

Molecular influence in the glass/polymer interface design: The role of segmental dynamics



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ABSTRACT

Recent observations of the high-velocity impact response in poly (urethane urea), PUU, elastomers has inspired a new inquiry on whether enabling molecular mechanisms could benefit dynamic impedance optimization at the interface of a glass/polymer bilayer, particularly at the moment of impulse interaction. In this work, we investigate the molecular influence on dynamic impedance using microballistic measurements on two bulk elastomers, a PUU and a polyurea, PU. Upon impact at strain rates $\sim 10^8/s$, PUU exhibits a moderate improvement in resistance against penetration than PU, that is more pronounced at higher speeds. The variation in dynamic stiffening corroborates well with the corresponding segmental dynamics data determined via broadband dielectric relaxation. Meanwhile, we calculate the shock impedance from the shock velocity data derived from the respective shock Hugoniot to discern the efficacy of dynamic impedance optimization between PUU and glass. New insight on molecular attributes will guide glass/polymer interface designs.

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1. Introduction

Over the last decade, nature has provided an inspiration towards the rational design of hybrid composites, where hierarchical architectures in structural biological materials such as shells and bones have been correlated with the robust mechanical strength characteristics that were deemed essential for protection against dynamic environmental threats [1–5]. One such concept of note is a gradient approach utilized in the design of graded composites, wherein incorporation of a bone-inspired hierarchy – a soft–stiff–soft–stiff material distribution pattern based on the bone-foramen and osteonal-bone material systems – demonstrated enhanced shock-wave mitigation capability [4]. Even so, neither nature nor prior experiments did explicitly reveal the role of

dynamics at the molecular level. Meanwhile, there is a lack of understanding of the underpinning molecular mechanisms and their influence on material deformation particularly at the moment of impulse interaction. Such knowledge can provide insights towards manipulating the physics of failure for design of robust material systems.

Recently, Veysset et al. used a laser-induced microballistic impact platform and demonstrated its capability of providing real-time, multi-frame imaging for *in-situ* visualization and differentiation of material deformation at strain rates on the order of $10^8/s$ [6–9]. In particular, the resulting dynamic stiffening phenomenon during such high-velocity impact was first revealed in hierarchical poly (urethane urea), PUU, elastomers but not in a polydimethylsiloxane elastomer, when impacted by silica micro-particles [6]. PUUs were noted to exhibit complex microstructure [10–13] along with a broad range of relaxation times [13,14], where the segmental mobility of the soft phase was shown to be strongly dependent upon the extent of intersegment mixing between soft

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and hard segments [13–15]. Among these PUUs, soft phases associated with greater phase-mixed regions revealed longer relaxation times on the order of microseconds at ambient conditions [6,13]. The presence of these slower dynamics components were found to be key to enabling dynamic stiffening, presumably via a high-rate deformation-induced glass transition mechanism [7,13], while those with nanosecond relaxation times at ambient conditions were presumably capable of providing additional energy absorption towards dynamic strengthening [6,7]. Furthermore, it was also noted that for PUUs a cooperative molecular relaxation mechanism, facilitated by the presence of intermolecular hydrogen bonding throughout the physically-crosslinked network, could be a plausible pathway towards both dynamic stiffening and dynamic strengthening [7,13,16]. In comparison, PUUs regardless of their respective composition exhibited greater dynamic stiffening during impact at strain rates on the order of $10^8/s$ than a glassy bisphenol A polycarbonate, despite the high fracture toughness and ballistic strength of the latter [7]. Dynamic stiffening over the same impact velocity range was not evidenced for bisphenol A polycarbonate; instead, plastic deformation was the predominant mode of deformation, presumably due to the lack of a cooperative intermolecular hydrogen-bond relaxation mechanism and a microsecond relaxation [7].

Our motivation for this study is to discern whether the high-rate dynamic stiffening phenomena observed in the bulk PUUs can serve as an effective energy dissipation pathway during ballistic impact at the interface of a glass/polymer bilayer, including the potential of its influence towards shock-wave propagation. Meanwhile, the shock Hugoniot is regarded as the most fundamental description of the thermodynamic state of a material following the passage of a shock wave [17]. Impedance, on the other hand, is a useful concept for better understanding of the flow of impact energy during the ballistic shock events [18,19], where shock-wave impedance differing from the acoustic wave impedance is determined by the product of density and the shock velocity determined at a given impact velocity, hereafter called shock impedance.

In this work, we focus on the molecular influence of polymers where material deformation upon ballistic impact at a glass/polymer interface could be a strong function of their corresponding segmental dynamics. First, we exploit laser-induced microballistic measurements and compare the high strain-rate deformation response of a bulk PUU against impact by silica as well as steel micro-particles, which are of higher impedance than silica micro-particles. With respect to the role of segmental dynamics, we utilize broadband dielectric relaxation measurements to further discern and differentiate its influence on the extent of dynamic stiffening observed upon microballistic impact between PUU and a polyurea, PU. In addition, we highlight the essence of high-rate deformation-induced glass transition observed in these bulk elastomers and determine its efficacy towards the dynamic impedance optimization at a glass/polymer interface. This is elucidated through the calculation of shock impedance based on the corresponding shock Hugoniot data.

2. Experimental

The model elastomers chosen for microballistic impact studies and broadband dielectric relaxation spectroscopy measurements included PUU 532–1000 and PU 1000. The PUU 532–1000 was prepared via a two-step, pre-polymer synthesis [20], which is composed of 4,4'-dicyclohexylmethane diisocyanate (HMDI), diethyltoluenediamine (DETA), and poly (tetramethylene oxide) (PTMO), with a molar ratio of 5:3:2 for [HMDI]:[DETA]:[PTMO], where the molecular weight of PTMO is 1000 g/mol. The PU 1000 was formed by reaction of poly (tetramethylene oxide di-

aminobenzoate) (Versalink P1000, Air Products) and a polycarbodiimide-modified diphenylmethane diisocyanate (Isolate 143 L, Dow Chemical) at a 4:1 weight ratio. The molecular weight given by the manufacturer for the PTMO-amine component is $M = 1238 \pm 72$ g/mol. It is noteworthy that the nominal hard segment contents of both PUU 532–1000 and PU 1000 are very similar, ~34 wt.%. More details on the synthesis of PUU and polyurea can be found in Ref. [20] and Ref. [21], respectively, so as on the materials characterization in Refs. [12–15,21–23] as well as in the [Supplementary Information](#) section.

The high-strain-rate deformation response of selected elastomers was investigated by using a laser-induced microballistic impact test platform as shown in Fig. 1 [6,24]. The launching pad assembly consists of a 210- μm glass substrate, a 60-nm gold film for laser absorption, a 30- μm layer of cross-linked polyurea (different from the PU 1000), and a sub-monolayer of either silica microspheres (diameter $D = 7.4 \mu\text{m}$) or steel microspheres ($D = 20 \mu\text{m} \pm 2 \mu\text{m}$) deposited on top of the assembly as described in Ref. [6]. Upon laser ablation of the gold film using a 10-ns duration, 532-nm wavelength laser pulse focused in a region of about 50- μm diameter, the polyurea layer expands and launches the particles into free space. The particle speed is adjusted from 100 to 800 m/s by varying the laser pulse energy from 2 to 60 mJ (Fig. 1). The projectiles are ejected into free space and impact a target sample at near-normal incidence ($\pm 5^\circ$). The launching pad and the target are separated by approximately 1.0 mm. Using a high-speed camera (SIMX16, Specialised Imaging), consisting of 16 CCDs, which are independently triggerable, with exposure times as short as 2 ns and variable inter-frame times, we visualized the micro-spheres as they impacted the surface of the samples and subsequently rebounded, providing insight into the high strain rate deformation response of these selected polymeric materials. Both impact and rebound velocities and maximum and residual (final) penetration depths were extracted from the 16-frame videos. The maximum depth of penetration occurs in the first instants following impact; thereafter, the polymer fully responds to the impact and the depth of penetration decreases. A more detailed description of the imaging setup and image analysis is available in Ref. [6].

Dielectric relaxation spectroscopy measurements were carried out using a parallel plate geometry, where samples in the form of disks (15–20 mm diameter, 0.1–0.3 mm thick) were sandwiched between 20 mm diameter brass electrodes to form a parallel plate

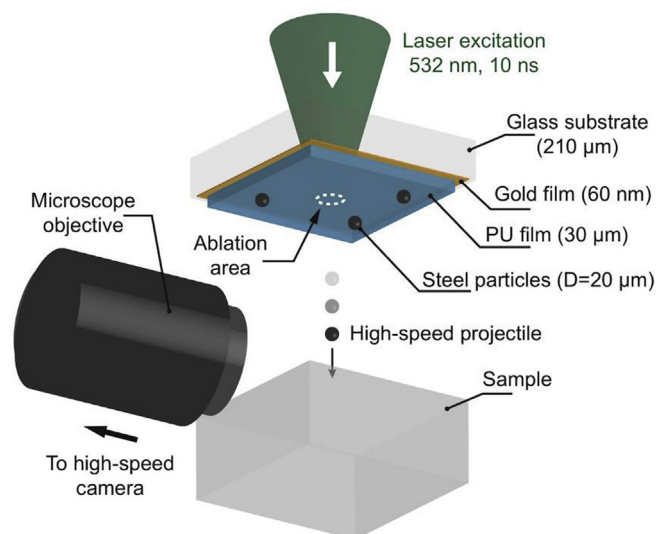


Fig. 1. Schematic of the laser-induced particle impact test.

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