



# Influence of nano-scale morphology on impact toughness of epoxy blends



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## ABSTRACT

The microstructure and ballistic impact toughness was investigated for a series of dynamically heterogeneous epoxy blends composed of diglycidyl ether of bisphenol A (DGEBA) that is cross-linked with stoichiometric mixtures of a rigid cycloaliphatic diamine and flexible polypropylene oxide based diamines. The ballistic impact resistance of the blends correlates with the presence of nano-scale structure, where blends that contain 2–5 nm domains exhibit nearly a doubling of impact toughness when compared to blends that exhibit large scale phase separation. The length scale of phase separation was manipulated by controlling the ratio of short chain to long chain propylene oxide diamines. At low long chain content, the materials nanoscale phase separate into 2–5 nm domains, resulting in a transparent epoxy that exhibits relatively good impact toughness. At high long chain volume fractions, the mixtures undergo macroscale phase separation and lose both optical clarity and impact performance. Interestingly, some of the macro-phase separated blends with intermediate long chain polypropylene oxide diamine content still exhibit high impact resistance if a nanoscale structure is still present in the rigid continuous phase. Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were used to characterize the phase separated structure in these blends. When the SAXS peak associated with nanoscale phase separation shifts to lower scattering vector and its intensity is reduced, the impact performance of the mixtures is likewise reduced. We hypothesize that the small scale structure in the blends facilitates rapid deformation during high rate ballistic impact events, which allows the material to absorb more energy before failure.

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## 1. Introduction

Epoxy-based thermosetting resins have found wide use throughout a variety of automotive, aerospace, and military applications. Epoxy thermosets are a particularly attractive material class for military applications due to their ease of processing, good environmental stability, and a relatively broad temperature window across which their modulus and impact behavior exhibit only modest changes. An example would be diglycidyl ether of bisphenol A (DGEBA) crosslinked with 4,4'-methylenebis(cyclohexylamine) (PACM). DGEBA/PACM exhibits a ~2–4 GPa modulus, and the modulus exhibits little change across the temperature range of interest for military applications. Epoxy thermosets for military

applications must meet additional requirements for high rate energy dissipation during ballistic events. A major drawback of epoxy thermosets such as DGEBA/PACM is their relatively poor high rate impact performance, and the temperature dependence of the high rate impact performance [1]. Although new thermosetting ring opening metathesis polymerization (ROMP) resins show promise for dramatically improved high rate impact performance at temperatures relevant for military applications [2], improving the performance of epoxy-based materials is still an important area of research. Both environmental degradation and catalyst availability are concerns for these ROMP resins, and the improvement over the performance of toughened epoxy resins [3,4] is marginal over a broad temperature range.

The fracture behavior and toughening mechanisms of these brittle materials have been areas of extensive research. Methods such as nanoparticle toughening with core-shell rubbers [3,5,6], silica nanoparticles [7–10], and block copolymers [11–13], as well

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as in-situ formation of rubber nanoparticles [14–16], have all been shown to enhance the fracture toughness and even ballistic performance [3] of otherwise brittle networks. A drawback of adding nanoscale fillers for property enhancement is the increased viscosity, which hinders standard epoxy processing techniques. Reaction-induced phase separation typically avoids this issue, and results in a material with micro-to-nano-phase separated domains which may be useful for improved toughness without sacrificing rigidity and thermal stability [14,17–21]. This mechanism has also been shown to impart additional useful properties such as reversible adhesion [22], as well as shape memory [20].

A previous investigation revealed a maximum in the high rate impact toughness at an amine volume fraction of 0.5, which was hypothesized to arise from nanoscale phase-separated soft domains in a rigid matrix [4]. The soft domains appear to preferentially deform [23,24], and the fine dispersion of these domains may be what gives rise to the improved ballistic performance [25]. This data is reproduced here in Fig. 1<sup>1</sup> including two additional mixtures with exactly 50 vol percent amines for both the D2000 and the D4000 blends. In both the D2000 and D4000 mixtures, the maximum in the high rate impact performance occurs at an amine volume fraction of 0.5. For the D2000 blends, small-angle X-ray scattering (SAXS) revealed the presence of nanometer scale domains [4].

In this study, we investigate the role of morphology in the ballistic performance in reaction-induced phase separating epoxy networks. Here, control of the size scale of the morphology was achieved by controlling the relative amounts of propylene oxide Jeffamines, D2000 and D4000, in DGEBA/PACM/D2000/D4000 mixtures. D2000 (see Fig. 2) does not phase separate during cure as strongly as D4000, as was previously observed [4]. This is likely due to its reduced chain length and favorable entropy of mixing relative to D4000. When no D4000 is included, nanoscale phase separation on the order of 2–5 nm is observed. As D4000 content is systematically increased, the materials eventually phase separate into hard and soft domains up to several hundred microns in diameter. Dynamic mechanical analysis, small-angle X-ray scattering, scanning electron microscopy, transmission electron microscopy, and even ballistic characterization of these mixtures all capture the transition from nanoscale phase separation to macroscale phase separation. The overriding factor governing the ballistic behavior of these materials, however, appears to be the presence of nanoscale phase separated material.

## 2. Experimental

The chemical structures of the materials used in this study are shown in Fig. 2. Diglycidyl ether of bisphenol-A (DGEBA, or EPON825) was purchased from Miller-Stephenson. The diamine 4,4'-methylenebis(cyclohexylamine) (PACM) was provided by Air Products. The propylene oxide-based Jeffamine diamines D2000 and D4000 were purchased from Huntsman. All materials were used as received. The critical difference in the systems investigated here is the degree of polymerization of D2000 versus D4000, with D2000 having an average of 33 propylene oxide segments, and D4000 having an average of 67 segments.

For each sample, the volume fraction ( $\Phi$ ) of DGEBA is 0.5. The amount of D4000 is systematically varied from a volume fraction of

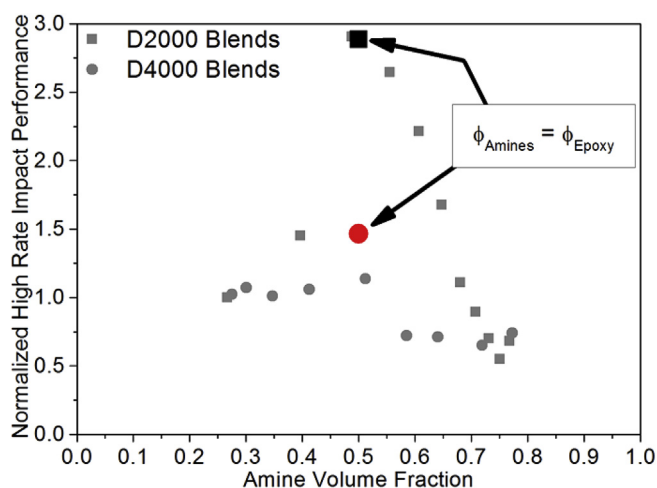


Fig. 1. Normalized high rate impact performance versus amine volume fraction for D2000 blends (squares) and D4000 blends (circles). The data is reproduced from Ref. [4]. The D2000 point and D4000 point at an amine volume fraction of 0.5 are highlighted for clarity.

zero (DGEBA/PACM/D2000 with 50 vol % DGEBA) to a D4000 vol fraction of 0.336, having no D2000 (DGEBA/PACM/D4000 with 50 vol % DGEBA). In each sample, stoichiometry was maintained such that no excess amine or epoxy groups are present in the final sample. This was accomplished by adjusting the amounts of PACM and D2000. The volume fraction of each component for each system is listed in Table 1. Throughout the manuscript, samples are designated by their volume fraction of D4000 ( $\Phi_{D4000}$ ) unless otherwise noted. As a means of a baseline comparison, a sample consisting of stoichiometric amounts of DGEBA and PACM was prepared, referred to as DGEBA/PACM. This material serves as a comparison to a standard structural epoxy material since it exhibits both a high glass transition temperature ( $T_g$ ) and high modulus at temperatures below  $T_g$ .

Compositions were formulated such that a total monomer mass of approximately 400 g was used, reducing the error when adding small amounts of one component. Over the composition range investigated, the maximum error in the amount of each component was always less than 1%. Samples were prepared by preheating appropriate amounts of each component to 60 °C under a nitrogen purge along with stainless steel molds. A small amount of mold release agent was coated onto the stainless steel molds to prevent strong adhesion between the cured epoxies and the molds. Prior to mixing, the monomers were degassed under vacuum at 60 °C. After degassing, the monomers were mixed and stirred vigorously for 2–3 min, then degassed under vacuum at 60 °C. The degassed monomer mixtures were then poured into the preheated stainless steel molds, degassed under vacuum, then cured under a nitrogen purge for 2 h at 80 °C, 8 h at 150 °C, then 2 h at 200 °C. The multiple

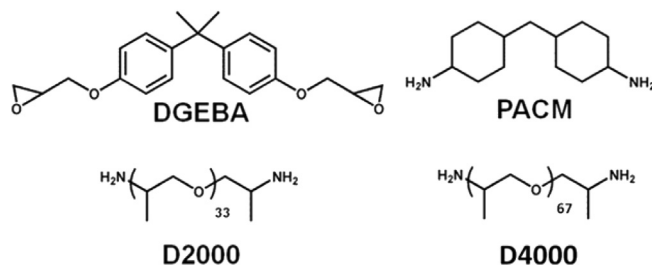


Fig. 2. Chemical structures of the materials used in this study.

<sup>1</sup> Reprinted from Polymer, 58 (0), Masser, KA; Knorr, DB; Hindenlang, MD; Yu, JH; Richardson, AD; Strawhecker, KE; Beyer, FL; Lenhart, JL, Relating structure and chain dynamics to ballistic performance in transparent epoxy networks exhibiting nanometer scale heterogeneity, 96–106, Copyright (2015), with permission from Elsevier.

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