



Relating structure and chain dynamics to ballistic performance in transparent epoxy networks exhibiting nanometer scale heterogeneity



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ABSTRACT

The ballistic performance was examined for a series of broad glass transition temperature epoxy formulations consisting of a di-epoxy monomer crosslinked with bi-modal mixtures of both a rigid, low molecular weight diamine and a flexible, high molecular weight diamine. Interestingly, the resins did not macro-phase separate during cure, but exhibited structural and dynamic heterogeneity on a length scale of a few nanometers, as confirmed by X-ray scattering, dynamic mechanical analysis, modulus-mapped atomic force microscopy, and broadband dielectric spectroscopy. The nano-structured resins were optically transparent and demonstrated a nearly 300% increase in ballistic energy dissipation relative to the neat resins, as well as when compared to epoxy formulations composed of similar bi-modal blends that exhibited a macro-phase separated structure. The ballistic performance is found to be insensitive to sub-glass transition temperature (T_g) relaxations, but appears to be dependent on both the nano-structure and the Vogel temperature of the high T_g component. The study demonstrates a new class of transparent protective materials composed of rigid and flexible components with a fine scale heterogeneous structure.

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1. Introduction

Thermosets are utilized in a broad range of structural applications throughout the aerospace community, defense applications, and industry in general [1–3]. Many of these applications possess strict structural requirements, including both a high modulus and glass transition temperature (T_g). For defense applications, materials and devices that use these polymers often need to function under broad operational temperature fluctuations, humidity extremes, and mechanical insults. Ballistic threats can impart effective strain rates greater than 10^4 s^{-1} , which are 5 or more orders of magnitude higher than typical quasi-static insults. While epoxy resins are common in protection systems, few studies have investigated the fundamental behavior of epoxies at these effective rates [4].

For structural applications, epoxy resins are often composed of a rigid or high functionality epoxy monomer cured with an aromatic, cyclic, or high functionality amine, to provide a T_g that is well above the highest operational temperature range for the system. A good example is a resin composed of diglycidyl ether of bisphenol A (DGEBA) crosslinked with PACM (see Fig. 1 for structures). The high T_g of DGEBA/PACM provides a modulus that does not vary substantially over a broad range of operational temperatures, an important characteristic for aerospace applications [5]. However, structural resins such as DGEBA/PACM exhibit poor ballistic performance, failing in a brittle manner at relatively low ballistic energies. Recent research has shown that epoxy resins with a T_g near room temperature exhibit the highest room temperature ballistic response [4]. Utilization of flexible spacer units, such as propylene oxide based diamines will reduce the T_g and potentially provide enhanced ballistic performance, but at the cost of a reduced modulus, and stronger temperature dependence of the modulus [6–8]. In addition, an epoxy resin with a T_g near room temperature is undesirable for most applications, because typical operational temperature fluctuations will cause pronounced changes in

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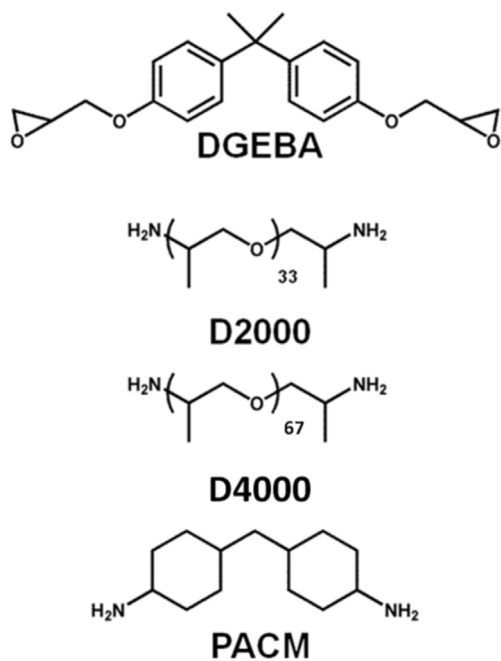


Fig. 1. Structure of the components of the epoxy mixtures.

mechanical response. With large flexible spacer contents and low resin crosslink density [9–13], epoxy systems exhibit both a low modulus and poor ballistic performance [4].

For protection applications, the high modulus requirements are often not as stringent as with structural applications. While polymeric materials for protective systems can potentially compromise on modulus to enhance high rate energy dissipation, there is a tremendous need for materials that exhibit improved ballistic response over broad operational conditions of temperature and humidity. Single component resins are unlikely to provide this performance breadth. However, heterogeneous networks with well controlled structure and chemistry may be beneficial.

The high rate mechanical performance of epoxies and cross-linked materials is extremely complex [1,2,14–16], and little insight exists into the fundamental mechanisms responsible for a given ballistic performance. Previous research [4,15,17] has examined the effect of the T_g on the ballistic performance of epoxies, finding that epoxies which are at or near their T_g during the ballistic test perform better than similar epoxies which are well below or well above their T_g during the ballistic test. The improved performance of the systems with a T_g near the ballistic testing temperature has been attributed to the dynamic nature of T_g , with materials which undergo a rubber-to-glass transition at impact rates exhibiting the best ballistic performance [15,17]. Materials which exhibit broadened or multiple T_g s are expected to exhibit improved ballistic performance over a broader temperature range due to the increased likelihood that a particular impact event will occur at a rubber-to-glass transition.

In the spirit of these challenges, we examine the ballistic performance of a series of broad T_g epoxies, consisting of blends of a single diepoxide monomer with diamine mixtures of varying rigidity and chain length. The pure diamine/epoxy systems exhibit very different T_g s, but similarly poor ballistic performance. However, mixtures of the diamines exhibit nano-scale structural and dynamic heterogeneity, and in some cases, dramatically improved ballistic performance. The increased ballistic performance of the formulations did not correlate with the glassy state relaxation behavior, but is attributed to the resulting nanoscale heterogeneity.

2. Experimental

Materials used in this study are shown in Fig. 1. Commercially available industrial diglycidyl ether of bisphenol A (DGEBA), i.e., EPON 825 (average molecular weight ~355 g/mol), was obtained from Miller–Stephenson. Polypropylene oxide based-Jeffamine diamines with a nominal molecular weight of 2000 g/mol (D2000) and 4000 g/mol (D4000) were provided by Huntsman. A cyclic diamine curing agent, 4,4'-methylenebis(cyclohexylamine) (PACM), was provided by Air Products. All epoxies and curing agents were used as received without further purification. All formulations were stoichiometric mixtures of the epoxy and diamine curing agent. Compositions are designated as the mole fraction of PACM amine hydrogens ('X'), relative to the total amount of reactive amine hydrogens in the system from both PACM and D2000. Therefore, a formation of $X = 1$ refers to a stoichiometric mixture of DGEBA and PACM, while $X = 0$ is a stoichiometric mixture of DGEBA and D2000 or DGEBA and D4000. $X = 0.5$ indicates equal mole fractions of amine hydrogens from both PACM and D2000, with the corresponding amine hydrogen total being stoichiometric for the amount of DGEBA.

For all sample preparations, epoxies and curing agents were preheated to 60 °C. If a diamine mixture was used, the two diamine components, e.g., PACM and D2000 were premixed at 60 °C for at least 1 h. Each epoxy and diamine (or diamine mixture) was then mixed and stirred vigorously at 60 °C for 5 min, then poured into molds and degassed under vacuum. Every epoxy mixture appeared uniformly mixed, with no large scale phase separation visible. Molds for ballistic testing samples were approximately 150 mm × 150 mm × 6 mm. Molds for Dynamic Mechanical Analysis were 3.3 mm thick and 1 mm thick. The 3.3 mm thick samples were used to determine the rubbery modulus, and the 1 mm thick samples were used to determine the glassy modulus. All epoxies were cured under a nitrogen purge with a cure cycle of 80 °C for 2 h, 150 °C for 8 h, and 200 °C for 2 h.

The extent of cure in the D2000 blends was evaluated via Fourier Transform Infrared (FTIR) spectroscopy. A Nicolet Nexus 870 infrared spectrometer was used to characterize the amine and epoxy cure in the wavenumber region spanning 7500 cm^{-1} to 4000 cm^{-1} . For each sample, 64 scans were co-averaged using a wavenumber resolution of 2. Due to the relatively low absorption in the specified wavenumber range, samples cured for DMA analysis (3.3 mm thick) were used. In addition to the PACM/D2000 mixtures, the neat starting materials, DGEBA, PACM, and D2000 were also measured for comparison.

Measurements of the ballistic performance were carried out with a 5.56 mm gas gun at room temperature (approximately 22 °C), with a relative humidity between 45 and 60 %. A 5.56 mm diameter steel ball bearing (Type 302, 0.69 g) was used as a projectile to impact the target. Projectile speed was tracked with a Doppler radar (BR-3502, Infinition Inc.), with a velocity resolution of 1 m/s. The polymer target (nominal 60 mm × 60 mm × 6 mm) was sandwiched in a target frame with a circular opening of 50.8 mm in diameter. The sample was oriented such that the projectile impacted the target normal to the sample surface. A witness plate (0.05 mm thick 2024-T3 aluminum foil) was placed 50 mm behind the target. The witness plate was examined for penetration after each shot, with any perforation of the witness plate indicating sample failure. Penetration of the witness plate does not necessarily require the projectile to penetrate the sample; backside fragmentation of the epoxy target may penetrate the witness plate and result in penetration, particularly for brittle samples. For each epoxy composition investigated, twelve targets were shot. The $V_{50-BL(P)}$ ballistic performance was calculated by taking the arithmetic mean of the three highest non-penetrating and the three lowest

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