-rate microparticle impact response of poly(urethane urea) elastomers



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## ABSTRACT

The dynamic deformation response of select model poly(urethane urea) elastomers (PUU) at high strain rates is investigated via an all-optical laser-induced projectile impact test (LIPIT). LIPIT measurements allow the direct visualization of the impact of micro-projectiles (silica spheres) on substrates and *in-situ* characterization, including depth of penetration and the extent of rebound of the micro-projectiles. PUUs are proven to be robust and the silica spheres are observed to rebound from them upon impact. In addition, for PUUs a strong correlation was noted between the coefficient of restitution and the maximum depth of penetration. Also, the coefficient of restitution data is comparable to that of glassy polycarbonate (PC), which is in great contrast to the comparison of the corresponding ambient storage modulus data obtained via dynamic mechanical analysis at 1 Hz. We hypothesize that high-rate deformation-induced glass transition is a plausible molecular relaxation mechanism towards macroscopic, dynamic stiffening/strengthening in PUUs.

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## 1. Introduction

Better understanding of the deformation of materials in extreme dynamic environments remains a great challenge among the research community across the Department of Defense (DoD) and academia. Recently, the development of a novel laser-induced particle impact platform has shown the capability of providing real-time *in-situ* visualization of the deformation response in a broad range of materials, from polystyrene-polydimethylsiloxane diblock copolymers (PS-*b*-PDMS) to graphene [1–4]. Upon impact, it was shown that PS-*b*-PDMS, consisting of a 40 nm periodic glassy-rubbery layered nanostructure, exhibited penetration and embedment of micro-spheres of silica particles, along with distinct microstructural changes, where the dissipation of impact energy was attributed to plausible pathways including layer kinking, layer compression, extreme chain conformational flattening, domain fragmentation, and segmental mixing [1]. Meanwhile,

work on LIPIT measurements of multilayer graphene revealed the presence of strong delocalization behavior and correspondingly, the potential of enhanced specific delocalized penetration energy, about eight to ten times higher than that of steel [2]. In addition, recent observations further highlighted the capability of LIPIT to enable differentiation with respect to the influence of molecular mechanism on the high strain-rate impact deformation response between select model poly(urethane urea), PUU, and polydimethylsiloxane (PDMS) elastomers [3].

PUUs are composed of urethane and urea linkages; the versatile chemistry and intrinsic intermolecular hydrogen bonding in these segmented PUUs like in segmented polyurethane and polyurea elastomers give rise to complex microstructure and a broad range of physical and mechanical properties [5–13]. The motivation towards hierarchical elastomers was derived from a novel molecular mechanism – high-rate deformation-induced glass transition, revealed by Bogoslovov et al. [14], which was successfully used to explain why a thin layer of polyurea coating on a steel plate was capable of providing ballistic protection against penetration by a 50 cal bullet [15]. These elastomeric materials have regained significant interest particularly for their potential in the areas of enhanced ballistic impact protection and shock wave mitigation

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capability [8,12–19]. However, challenges remain to fully understand the efficacy of molecular attributes that would provide guidance to enable better selection of the proper high performance elastomers required for the overall dynamic impact deformation optimization. For example, Hsieh et al. successfully characterized ultrahigh molecular weight polyethylene (UHMWPE) prepreg and composite materials, and found a strong correlation between the molecular dynamics of matrix elastomers used in the prepreps and the macroscale back-face-deformation (BFD) response of the corresponding composites observed upon ballistic impact. In practice, ballistic helmets are produced through consolidation of prepreg materials, where the UHMWPE prepreps of interest are composite materials consisting of UHMWPE fibers in the form of unidirectional, 0/90/0/90, wherein each fiber is impregnated with either polyurethane-based or Kraton®-based matrix elastomers. These prepreg materials are in the form of sheets, where the role of matrix elastomers is to bond the fibers. It was shown that UHMWPE prepreg composites composed of polyurethane matrix elastomers outperformed in the BFD reduction compared to those composed of Kraton® based matrix elastomers [20]. These results are of critical importance when the performance requirements for helmets are considered; it is noteworthy that the extent of BFD upon impact is detrimental if the deformation exceeds the helmet standoff (distance from helmet to head) as it can transfer large forces to the skull, thus potentially causing great concern towards blunt impact trauma [21,22].

With respect to the molecular attributes that are important towards energy absorption and dissipation, it is envisioned that for hierarchical elastomers multiple time constants for energy relaxation and dissipation are required, which could be associated with various relaxation modes within either microphase-separated or a co-continuous phase domains. Thus, a full multiscale characterization approach is required for building a better scale-bridging understanding of the segmental dynamics in order to provide a full picture of the dynamic response, particularly when these hierarchical elastomers are exposed to a broad range of external stimuli, ranging from ballistic impact, shock and other extreme dynamic environments, regardless of being in the bulk or as matrix elastomers in composites.

Segmental relaxation dynamics can be characterized in dielectric measurements, in the case where absorption maximum occur when dipole relaxation time,  $\tau$ , (due to molecular relaxation) matches the inverse frequency ( $1/\omega$ ) of the alternating electric field impulse, i.e. when  $\omega\tau = 1$  [23]. Broadband dielectric spectroscopy measurements revealed a drastic difference in dielectric relaxation and the corresponding segmental mobility among three select PUUs, which consist of 4,4'-dicyclohexylmethane diisocyanate (HMDI), diethyltoluenediamine (DETA), and poly(tetramethylene oxide) (PTMO), having the same stoichiometric ratio, 2:1:1 of [HMDI]:[DETA]:[PTMO] but varying in the molecular weight of PTMO (650, 1000 and 2000 g/mol), namely 211-650, 211-1000, and 211-2000, respectively [8]. The 211-650 PUU exhibited a strong relaxation at  $\sim 8$  Hz along with a second loss maximum at  $\sim 4600$  Hz. The former presumably corresponds to the most phase-mixed regions, where the formation of co-continuous, highly intermolecular hydrogen bonded hard segment (HS)/soft segment (SS) networks could be a plausible attribute. For 211-1000, a strong relaxation occurred at  $\sim 21,200$  Hz, and additionally there was a small shoulder at  $\sim 8$ -10 Hz, though the latter was found to be less significant than the strong relaxation seen in 211-650 [8]. However, for 211-2000, it was not until  $\sim 10^6$  Hz that an apparent relaxation was noted. The segmental mobility calculated based on broadband dielectric analysis varied over five orders of magnitude among these three PUUs, where the segmental relaxation time  $\tau$  at 298 K was determined to be  $\sim 0.02$  s,  $7.5 \times 10^{-6}$  s and  $5 \times 10^{-8}$  s for 211-650, 211-

1000 and 211-2000, respectively [8]. Additionally, the trend in segmental dynamics associated with the glass transition of soft segments, determined from the dielectric measurements, appears to correspond very well with the phase-mixed relaxation data obtained from dynamic mechanical analysis (DMA) [8].

Furthermore, studies from solid-state nuclear magnetic resonance (ssNMR) spectroscopy measurements revealed new insight into the dynamics on the molecular level among the three select PUUs, 211-650, 211-1000, and 211-2000 [24,25]. In ssNMR, the time-domain wideline separation (TD-WISE) data clearly elucidated that segmental dynamics associated with soft segments in the phase-mixed regions were at least an order of magnitude slower than those obtained for the mobile, soft-segment-rich regions in these PUU elastomers [8,25]. Thus, when considering dynamic strengthening in a temporal scale on the order of microsecond at ambient temperature, it would most likely be dominated by the molecular motion associated with soft segments within the phase-mixed regions [8,24,25].

Impulsive stimulated scattering (ISS) measurements, on the other hand, allow for characterization of relaxation behavior at the nanoscale, where absorption of two laser excitation pulses, which are crossed in the sample, results in localized sample heating and fast thermal expansion, which subsequently generates a coherent acoustic wave with oscillation on the order of 300 MHz frequency ( $\sim 10^8$ /s) [26]. In ISS, the speed of sound can be obtained based on the acoustic wave oscillation measurements, where the frequency of impulse is closer to the segmental mobility ( $1/\tau$ ) of PUU 211-2000 but much greater than that of PUU 211-1000 and 211-650. Thus, it is expected that high-rate deformation-induced glass transition would occur in these PUUs. This was validated from the apparent (frequency-dependent) modulus measurements, which was calculated based on the respective speed of sound derived from the 300 MHz acoustic wave oscillation measurements in ISS. For example, the apparent modulus of PUU 211-650 from ISS was only about 60% larger than that of PUU 211-2000, whereas for the former the ambient storage modulus measured at 1 Hz in DMA was about 17 times larger than that of the latter. Additionally, in ISS all of these PUUs exhibit about the same decay time  $\sim 8$  ns, regardless of their compositions. It is noteworthy that even for the most rubbery PUU 211-2000 the calculated speed of sound, 1770 m/s, was still faster than that of PDMS, 1074 m/s, presumably due to the fact that PUU 211-2000 exhibits a greater glass-like response than PDMS. This is consistent to the aforementioned molecular influence upon high strain-rate impact response observed under LIPIT [3].

To further validate our hypothesis with respect to the influence of molecular mechanism upon dynamic deformation response of hierarchical elastomers at large strains and at the nano-second timescale, a better choice of *in-situ* experimental techniques is needed. In this work, we exploit LIPIT for a comprehensive investigation of the supersonic microparticle impact response of PUU elastomers, where real-time characterization of mode of deformation, including the extent of depth of penetration and extent of projectile rebound, will be used to determine the coefficient of restitution with respect to the PUU molecular composition and projectile impact velocity.

## 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 molecular weight (MW) of the PTMO soft segment (SS), 650, 1000 and 2000 g/mol, prepared via a two-step, pre-polymer synthesis [5], were

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