

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



Kevin A. Masser¹, Daniel B. Knorr Jr.¹, Mark D. Hindenlang, Jian H. Yu, Adam D. Richardson, Kenneth E. Strawhecker, Frederick L. Beyer, Joseph L. Lenhart^{*}

Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 21005, United States

ARTICLE INFO

Article history:

Received 23 September 2014

Received in revised form

8 December 2014

Accepted 13 December 2014

Available online 23 December 2014

Keywords:

Polymer networks

Nanoscale heterogeneity

Nanostructure

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.

Published by Elsevier Ltd.

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

^{*} Corresponding author.

E-mail address: joseph.l.lenhart.civ@mail.mil (J.L. Lenhart).

¹ These authors contributed equally to the publication.

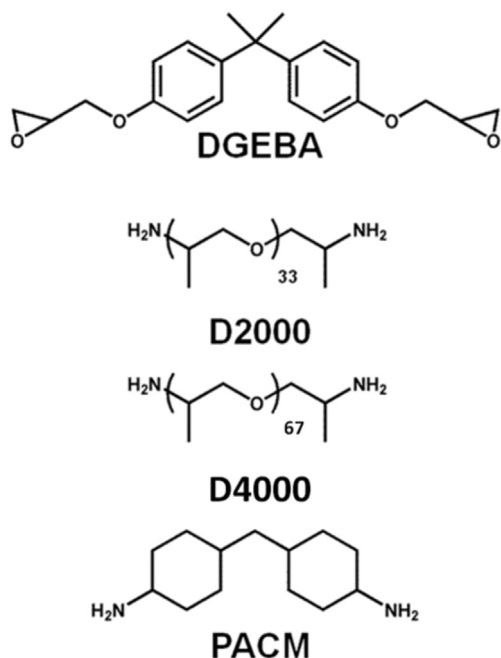


Fig. 1. Structure of the components of the epoxy mixtures.

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

penetrating impact velocities on the witness plate. In this way, the V_{50} refers to the velocity required for a penetration probability of 0.5. From these velocities, the kinetic energy at a failure probability of 0.5 (KE50) is then calculated. It is important to note the reported KE50s are relevant for only the thickness listed (6 mm), as a thicker or thinner sample will require a higher or lower projectile energy, respectively. All reported KE50s are normalized by the KE50 of DGEBA/PACM. Normalized KE50 values provide trends that are valid over broader thickness ranges than reported here.

Dynamic mechanical analysis (DMA) was performed using a TA instruments Q800 on samples that were nominally 30 mm × 12 mm × 3.3 mm for the rubbery modulus ($T > T_g$), and 30 mm × 12 mm × 1 mm for the glassy modulus ($T < T_g$), all in 17 mm single cantilever mode. A constant displacement was set at 7.5 μ m, and measurements were taken at a rate of 1 Hz. The storage and loss modulus were measured from −140 °C to 200–220 °C at a heating rate of 1 °C per minute, with a low temperature equilibration time of 10 min.

Atomic Force Microscopy (AFM)-modulus imaging was utilized to determine the local elastic modulus (AFM-modulus) of the sample surfaces. Images were obtained using a MultiMode8 AFM with a Nanoscope V controller using PeakForce Quantitative Nanomechanical Mapping mode. Commercial AFM tips including TAP150A, FESPA and TESPA (Bruker), and AC200TS (Asylum Research), were used as received. Modulus map images were obtained using the relative method described elsewhere [18]. The spin-cast polystyrene (PS) reference sample employed for this method (Bruker-Nano) has a reported modulus of 2.7 GPa. AFM-modulus was determined using the PS as a reference and the PF QNM method, using the Derjaguin-Muller-Toporov (DMT) modulus model [19]. AFM-modulus values were obtained without modification to images, using the average pixel modulus values over a 1 micron square region. Other applications, including a discussion of the utility of this technique have been published previously [20–23].

Small-angle X-ray scattering (SAXS) data were collected using a pinhole-collimated camera equipped with a two-dimensional (2D) multiwire area detector (Molecular Metrology). Photons having wavelength of 1.54 Å were generated using an Ultrax18 rotating Cu anode X-ray generator (Rigaku Americas, Inc.) operated at 4.5 kW and equipped with a Ni filter. Two-dimensional data were collected at sample-to-detector distances of 1.5 m and 0.5 m, then azimuthally averaged to yield intensity, I , as a function of scattering vector magnitude, q , where $q = 4\pi\sin(\theta)/\lambda$, 2θ is the scattering angle, and λ is wavelength. Sample-to-detector distance and beam center were calibrated using silver behenate [24]. The averaged data were then corrected for background noise and scaled to absolute intensity using glassy carbon as a secondary standard, previously calibrated at the Advanced Photon Source, Argonne National Laboratory [25]. All data manipulation and analysis were performed using Igor Pro v. 6.22A (Wavemetrics, Inc.) [26].

Broadband dielectric relaxation spectroscopy measurements were performed on a Novocontrol Concept 40 impedance analyzer system. Parallel-plate capacitor samples were prepared by sputter-coating 30 mm diameter gold–palladium electrodes onto the sample surfaces with a Denton Vacuum Desk V sputter unit. At least 40 nm of metal were sputtered onto the sample surfaces to avoid complications of resistive sample contacts. The prepared samples were measured isothermally from −150 °C to well above the T_g of the material in 5° increments. Samples were measured on heating to preserve the thermal history imparted by the curing process. Samples were allowed to equilibrate at temperature for 15 min prior to the start of each frequency sweep to ensure thermal stability. Temperature was controlled by heating evaporated liquid nitrogen and passing it over the sample in a vacuum-insulated

chamber, allowing a temperature precision of greater than 0.05°. At each temperature, 64 frequencies were measured, evenly spaced on a logarithmic scale within the range of 10 MHz–10 mHz. At each frequency point, a reference measurement was performed to improve accuracy. Samples were measured on cooling after the initial heating run to ensure no changes in the dynamics had occurred. The in-phase (ϵ') and out-of-phase (ϵ'') components of the complex dielectric constant ($\epsilon^* = \epsilon' - i\epsilon''$) were calculated at each frequency point from the measured impedance and the sample geometry.

3. Results and discussion

Shown in Fig. 2 is the projectile kinetic energy required for a penetration probability of 0.5 (KE50) as a function of PACM mole fraction (a) and the volume fraction of PACM + D2000 or PACM + D4000 (b). In this and subsequent figures, the kinetic energy of each system has been normalized to pure DGEBA/PACM ($X = 1$) for clarity. With the exception of the $X = 0.1$ sample, every DGEBA/PACM/D2000 blend investigated exhibited an increased KE50 relative to the DGEBA/D2000 ($X = 0$). The KE50 gradually increased with increasing D2000 content until reaching a maximum of nearly 300% greater than neat DGEBA/PACM at a PACM fraction of $X = 0.8$. At a PACM fraction of $X = 0.9$, KE50 has

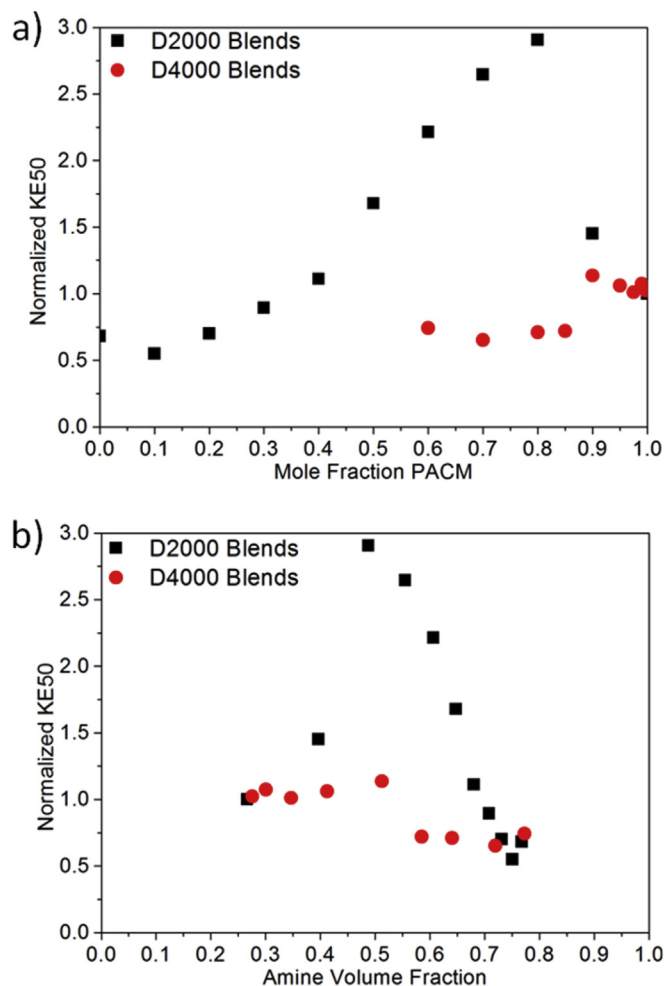


Fig. 2. Normalized kinetic energy at a failure probability of 0.5 (KE50) versus PACM fraction (a) and versus total amine (PACM + D2000 or PACM + D4000) volume fraction (b). The standard deviation of the points is less than the size of the datapoints.

again decreased by more than half the maximum in the DGEBA/PACM/D2000 blends. To obtain a similar decrease in ballistic performance moving to lower PACM compositions, the PACM fraction must be decreased to $X = 0.5$ or less. Fig. 2(b) shows the KE50 as a function of the total volume fraction of amine monomers (both PACM and D2000) in the system. Interestingly, the maximum in KE50 occurs at an amine volume fraction near 0.5, suggesting that an interconnected structure near a phase inversion point might be responsible for the improved ballistic performance.

Examining the ballistic performance of the DGEBA/PACM/D4000 blends in Fig. 2(a–b), a relatively small increase in KE50 is observed at a similar amine volume fraction of ~0.5, but the increase is substantially lower than with the DGEBA/PACM/D2000 blends. As shown in Fig. 3(a–c), the DGEBA/PACM/D2000 blends are optically transparent, whereas every DGEBA/PACM/D4000 blend composition (Fig. 3(d)) is opaque, indicating large scale phase separation. Chemically, the DGEBA/PACM/D2000 systems and the DGEBA/PACM/D4000 systems are nearly identical; the only difference (see Fig. 1) being the length of the propylene oxide segment in D2000 or D4000. This suggests the phase behavior of these materials strongly dictates the overall ballistic performance, and miscibility on some length scale is required for improvements in ballistic performance to be realized. The occurrence of the maximum in KE50 at 50 volume percent amines for both the D2000 and the D4000 systems in Fig. 2(b) adds further support to the importance of phase behavior. At a volume fraction of 50 %, neither component (amines or epoxy) is the majority phase in either the D2000 or the D4000 systems. Although the DGEBA/PACM/D4000 systems form a distinctly two-phase system, as shown in Fig. 3(d), being at or near what is likely the phase inversion point [27,28] still improves the ballistic performance. Although the DGEBA/PACM/D2000 mixtures form single phase mixtures at all compositions and exhibit improved ballistic performance at nearly all compositions, the maximum in KE50 still occurs at an amine volume fraction of approximately 50 %.

The improved ballistic performance observed in the DGEBA/PACM/D2000 systems is not due to the presence of uncured materials. Samples of the cured epoxies were measured in the near IR region, where changes in the epoxy and amine cure are readily observed. Shown in Fig. 4 are the FTIR results for each of the DGEBA/PACM/D2000 systems, along with pure DGEBA, PACM, and D2000. Peaks corresponding to the primary amines of PACM and

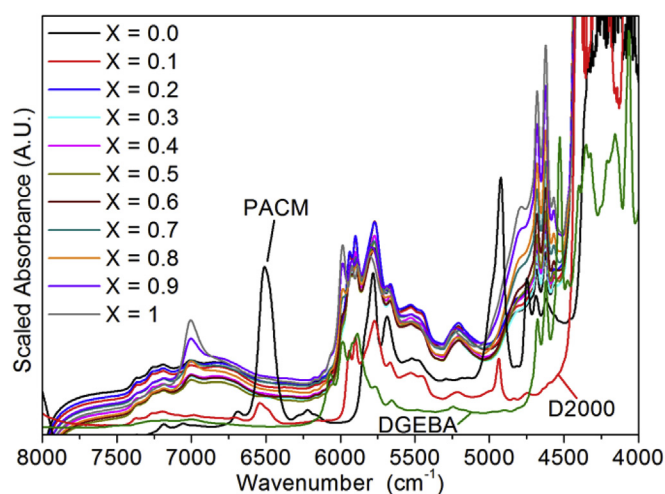


Fig. 4. FTIR spectra of the DGEBA/PACM/D2000 systems, as well as the DGEBA, PACM, and D2000 starting materials.

D2000 occur at approximately 6500 cm^{-1} and 4900 cm^{-1} , respectively. In each of the DGEBA/PACM/D2000 systems, these peaks are absent, indicating the primary amines of PACM and D2000 are not present in the final cured epoxies. A peak centered at approximately 4530 cm^{-1} in neat DGEBA is due to the epoxide ring, and is similarly absent in all of the cured epoxies. This result suggests that the observed structure, dynamics and ballistic performance of these materials is not due to incomplete resin cure. As a further check of the extent of cure, Differential Scanning Calorimetry (DSC) was employed, and no evidence of additional cure was detected up to $200\text{ }^{\circ}\text{C}$. See Fig. S1 in the Supplemental Information for a representative DSC curve.

To further investigate the impact of phase behavior and dynamics on the ballistic performance, DMA measurements were performed on the DGEBA/PACM/D2000 systems. Shown in Fig. 5 are the DMA results for each system. With the exception of the neat materials (DGEBA/PACM and DGEBA/D2000), each system exhibits a broadened transition region in the storage modulus, indicating the presence of two glass transitions. Similarly, the loss modulus (Fig. 5(b)) and $\tan \delta$ (Fig. 5(c)) exhibit two peaks in the transition region of each PACM/D2000 mixture, indicating two glass transitions. This suggests the DGEBA/PACM/D2000 mixtures are heterogeneous at some length scale, although the transparency of the DGEBA/PACM/D2000 systems suggests miscibility at least on the length scale of visible light. Interestingly, the lower temperature glass transition occurs at approximately the same temperature for each composition, while the higher temperature glass transition changes systematically with composition. For neat D2000, the glass transition is centered at approximately $-20\text{ }^{\circ}\text{C}$, and for neat DGEBA/PACM, the glass transition is centered at approximately $180\text{ }^{\circ}\text{C}$. In addition to the dual T_g s, a broadened peak, centered at approximately $-40\text{ }^{\circ}\text{C}$ in the $\tan \delta$ results for the $X = 1$ sample is from a glassy state, or β relaxation from the PACM component, since it is not present in pure DGEBA/D2000. A small peak in the loss modulus is centered at approximately $60\text{ }^{\circ}\text{C}$ in the high PACM compositions. The molecular origins of this peak are unknown, but it is likely from the PACM component, as only the high PACM content systems exhibit this peak. Two glassy state relaxations are present, a β relaxation from PACM centered at approximately $-40\text{ }^{\circ}\text{C}$, and a β relaxation from the D2000 component, centered at approximately $-140\text{ }^{\circ}\text{C}$. Additional details of these relaxations will be presented in the dielectric spectroscopy section below.

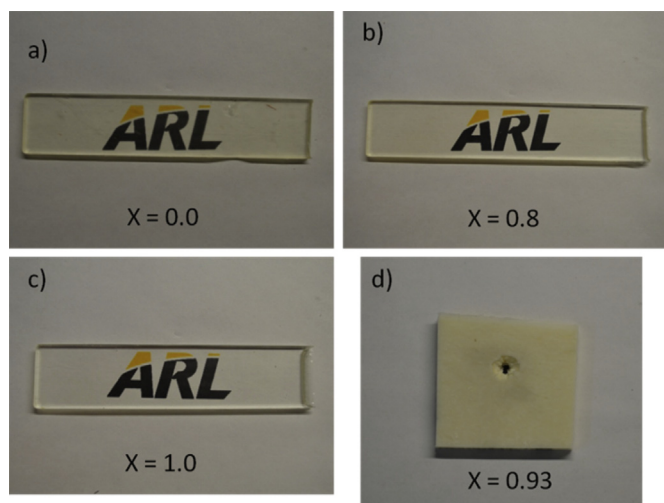


Fig. 3. Optical images of select DGEBA/PACM/D2000 compositions (a–c) and the $X = 0.93$ DGEBA/PACM/D4000 blend (d).

Examining the glassy and rubbery state modulus of each epoxy system in Fig. 5(a), it is clear that, within the experimental error of the measurement, the modulus in both the glassy state and the rubbery plateau increases approximately linearly with PACM mole fraction. From the rubbery plateau modulus, an approximation of the molecular weight between crosslinks can be determined, as shown previously [29]. Since the calculated molecular weight between crosslinks decreases linearly with increasing PACM mole fraction, there is no clear correlation between the molecular weight between crosslinks with the ballistic performance.

Shown in Fig. 6 are the KE50 values of the DGEBA/PACM/D2000 systems versus the storage and loss modulus from DMA

measurements at the ballistic test temperature, i.e., 22 °C. With the exception of the X = 0.9 blend and pure DGEBA/PACM (X = 1), the KE50 values increase with increases in both the storage and the loss modulus. The lower KE50 values of X > 0.9 formulations highlight the tradeoff between high modulus and ballistic performance. For example, pure DGEBA/PACM (X = 1) exhibits a room temperature storage modulus of approximately 2.5 GPa. In contrast, the X = 0.8 composition exhibits a room temperature storage modulus of approximately 1.2 GPa. If the target application can tolerate a slightly reduced room temperature storage modulus and a stronger temperature dependence of the modulus, the X = 0.8 composition has the benefit of a nearly 300% improvement in ballistic performance.

Several studies have examined the link between mechanical performance and glassy state relaxations [30–32]. It has been proposed that relaxations in the glassy state involving individual repeat units or portions of these repeat units improves mechanical performance, since the relaxation rate of β relaxations is typically far faster than the mechanical rate at room temperature [30,31]. Examining the glassy state relaxation behavior of these materials in Fig. 5, the β relaxation of PACM, centered at approximately –40 °C, is most intense in the X = 1.0 and X = 0.9 blends. However, as shown in Fig. 2, the X = 0.9 and X = 1.0 compositions exhibit among the poorest ballistic performance. This suggests the glassy state relaxations in these materials play a secondary role in the ballistic response.

The DMA results of Fig. 5 suggest the materials are at least dynamically heterogeneous, and may be structurally heterogeneous on some length scale. Each blend exhibits a broadened transition region, consisting of what appears to be two distinct glass transitions. Optically, these blends are transparent, as shown in Fig. 3. This suggests that if the epoxies are phase separated, the domain sizes must be smaller than the wavelength of visible light, or the two phases have matched refractive indices. A refractive index match is unlikely, since the X = 0 and X = 1 samples, as will be shown below, exhibit different dielectric constants.

Atomic force microscopy (AFM) was employed to map the phase behavior of the fracture surfaces of the DGEBA/PACM/D2000 systems, and is summarized in the Supplemental Information in Figs. S2 and S3. No heterogeneity was detected in these materials, but this is likely due to the 15 nm resolution limit of the technique. Since any phase separation in these systems is smaller than the wavelength of visible light and the resolution of the AFM, SAXS was employed to further investigate possible structure in these systems. Shown in Fig. 7 are the SAXS results for each system. All DGEBA/PACM/D2000 mixtures exhibit a weak scattering peak centered at approximately 0.02 Å⁻¹ to 0.2 Å⁻¹. This appears to be indicative of nanophase separation of small domains comprised of the poly(propylene oxide) backbone of D2000, and would therefore be well described by the Guinier approximation for form factor scattering from isolated particles or domains [33]. The Guinier approximation is given as $I(q) = \rho_0^2 \nu^2 \exp(-q^2 R_g^2/3)$, where ρ_0 is the average scattering length density of the material, ν is the volume of the particle, and R_g is the radius of gyration of the particle or domain. This approximation fits the characteristic “Guinier knee” observed in the SAXS data well.

By combining the Guinier approximation with a power law scattering function to characterize the scattering from the interface between the microphase separated domain or particle, the Unified approach of Beaucage provides a simple analysis of domain size for dilute, non-periodic additives or domains in the small-angle regime [34,35]. The Unified model of Beaucage is given in Equation (1), where G is the Guinier exponential prefactor, $G = n^2 N_p I_e$, n is the number of electrons per particle, N_p is the average number of

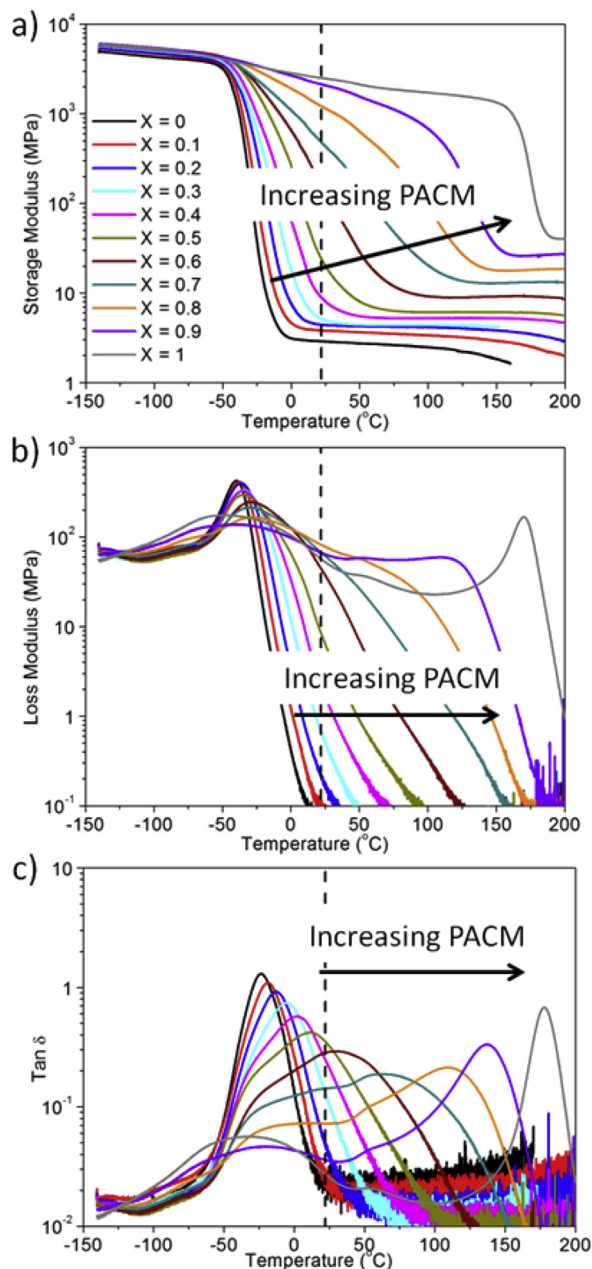


Fig. 5. Dynamic mechanical analysis at 1 Hz of the systems investigated. The storage modulus (a) loss modulus (b) and $\tan \delta$ (c) are shown. The vertical line represents the approximate ballistic measurement temperature. The compositions are listed in the legend of (a). The D2000 β is located at approximately –140 °C, the PACM β is located at approximately –50 °C, the D2000 α is located at approximately –20 °C, and the PACM α is located at approximately 180 °C.

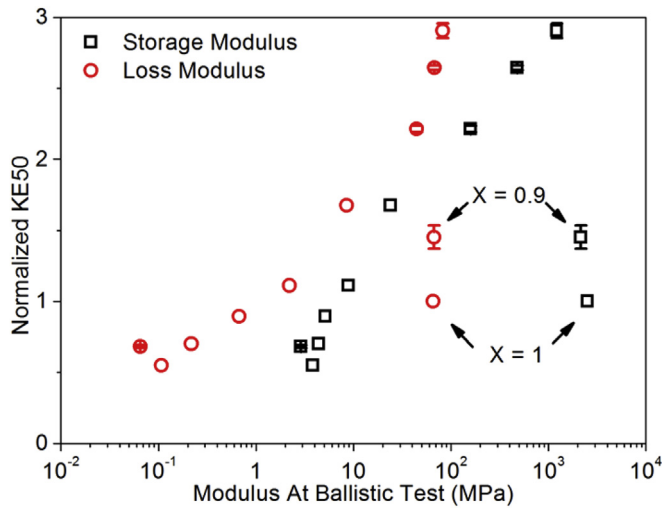


Fig. 6. KE50 versus the storage modulus and loss modulus at the ballistic testing temperature for the DGEBA/PACM/D2000 systems.

particles per unit scattering volume, and I_e is the scattering factor for a single electron.

$$I(q) = G \exp\left(-\frac{qR_g^2}{3}\right) + B \left\{ \frac{\left[\text{erf}\left(\frac{qR_g}{\sqrt{6}}\right) \right]^3}{q} \right\}^p \quad (1)$$

Fits of a Guinier model to this peak suggest a characteristic length scale (R_g) ranging from 17 to 45 Å, as shown in Fig. 7(b). These values are consistent with domain sizes previously observed for other D2000-containing systems [36,37]. An example fit is shown in Fig. S4 of the Supplemental Information. This analysis does not provide information on the specific shape of the micro-phase separated domains. Because no actual peaks are observed in the scattering data, it is clear that interdomain scattering is minimal, indicating that the domains are dilute within the epoxy matrix. Previous studies of poly(propylene oxide), a D2000 analog [38], showed the radius of gyration was 33 Å for a molecular weight of 2000 g/mol. As such, the phase segregation here is on the order of the molecular size of D2000 and therefore may not strictly be considered phase separation, but rather the existence of spacing comparable to the regions required for D2000 to exist by itself.

Of interest is the correlation between the calculated SAXS parameters and the KE50, particularly the R_g and the scattering invariant, which is discussed below. As shown in Fig. 8, the $X = 0.8$ sample exhibits the largest domain sizes (R_g s), and the largest KE50, with KE50 generally increasing with increasing R_g . The correlation is not perfect, however, since the $X = 0.9$ sample has the second largest R_g , but exhibits a much lower KE50 than the $X = 0.7$ and $X = 0.6$ samples. Thus, the phase separation domain size of the D2000 is not the only factor governing the ballistic performance of these materials.

The scattering invariant relates to the total scattering power of the sample, and can be related to the total amount of scattering surface within a material. Porod described the scattering invariant (Q) as [39]

$$Q = \int I(q) q^2 dq \quad (2)$$

In the case of the systems investigated here, it is likely related to the extent of nanophase separation within the materials, with

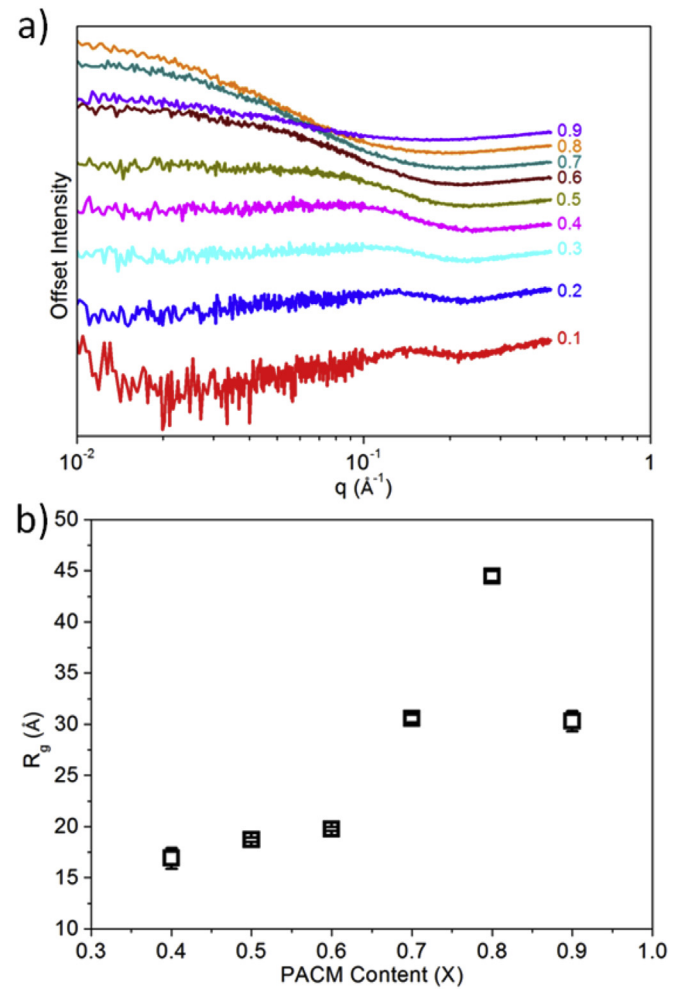


Fig. 7. SAXS scattering intensity as a function of q for the DGEBA/PACM/D2000 mixtures (a) and the characteristic size scale determined from a Guinier fit to the data (b). SAXS curves in (a) are offset for clarity.

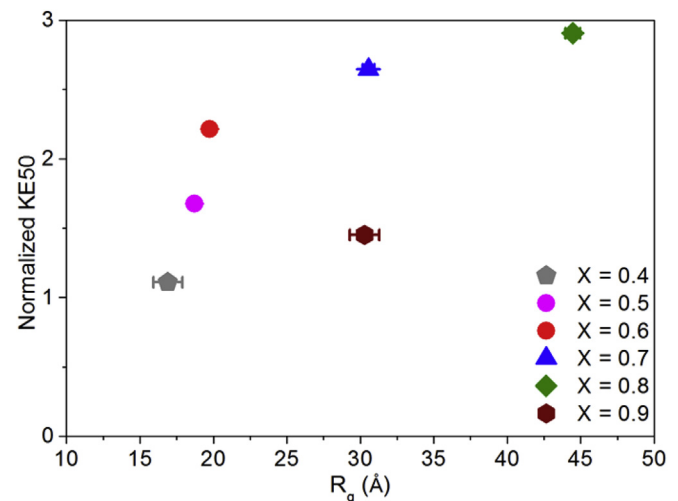


Fig. 8. KE50 versus R_g , calculated from the SAXS fitting procedure for the DGEBA/PACM/D2000 systems.

scattering arising from the phase separated D2000 regions. Due to the lack of a low- q upturn in the SAXS data (Fig. 7(a)), the invariant analysis could be performed with reasonable accuracy within the given q range by a simple integration of the $I(q) \cdot q^2$ vs q data. A rigorous analysis of the scattering invariant requires the broadest q range possible, so the calculated invariant shown here serves as a comparison only over the studied q range. To test the reproducibility of this analysis, the $X = 0.5$ sample was re-formulated, cast, then measured. The differences between the two $X = 0.5$ samples (not shown) were within the error of the measurement, so the comparisons shown here should be valid over the examined q range.

Shown in Fig. 9(a) is the scattering invariant, calculated from the integral of the non-scaled SAXS curves taken from Fig. 7. Unlike the relaxation behavior (storage and loss modulus) and the characteristic length scale R_g , the ballistic performance of the DGEBA/PACM/D2000 blends correlates well with the scattering invariant, exhibiting a reasonably linear relationship over the compositional range of the mixtures. Fig. 9(b) shows the scattering invariant versus the D2000 volume fraction. The peak in the invariant occurs near a D2000 volume fraction of 0.5, suggesting that the scattering occurring in these materials is from the nanophase separated D2000 interface with the DGEBA/PACM matrix. Interestingly, the peak in the scattering invariant is slightly shifted from a D2000 volume fraction of 0.5, which could be due to intermixing of the soft and hard domains. For example, Runt et al. observed intermixing

hard-soft segment networks composed of polydimethylsiloxane/poly(hexamethylene oxide diol)-based polyurethanes, which consist of soft segment regions with some hard segments, and hard segment regions with some soft segments [40,41]. The chain relaxation behavior shown below for the DGEBA/PACM/D2000 supports this physical picture. The data in Figs. 8 and 9 indicate that the ballistic performance of these materials is not only dependent on the size of the nanophase separated regions, but also the volume fraction of the system that is nanophase separated. It is important to note that the maximum in ballistic performance occurs at a total amine (PACM + D2000) volume fraction of approximately 0.5, and the scattering invariant appears to be related to the D2000 component. When the total amine (PACM + D2000) volume fraction is 0.5, the D2000 volume fraction is approximately 0.35.

While more investigation is warranted, the larger volume fraction of D2000 required to obtain optimal ballistic performance suggests that soft domain connectivity is important for high rate energy dissipation in these systems. We therefore hypothesize that the presence of the rubbery D2000 component facilitates shear yielding, as is observed in cocontinuous blends [42,43]. The interconnectivity of soft/hard domains may be critical for both the yielding behavior and the mechanical rigidity. Further research is necessary to determine the exact origins of the improvement in ballistic performance, whether void formation and growth [44,45] is the dominant mechanism, or simple shear yielding.

To further probe the dynamic heterogeneity and relaxation behavior of these systems, and how it relates to the ballistic performance, dielectric relaxation spectroscopy was performed. Due to its relatively broad accessible frequency range (MHz to mHz), it is able to probe relaxation dynamics at frequencies well above those of a ballistic impact ($\sim 10^4 \text{ s}^{-1}$), as well as quasi-static rates. It is important to note, however, that this and techniques such as DMA probe the linear elastic response of these materials, whereas a ballistic impact is certainly strongly nonlinear. Shown in Fig. 10 is the conductivity-free dielectric loss (ϵ''_D) for selected DGEBA/PACM/D2000 systems. ϵ''_D is calculated using an approximation of a Kramers-Kronig transform, as shown previously [46]. It has the advantage of removing the contribution of impurity ion motion from the dielectric loss while preserving the features related to dipole reorientation. As shown in Fig. 10, four individual relaxations are observed. Centered around -140°C at 1 Hz, a glassy state (sub T_g) relaxation is present, denoted γ , in the $X = 0$ sample as well as

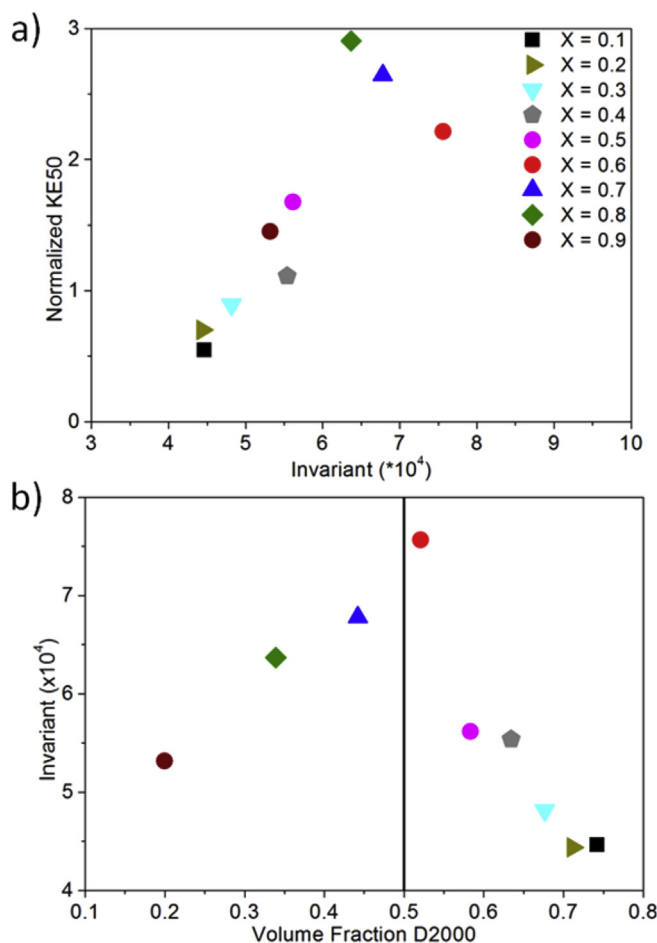


Fig. 9. KE50 versus scattering invariant for each DGEBA/PACM/D2000 blend (a) and the invariant (b) versus the D2000 volume fraction. The vertical line in (b) is 50 volume % D2000.

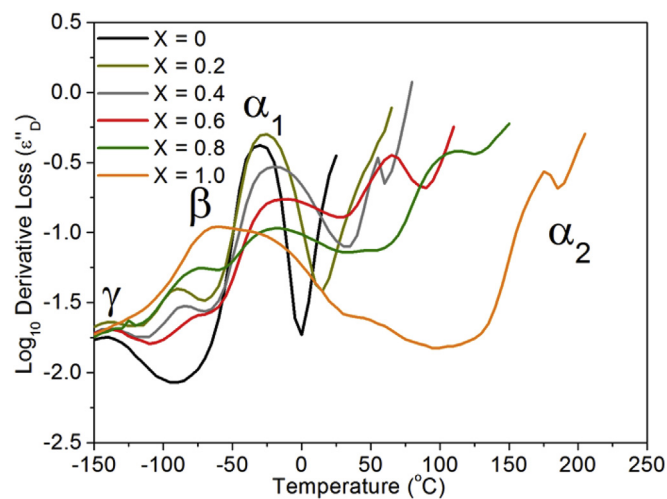


Fig. 10. Conductivity-free dielectric loss (ϵ''_D) at 1 Hz as a function of temperature for selected systems. The approximate locations of the observed relaxations are indicated on the plot.

each diamine mixture, but not in $X = 1$, indicating that the γ relaxation is associated with the D2000 component. Conversely, the β relaxation, centered around -75°C , is present in $X = 1$ as well as each diamine mixture, but not $X = 0$, indicating that this β relaxation is associated with PACM. At higher temperatures, the α_1 relaxation and/or the α_2 relaxation are present in each blend system. At the highest temperatures, the increase in ϵ''_{D} is due to the accumulation of impurity ions at the blocking Au/Pd electrodes, a ubiquitous feature of both the raw dielectric loss and the derivative dielectric loss at temperatures well above T_g [47].

To determine the characteristic relaxation times of the relaxations present in these systems, the isothermal dielectric loss was modeled with a Havriliak-Negami function [48].

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau)^m)^n} + \frac{\sigma_0}{\omega} \quad (3)$$

$\Delta\epsilon$ is the relaxation strength, or the difference between the static dielectric constant and the infinite frequency dielectric constant (ϵ_∞). It is related to the number density of dipoles participating in the relaxation, as well as their dipole moment and how they are correlated [47]. The shape of the relaxation is described by m and n , which are the breadth and high frequency asymmetry, respectively. For glassy state relaxations (β and γ), the high frequency asymmetry shape parameter is fixed at 1, making equation (3) a Cole–Cole function [46,47]. ω and τ refer to the angular frequency and relaxation time, respectively. The third term accounts for dc conductivity at temperatures above T_g with σ_0 representing the dc conductivity. In cases where the conductivity-free loss (ϵ''_{D}) is used, an appropriate fitting function was used [46]. From these fitting parameters, the characteristic relaxation frequencies (f_{Max}) are calculated. In equation (4), the parameters are the same as in equation (3).

$$f_{\text{Max}} = \frac{1}{2\pi f} \left[\frac{\sin \frac{\pi m}{2+2n}}{\sin \frac{\pi mn}{2+2n}} \right]^{\frac{1}{m}} \quad (4)$$

In addition to fitting isothermal dielectric spectra, the relaxation times of the α_1 and α_2 relaxations can be estimated from isochronal dielectric spectra, similar to the data shown in Fig. 10.

Shown in Fig. 11 are the characteristic relaxation frequencies for the γ and β relaxations. As is typical of local, glassy state relaxations, the β and γ relaxations exhibit only subtle changes in their temperature dependence with composition. Changes in local relaxation behavior typically require the presence of strong specific interactions. Weak hydrogen bonding between ether oxygen atoms of D2000 and residual hydroxyl groups from the reacted epoxy ring on DGEBA is expected, but it is unlikely strong enough to alter relaxation behavior [49,50].

The frequency-maxima of the γ and β relaxations were modeled with an Arrhenius function (see equation (5)). In equation (5), E_a is the activation energy, f_0 is the frequency prefactor, R is the universal gas constant, and T is temperature. Examining Figs. 10 and 11, it is clear the γ relaxation is related to motions of the propylene glycol segments in the D2000, since it is not present in the $X = 1$ sample, but is present in the remaining samples. The γ relaxation has an activation energy of 31 ± 5 kJ/mol, which is in agreement with previous work investigating the temperature dependence of the propylene glycol glassy state relaxation [51]. The β relaxation, present only in systems containing PACM, has an average activation energy of 61 ± 5 kJ/mol. This relaxation is likely due to ring motion of the PACM portion, and its activation energy is similar to local relaxations of hexane-ring containing systems [52,53].

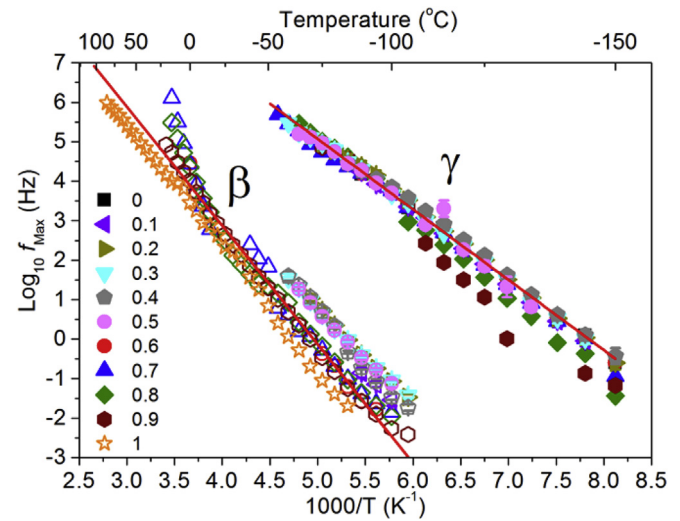


Fig. 11. Arrhenius plot of the β and γ relaxations. Filled symbols indicate the γ relaxation. Open symbols indicate the β relaxation. Solid lines are Arrhenius fits to the PACM β relaxation and the D2000 γ relaxation. The standard deviation of each point is 5 %.

$$f_{\text{Max}} = f_0 \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

The presence of sub T_g relaxations has been attributed to improved mechanical performance, since these relaxations dissipate energy, and their relaxation times are often much shorter than a ballistic impact at room temperature [30–32]. A classic example would be polycarbonate, whose strong β relaxation has been attributed to polycarbonate's superior ballistic performance [30,54]. Fig. 12 shows the KE50 values versus the average relaxation strength for the β and the γ relaxations. The $X = 0.9$ and $X = 1.0$ compositions exhibit the greatest total relaxation intensity, similar to what is observed in the DMA, and the remainder of the compositions exhibit approximately the same relaxation intensity. No correlation exists between the γ and β relaxation intensities in these epoxy blends and the resulting ballistic performance, demonstrating that local relaxations do not control the ballistic response in these materials. These relaxation strengths are

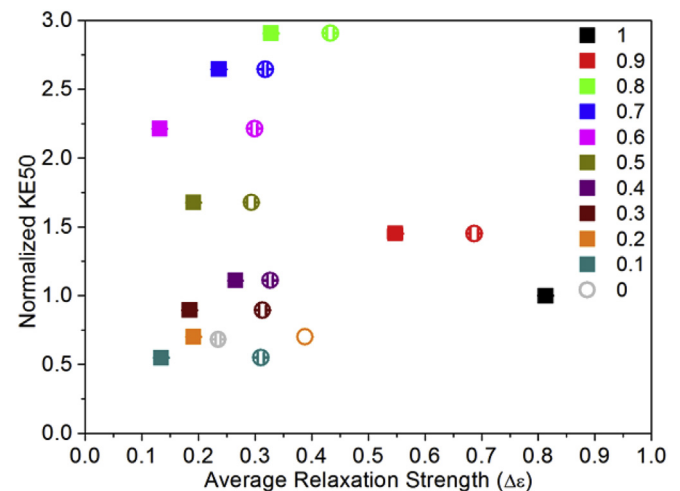


Fig. 12. KE50 versus average relaxation strength for the beta relaxation (filled squares) and the gamma relaxation (open circles). The legend refers to the PACM content (X) in the DGEBA/PACM/D2000 systems.

determined from dipole rotations, not the mechanical response. They do, however, represent the relative amounts of each chemical unit undergoing motion. If the sub T_g relaxations in these systems were controlling the ballistic performance, the compositional dependence of the ballistic performance would be captured in Fig. 12.

A segmental (α) relaxation is the chain motion associated with the glass transition [47]. Unlike the glassy state relaxations, the segmental relaxation(s) of each system are dependent on the blend composition. Shown in Fig. 13 are the relaxation frequencies for the two segmental relaxations (α_1 and α_2). The $X = 1$ and $X = 0$ samples exhibit a single segmental relaxation, following a characteristic Vogel-Fulcher-Tammann (VFT) shape. Each DGEBA/PACM/D2000 blend exhibits two segmental (α) relaxations, consistent with the DMA in Fig. 5 and supported by the SAXS data showing segmental-level heterogeneity. The higher temperature α_2 relaxation is more sensitive to composition compared to the α_1 relaxation, and moves to systematically lower temperatures with increasing D2000 content. The α_1 relaxation exhibits a relatively small change with composition. This is in agreement with the DMA results and the scattering results, suggesting the blends consist of dynamically heterogeneous D2000 regions whose T_g changes only slightly with composition, and a DGEBA-rich phase whose T_g is strongly influenced by the presence of the D2000 links.

The α_1 and α_2 relaxations of each system were modeled with a Vogel-Fulcher-Tammann (VFT) function, which is equivalent to the Williams-Landell-Ferry (WLF) function. In equation (6), B is a material specific parameter related to the dynamic fragility [55,56], f_0 is the frequency prefactor and T_0 is the Vogel temperature. T_0 is typically described as the temperature at which the segmental relaxation time diverges [47], although recent work questions this assumption [57–59]. The Vogel temperature is typically about 20° below T_g . Since it represents the temperature at which segmental relaxations are essentially “frozen” on a relevant experimental time-scale, the Vogel temperature is potentially critical for ballistic performance if segmental relaxations are playing a key role in the deformation response. From the VFT equation (Equation (6)), the T_g of the material can be calculated, taking T_g as the temperature at which f_{Max} is 0.0016 Hz, or where the relaxation time is 100 s. This method has been shown to accurately represent the calorimetrically-determined T_g in a broad range of polymeric materials [46,47].

$$f_{Max} = f_0 \exp\left(-\frac{B}{T - T_0}\right) \quad (6)$$

The VFT-determined T_g s for the α_2 and α_1 relaxations for the DGEBA/PACM/D2000 systems are shown in Fig. 14 as a function of the volume fraction of D2000. For both the α_2 and α_1 relaxations, the calculated T_g s do not appear to correlate with the ballistic performance. The highest α_2 T_g occurs at a composition of $X = 0.7$, or a D2000 volume fraction of 0.44. Due to the error of the determination, however, it is possible the maximum in the T_g of the D2000 component occurs at a different volume fraction. The change in T_g with composition does suggest that the D2000 component is not phase separated in the traditional sense. A completely phase separated system would exhibit two distinctly different T_g s, each being essentially independent of composition. The compositional dependence of the segmental relaxations shown in Fig. 13 clearly shows this is not the case, with the α_2 relaxation exhibiting a particularly strong dependence on composition. As shown in Fig. 14(b), at intermediate D2000 compositions, the T_g of the D2000 component (α_1) is increased above neat DGEBA/D2000 by approximately 15°. This suggests some level of mixing with the DGEBA/PACM component. At low D2000 compositions, the T_g of the D2000 component is nearly the same as the pure DGEBA/D2000 sample. This suggests that at high D2000 content, the D2000 segments are less intimately mixed than the intermediate

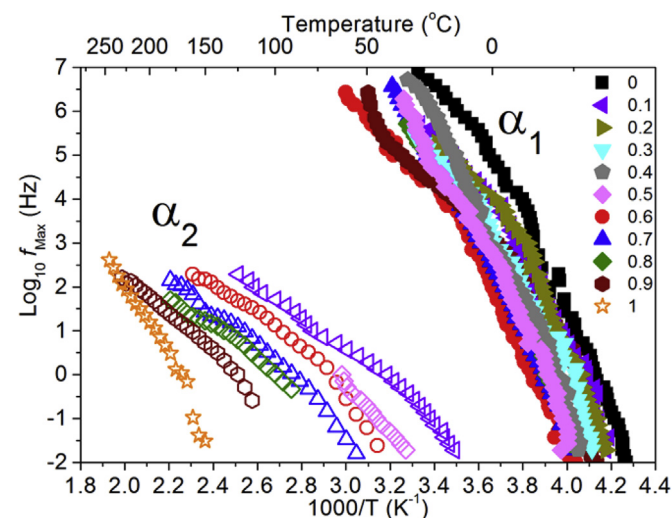


Fig. 13. Arrhenius plot of the α_1 (filled symbols) and α_2 (open symbols) relaxations for each system investigated. The standard deviation of each point is 10 %.

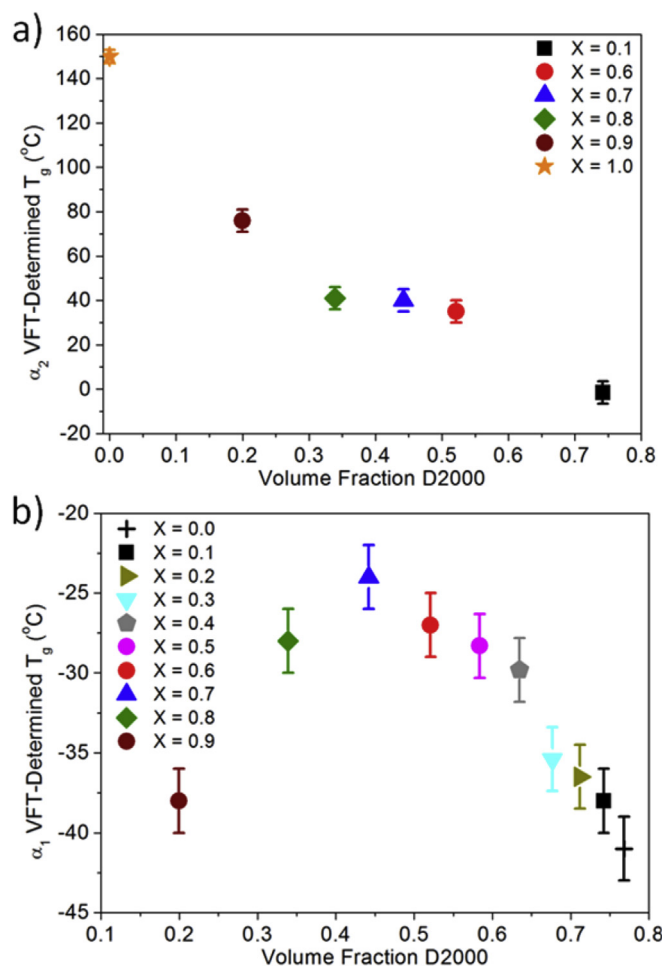


Fig. 14. VFT-determined glass transition temperature versus the volume fraction of D2000 in the DGEBA/PACM/D2000 systems for the α_2 relaxation (a) and the α_1 relaxation (b).

compositions. The sudden decrease in the D2000 T_g at higher PACM contents, if caused by a greater degree of phase separation, suggests that more strongly phase-segregated systems are not desirable, since a decrease in the ballistic performance also occurs at this composition.

Considering the dynamic heterogeneity of these systems, or the difference in timescales between two segmental relaxations, the $X = 0.1$ composition is the least dynamically heterogeneous. The difference in dynamic T_g of the two α relaxations is approximately 37° . The better ballistic-performing systems $X = 0.6, 0.7$, and 0.8 all exhibit differences in T_g of 60 – 70° . The $X = 0.9$ system exhibits the greatest degree of dynamic heterogeneity, having a difference in T_g of the two α relaxations of approximately 114° . It is unclear how important dynamic heterogeneity is to the ballistic performance, but the best performing systems exhibit neither the highest nor the lowest heterogeneity.

The degree of phase mixing can be examined by comparing the D2000 VFT-determined T_g (α_1) and the scattering invariant, shown in Fig. 15. As the scattering invariant increases, the T_g of the D2000 phase increases. This suggests that, as the interfacial area increases, creating more D2000 interface with DGEBA/PACM, the segmental motion of the D2000 phase becomes more restricted, increasing the T_g . $X = 0.6$ and $X = 0.7$ both appear to exhibit a more finely dispersed D2000 phase than the best ballistic performer ($X = 0.8$).

Shown in Fig. 16 are the scaled KE50 results as a function of temperature which has been normalized by the Vogel temperature (T_0 from Equation (6)) of the α_2 relaxation from Fig. 13. The α_2 relaxation was used because the Vogel temperature of the α_1 relaxation exhibits relatively little change with composition and the α_2 relaxation is strongly dependent on composition. The ballistic performance increases to some critical value ($T/T_0 > 1.45$), beyond which the ballistic performance drops. The DGEBA/D2000 sample is at nearly twice its Vogel temperature during the ballistic experiment, and the DGEBA/PACM sample is below its Vogel temperature.

Being above or below the Vogel temperature is not likely the most important factor when selecting a system. The apparent dependence of KE50 on T_g [4] and T_0 (Fig. 16) is most likely a coincidence, with these systems exhibiting some degree of phase and dynamic separation, which appears to strongly influence the ballistic behavior. The glass transition temperature is often 1.3 – 1.5 times the Vogel temperature, so the trend in Fig. 16 is expected,

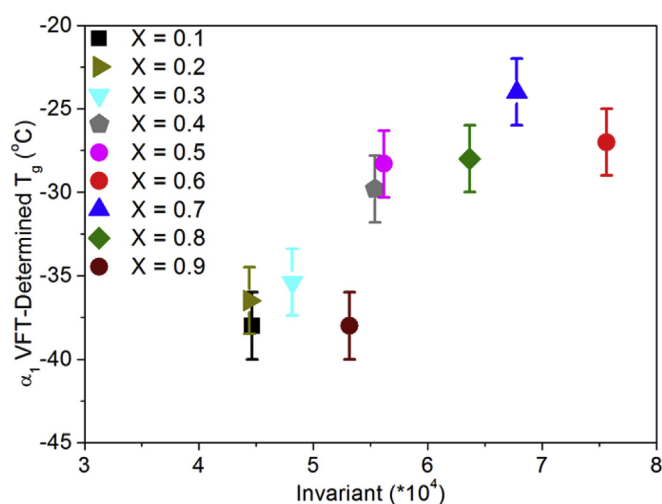


Fig. 15. VFT-determined T_g for the D2000 component (α_1) as a function of the scattering invariant for the DGEBA/PACM/D2000 systems. The legend lists the PACM content (X).

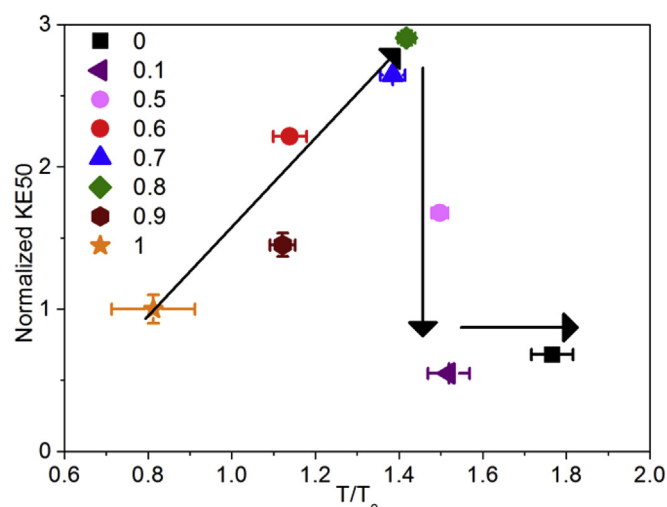


Fig. 16. Normalized kinetic energy at a failure probability of 0.5 versus temperature which has been scaled by the Vogel temperature (T_0) of the α_2 relaxation. Arrows serve to guide the eye.

considering previous results [4]. Knowledge of T_g and T_0 should be useful when selecting a system for a specific operational temperature range, as well as selecting epoxy compositions for a particular application. The long chain D2000 provides the ability to nanophase separate without macro-phase separating, which seems to aid in dissipating impact energy. In the $X = 1$ sample, no detectable nanophase separation exists, so small deformations require covalent bond breakage, leading to brittle failure. The DGEBA/PACM/D2000 blends provide the high modulus of PACM and the ability to form nanoscale heterogeneity. Improving ballistic performance for a specific application will require an understanding of the nanostructure, the desired dynamic modulus, the glass transition behavior, and least importantly, the relaxation behavior in the glassy state. Future publications will examine these effects in a broader range of epoxy chemistry.

4. Conclusions

The ballistic performance of a series of optically transparent, yet nanophase separated diamine mixtures with an epoxy hardener were investigated. The ballistic performance in the nanophase separated systems appears to be correlated to the total interfacial area, as determined by X-ray scattering. The ballistic performance was also found to be correlated to the characteristic length scale of the nanoscale morphology, R_g . The dynamic heterogeneity exhibited by the nanophase separated systems was examined by DMA and dielectric relaxation spectroscopy. Each blend exhibited dual glass transitions, or segmental relaxations, due to nanometer-sized phase separated domains, and the temperature dependence of these relaxations was strongly influenced by the composition. It was found that the magnitude or number of glassy state relaxations in these systems exhibits no correlation with the ballistic performance. The Vogel temperature of the higher temperature segmental relaxation was found to be a factor in the ballistic performance, but the overriding feature in the ballistic performance of these materials seems to be the nanoscale morphology.

Acknowledgment

MDH and ADR acknowledge the ORISE Postdoctoral Research Program and the Army Research Laboratory for funding. The

authors thank Ian McAninch for providing infrared data on the neat epoxy materials.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2014.12.027>.

References

- [1] Morye SS, Hine PJ, Duckett RA, Carr DJ, Ward IM. *Compos Sci Technol* 2000;60(14):2619–756.
- [2] Deka LJ, Bartus SD, Vaidya UK. *J Mater Sci* 2008;43(13):4399–410.
- [3] McGrath LM, Parnas RS, King SH, Schroeder JL, Fischer DA, Lenhart JL. *Polymer* 2008;49(4):999–1014.
- [4] Knorr Jr DB, Yu JH, Richardson AD, Hindenlang MD, McAninch IM, La Scala JJ, et al. *Polymer* 2012;53(25):5917–23.
- [5] Faur-Csukat G. *Macromol Symp* 2006;239(1):217–26.
- [6] Blanco M, López M, De Arcaya PA, Ramos JA, Kortaberria G, Riccardi CC, et al. *J Appl Polym Sci* 2009;114(3):1753–60.
- [7] Puig J, Zucchi IA, Hoppe CE, Pérez CJ, Galante MJ, Williams RJJ, et al. *Macromolecules* 2009;42(23):9344–50.
- [8] Zucchi IA, Hoppe CE, Galante MJ, Williams RJJ, López-Quintela MA, Matějka L, et al. *Macromolecules* 2008;41(13):4895–903.
- [9] Franco M, Mondragon I, Bucknall CB. *J Appl Polym Sci* 1999;72(3):427–34.
- [10] Aizpurua B, Franco M, Corcuera MA, Riccardi CC, Mondragon I. *J Appl Polym Sci* 2000;76(8):1269–79.
- [11] Franco M, Corcuera MA, Gavalda J, Valea A, Mondragon I. *J Polym Sci Part B Polym Phys* 1997;35(2):233–40.
- [12] Zubeldia A, Larrañaga M, Remiro P, Mondragon I. *J Polym Sci Part B Polym Phys* 2004;42(21):3920–33.
- [13] Ma J, Mo M-S, Du X-S, Dai S-R, Luck I. *J Appl Polym Sci* 2008;110(1):304–12.
- [14] Roland CM. *Rubber Chem Technol* 2006;79(3):429–59.
- [15] Roland CM, Fragiadakis D, Gamache RM. *Compos. Struct* 2010;92(5):1059–64.
- [16] Roland CM, Fragiadakis D, Gamache RM, Casalini R. *Philos Mag* 2012;93(5):468–77.
- [17] Bogoslovov RB, Roland CM, Gamache RM. *Appl Phys Lett* 2007;90(22).
- [18] Bruker. In: Bruker, editor. *Peakforce QNM user guide*; 2011. p. 84.
- [19] Derjaguin BV, Muller VM, Toporov YP. *J Colloid Interface Sci* 1975;53(2):314–26.
- [20] Schön P, Dutta S, Shirazi M, Noordermeer J, Julius Vancso G. *J Mater Sci* 2011;46(10):3507–16.
- [21] Dokukin ME, Sokolov I. *Langmuir* 2012;28(46):16060–71.
- [22] Strawhecker KE, Hsieh AJ, Chantawansri TL, Kalciglu ZI, Van Vliet KJ. *Polymer* 2013;54(2):901–8.
- [23] Strawhecker KE, Cole DP. *J Appl Polym Sci* 2014;131(19) [n/a–n/a].
- [24] Huang TC, Toraya H, Blanton TN, Wu Y. *J Appl Crystallogr* 1993;26(2):180–4.
- [25] Dreiss CA, Jack KS, Parker AP. *J Appl Crystallogr* 2006;39(1):32–8.
- [26] Ilavsky J, Jemian PR. *J Appl Crystallogr* 2009;42(2):347–53.
- [27] Jeon HS, Nakatani AI, Hobbie EK, Han CC. *Langmuir* 2001;17(10):3087–95.
- [28] Kitayama N, Keskkula H, Paul DR. *Polymer* 2000;41(22):8041–52.
- [29] van der Sanden MCM, Meijer HEH. *Polymer* 1993;34(24):5063–72.
- [30] Shuster M, Narkis M, Siegmund A. *Polym Eng Sci* 1994;34(21):1613–8.
- [31] Boyer RF. *Polym Eng Sci* 1968;8(3):161–85.
- [32] Mulliken AD, Boyce MC. *Int J Solids Struct* 2006;43(5):1331–56.
- [33] Roe RJ. *Methods of X-ray and neutron scattering in polymer science*. New York: Oxford University Press; 2000.
- [34] Beaucage G. *J Appl Crystallogr* 1995;28(6):717–28.
- [35] Beaucage G, Kammler HK, Pratsinis SE. *J Appl Crystallogr* 2004;37(4):523–35.
- [36] Beck Tan NC, Bauer BJ, Plestil J, Barnes JD, Liu D, Matějka L, et al. *Polymer* 1999;40(16):4603–14.
- [37] Wu W, Bauer BJ. *Macromolecules* 1986;19(6):1613–8.
- [38] Schonhals A, Rittig F, Karger J. *J Chem Phys* 2010;133(9).
- [39] Porod G. *Kolloid-Zeitschrift And Zeitschrift Fur Polymere* 1951;124(2):83–114.
- [40] Hernandez R, Weksler J, Padsalgikar A, Runt J. *Macromolecules* 2007;40(15):5441–9.
- [41] Hernandez R, Weksler J, Padsalgikar A, Choi T, Angelo E, Lin JS, et al. *Macromolecules* 2008;41(24):9767–76.
- [42] Mamat A, VuKhanh T, Cigana P, Favis BD. *J Polym Sci Pt B Polym Phys* 1997;35(16):2583–92.
- [43] Li K, Huang HX. *Polym Eng Sci* 2012;52(10):2157–66.
- [44] Mukherji D, Abrams CF. *Phys Rev E* 2008;78(5).
- [45] Zhang H, Scholz AK, Vion-Loisel F, Merckel Y, Brieu M, Brown H, et al. *Macromolecules* 2013;46(3):900–13.
- [46] Wübbenhorst M, van Turnhout J. *J Non Cryst Solids* 2002;305(1–3):40–9.
- [47] Kremer F, Schonhals A. *Broadband dielectric spectroscopy*. Springer; 2003.
- [48] Havriliak S, Negami S. *Polymer* 1967;8(4):161–210.
- [49] Coleman MM, Graf JF, Painter PC. *Specific interactions and the miscibility of polymer blends*. Taylor and Francis; 2003.
- [50] Masser KA, Runt J. *Macromolecules* 2010;43(15):6414–21.
- [51] Leon C, Ngai KL, Roland CM. *J Chem Phys* 1999;110(23):11585–91.
- [52] Atorngitjawat P, Klein RJ, McDermott AG, Masser KA, Painter PC, Runt J. *Polymer* 2009;50(11):2424–35.
- [53] Castagna AM, Pangon A, Choi T, Dillon GP, Runt J. *Macromolecules* 2012;45(20):8438–44.
- [54] Grellmann W, Lach R. *Angew Makromol Chem* 1996;237:191–208.
- [55] Angell CA. *Science* 1995;267(5206):1924–35.
- [56] Huang DH, McKenna GB. *J Chem Phys* 2001;114(13):5621–30.
- [57] Hecksher T, Nielsen AI, Olsen NB, Dyre JC. *Nat Phys* 2008;4(9):737–41.
- [58] McKenna GB. *Nat Phys* 2008;4(9):673–4.
- [59] Zhao J, Simon SL, McKenna GB. *Nat Commun* 2013;4:1783.