HIGH VELOCITY IMPACT OF TOUGHENED EPOXY RESIN SYSTEMS IN GLASS FIBER REINFORCED COMPOSITES

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ABSTRACT

Toughening mechanisms of different polymer resins were explored for fiber reinforced composites under high velocity impact testing. Previous research demonstrated the critical importance of polymer molecular architecture and temperature-dependent viscoelastic behavior on impact performance by altering the damage mechanisms observed in both polymer-only and fiber reinforced composite testing. Combining these aspects creates a design space for performance optimization, particularly for reducing damage area due to delamination while retaining energy absorption over a broad range of temperatures. Epoxy resins that were either rubber toughened or intrinsically tough (i.e., a nanoscale phase-separated epoxy) were used to fabricate fiber reinforced composites with plain weave S-2 glass fibers using VARTM. The resulting composites were tested under high velocity impact over a temperature range of -50°C to 75°C and were compared to composites made from conventional, non-toughened epoxy resins. Overall, the total energy absorption stayed fairly constant for each toughened resin system over the temperature range of interest and were comparable from system to system. The damage area, however, decreased by more than 50% for the phase separated epoxy relative to the rubber toughened system, because of a change in deformation mechanism. The change in damage area without a decrease in total energy absorption implies that composite deformation mechanisms can be tailored by rational design of the polymer matrix molecular architecture to improve high-rate impact performance of fiber reinforced composites.

1. INTRODUCTION

Composite materials have the potential to displace heavier metal materials in various applications including automobiles, vehicles, robotic systems and aerospace applications. Military applications are particularly unique in that nearly all fielded materials may experience high velocity impact (>~100 m/s) either due to blast from an improvised explosive device, ballistic impact from a projectile, or impact from shrapnel. Glass fiber reinforced polymer (GFRP) materials have been developed to provide good impact resistance against these high velocity events. Research on the ballistic performance of GFRPs goes back more than 50 years, when GFRPs were identified as good backing materials for vehicle armor[1], where they are effective because they are stiff to deflection but can still experience large deflection, which prevents high shear or punching stresses at the impact surface[2]. This area of research has continued to be of interest as reducing vehicle weight becomes more important and different types of vehicles (e.g., autonomous vehicles) that require some means of ballistic protection but cannot bear the weight of metal-based armors are being considered.

SAMPE neXus Proceedings. Virtual Event, June 29 – July 1, 2021. Society for the Advancement of Material and Process Engineering – North America.

Unfortunately, GFRPs can demonstrate large ballistic damage zones, making the extent of damage area a primary design concern[3]. The high damage area and poor response fiber reinforced polymer composites to impulsive loads is often blamed on the brittle nature of the resins used[4]. In addition, the highest ballistic performances are typically observed with laminates that have relatively low flexural stiffness[5], which depends on the modulus and the fracture behavior of the neat resin. Therefore, a better understanding of how matrix systems with an improved fracture toughness influences the high velocity impact performance of a composite is crucial.

Polymer toughening techniques have been of research interest for several decades[6,7]. Structural epoxies typically demonstrate the capacity for high loading (high modulus and strength) but at the cost of brittle failure. Toughening mechanisms have been used to combat this brittle failure through resistance to crack initiation and propagation without affecting the advantageous structural properties and process-ability. Toughening through the formulation of multiple-phase systems and the dispersion of inorganic nanoparticles, core-shell rubbers, clays, other micro/nano-fillers, and various hybrid systems have been demonstrated[7-12].

One toughening method is formulation of stoichiometric blends of amines to form interpenetrating polymer networks[13]. The introduction of various rigid and elastomeric amines has been shown to create both phase-separated and heterogeneous epoxy networks with improved ballistic performance[14,15]. This research has shown the tailorability of phase-separated systems from microscale to nanoscale depending on the amine formulation[16]. The ballistic performance, as well as other high-rate mechanical performance was demonstrated to be dependent on the morphology of the epoxy blends as well as the testing temperature[17-20]. Transitioning these epoxy blends that were optimized for superior fracture toughness to fiber reinforced composites may provide measureable improvements to impact performance.

Using the previous resin work as a guide, we seek to explore the effect of polymer toughening mechanisms on the high velocity impact performance of GFRPs. We accomplish this by measuring the composite ballistic energy absorption and damage area over a wide temperature range (i.e., -50ºC to 75 ºC) for a model structural epoxy resin system and two toughened epoxy systems, each using different toughening mechanisms. Our results show that the total energy absorption, as quantified by KE_{50}, is independent of temperature and similar from each of the epoxy systems. However, the damage area is reduced by 50% for phase-separated epoxy systems because of the inherently different properties and absorption mechanisms.

2. EXPERIMENTATION

2.1 Materials and Fabrication

Diglycidyl ether of bisphenol-A (DGEBA) was obtained from Miller-Stephenson (Hexion, EPON 825) and used as received. Oxypropylene diamine was provided by Huntsman (Jeffamine D230 and D2000) and was used without modification. Diamine 4,4'methylenebis(cyclohexamine) (PACM) was provided by Air Products. Resin systems were prepared by preheating components to 60°C, mixing at stoichiometric ratios of amine and epoxy, followed by degassing for 10-20 minutes under vacuum (~27 inHg) to remove dissolved gasses. The resin was then used without further modification in composite fabrication or alone to fabricate resin-only panels.

S2 glass fabrics with a 0°/90° plane weave and epoxy-based sizing were acquired from PW composites. Fabrics were cut into 13" by 13" square plies using a Gerber cutting table and stacked to create panels of the appropriate dimensions per testing requirements. Composite panels were fabricated using vacuum-assisted resin transfer molding (VARTM) and a double vacuum bag system to debulk the system pre-transfer. Resin transfer across the composite panel was performed under a constant pressure of 29 inHg and typically occurred in under a minute. Panels were cured under vacuum with the following cure profile: 2 hours at 80° C, 8 hours at 150° C, and 2 hours at 200° C. Individual specimen were cut from each panel using a water-jet. More details of the composite are listed in Table 1.

Table 1 - List of Composite Physical Properties.

Resin	Fibers	Orientation	No. of Plies	Thickness (mm)	Areal Density (kg/m^2)
DGEBA/D230	S2 Glass	0°/90°	5	3.54 ± 0.13	6.01 ± 0.12
Rubber Toughened	S2 Glass	0°/90°	5	3.47 ± 0.11	5.95 ± 0.08
DGEBA/PACM/D2000	S2 Glass	0°/90°	5	3.29 ± 0.05	5.62 ± 0.10

2.2 Impact Measurements

High velocity impact performance was evaluated using the V_{50} ballistic limit, which is detailed elsewhere[21]. The V_{50} is the velocity of the ballistic limit at which a witness foil, spaced 2 inches behind the target, has a 50% probability of perforation by either the projectile or spall from the target. The associated kinetic energy of projectile at V_{50} is presented as the KE_{50} and calculated using the following equation:

$$KE_{50} = 0.5 * m * V_{50}^2$$

where m is the mass of the projectile. The impact performance (i.e. the KE_{50} and the resultant damage area) of composite panels was tested using a variable-pressure gas gun and a 0.22 caliber stainless steel projectile (5.52 mm, 0.69 g, sphere) at a temperature range from -50°C to 70°C. Testing specimen dimensions were typically machined to 3" by 3" with nominal thicknesses of 3 mm created by the resin-infused 5 plies. Specimens were packaged between two steel plates with 50.8 mm diameter windows and mounted in front of an aluminum foil witness to detect perforation. Any perforation through the foil witness was considered complete penetration; otherwise, the sample was considered to be non-penetrating. The V_{50} was measured by taking the average velocity between the highest velocity non-penetrated shots and the lowest complete penetrating shots. The data presented here is normalized to the composite areal density and the room temperature KE_{50} for D230. For variable temperature testing, samples were allowed to equilibrate in an oven at the measurement temperature for at least an hour prior to testing. Then, the fixture was mounted in an environmental chamber for impact testing.

2.3 Damage Area Assessment

The damage area was quantified for each tested panel by measuring the area of the damage caused by the projectile through non-destructive imaging. To do so, samples were back-lit, imaged, and processed to calculate the area. Areas were calculated using a thresholding tool within Image J software.

3. RESULTS

3.1 Polymer Impact and Fracture Properties

A plethora of work exists on toughening mechanisms for polymer-only applications, as previously discussed[6,8]. Candidates for the composite matrix resin were chosen based on previous work on polymer impact to determine if the same toughening mechanisms translated to fiber-reinforced composites[19]. Resins here demonstrated either a high V_{50} performance or high fracture toughness, as defined by the critical stress intensity factor (K_{1c}) and the critical strain energy release rate (G_{1c}). Resins candidates were also required to have a high T_g to maintain structural integrity and ensure durability throughout the large temperature range tested (i.e. a structural resin). To understand the role of toughening mechanisms, two different mechanisms were selected: rubber toughened and nanophase separated epoxies, as seen in Table 2. The rubber toughened epoxy exhibited significant improvements to K_{1c} and G_{1c} of 144% and ~600%, respectively, relative to the control resin (DGEBA cured with D230). While the nanophase separated epoxy showed improvement to fracture toughness (50% and >200%), the improvement to polymer-only V_{50} measurements were remarkably higher (43% increase), relative to the rubber toughened epoxy system (7%). Because of the stark contrast in impact and fracture performance, the two epoxy resin systems should display different impact performance and energy absorption mechanisms.

Table 2 - Polymer impact and fracture properties from literature. V_{50} tests of the polymer only were measured in-house primarily for separate studies and are normalized to the D230 control.

Resin	T_g (°C)	V_{50} at 20°C (normalized)	K_{1c} ($MPa*m^{1/2}$)	G_{1c} (J/m^2)	Reference
D230 (control)	93±1	1.00±0.01	0.86±0.09	210±50	[22]
Rubber Toughened	96±2	1.07±0.02	2.08±0.09	1460±120	[9]
Nanophase Separated	102±2	1.43±0.03	1.29±0.07	670±52	[19]

3.2 Impact Performance Results

The impact performance was evaluated using the KE_{50} of the projectile at V_{50}, i.e. the velocity at which the probability of penetration is 0.5. These measurements were normalized by the areal density of the composite, which are listed in Table 1 and dependent on the density of the polymer matrix. This normalization creates a fair comparison between sample sets because the literature has shown that ballistic limit, V_{BL} or V_{50}, are dependent on the mass and geometry of the projectile and mass of the target behind the projectile[23]. KE_{50} measurements were performed over a large temperature range (-50 to 70°C) that was used to encompass the operating temperature seen in a wide range of environments for composite applications. As seen in Figure 1, the normalized KE_{50} results were independent of the testing temperature. Also, the relative difference between each resin candidate remained insignificant as well. This result shows that for structural resins (i.e. high T_g), the overall impact resistance is not dictated by the matrix of the composite at sub-T_g temperatures. In fact, previous literature has modeled the total impact resistance, as quantified by the energy absorption, and shown that fiber-dominated mechanical properties and out-of-plane deformation of the composite, not fracture-toughness of the matrix, contribute the most to energy absorption[24,25].

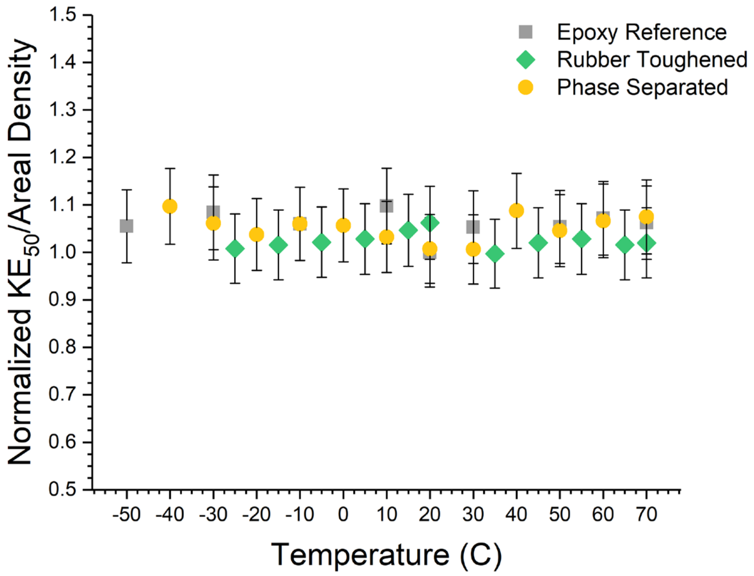

Figure 1 - Impact results for reference epoxy, a rubber toughened system, and an inherently tough polymer

3.3 Damage Area Assessment

Although the total impact energy absorption was not affected, the damage area was significantly changed between the three epoxy systems. The damage area was measured for each test specimen by evaluating the superficial area (i.e. 2-D planar area, optically visible) at the composite V_{50}. While this does not account for multiple layers of damage within the composite, it is a fair representation of the matrix cracking and interlaminar delamination energy absorption mechanisms observed in composites. On-going work is being done to re-evaluate this procedure using additional non-destructive imaging techniques, such as x-ray computed tomography (CT).

As seen in Figure 2, the damage area is dependent on the type of toughening mechanism. The rubber toughened epoxy composites demonstrated an increase in damage area over the tested temperature range, while the nanophase separated epoxy system decreased the damage area by ~50%. Previous, research has shown that the damage area may also be reduced by testing at temperatures above the T_g of the epoxy, and thereby, decreasing the out-of-plane stiffness and increasing the back-face deformation of the composite[26]. However, each of these epoxy systems maintain a high T_g and a decrease in damage area is still observed for the nanophase separated matrix. The combination of these results may suggest that a maximized fracture toughness is not essential for limiting composite delamination, but instead may rely more on inherent toughness than absorbs a high degree of strain energy – shown through the back-face deformation – when impacted with the projectile. Other aspects such as matrix/fiber adhesion should be considered, but were not a part of this particular study.

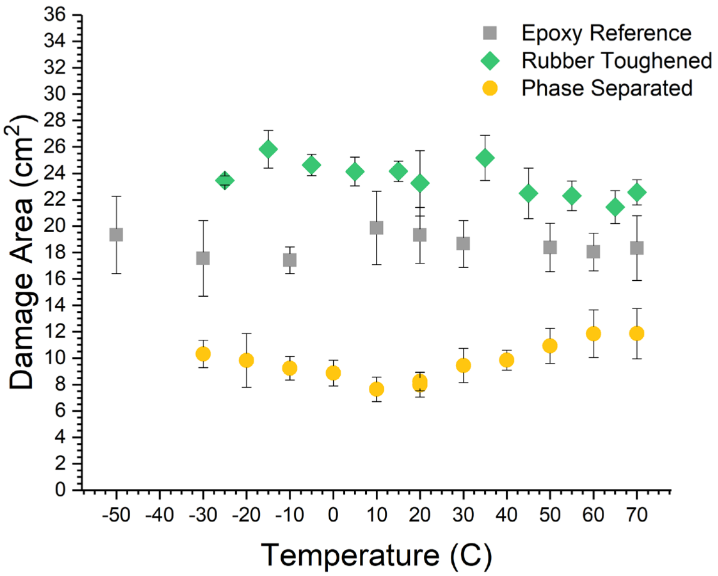

Figure 2 - Measured damage area of composites at V_{50} velocity.

Clues to the ballistic response and energy absorption mechanisms may also be drawn from images of the tested composites. Figure 3 shows images of the damage area for the three epoxy systems. The structural epoxy and rubber toughened epoxy, shown in Figure 3a and b, depict damage area in a circular shape that is representative of composites with stiff shear moduli; whereas, the diamond shape depicted in Figure 3c is more characteristic of composites with lower shear modulus. While no empirical evidence of this currently exists, the back-face deformation (through a reduced shear modulus) of the nanophase toughened epoxy can be assumed to be much greater than the other two systems, leading to less energy absorption through delamination and ultimately, lower damage areas. Measurement of the back-face deformation through DIC imaging techniques is a future research area of interest to support the hypotheses in this study.

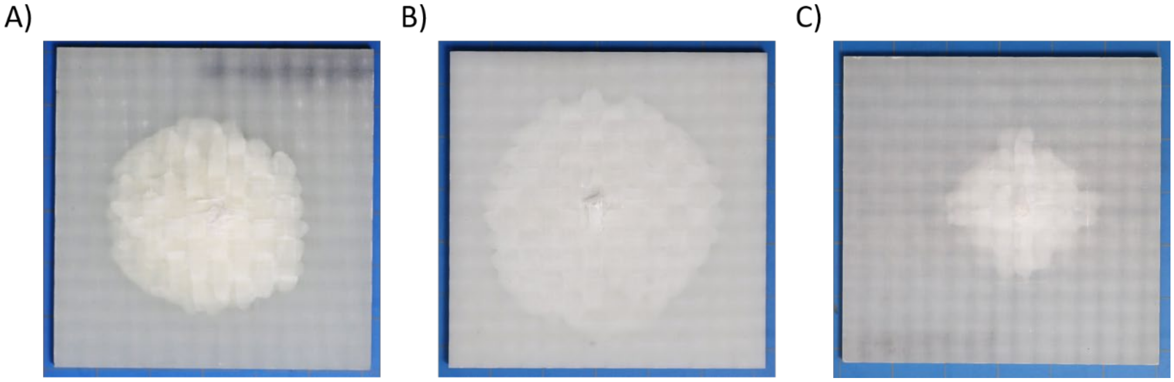

Figure 3 - Images of damage area for the impacted composite systems: A) D230, B) rubber toughened epoxy, C) phase-separated epoxy

4. CONCLUSIONS

Here, we summarize our work on the transition of polymer toughening mechanisms to the impact performance of fiber-reinforced composites. The ballistic performance of a model structural epoxy and two toughened epoxy systems were characterized by KE_{50} and the resultant damage area over a wide temperature range. The KE_{50} impact performance was shown to be independent of temperature and independent of the resin system used. The damage area, however, showed strong dependence on the type of toughening mechanism used. Inherently tough polymers, as exemplified by nanophase separated epoxies, demonstrated significantly reduced damage areas compared to the rubber-toughened and non-toughened system. This improvement is hypothesized to be from increased matrix fracture toughness and back-face deformation upon impact.

Acknowledgements

Research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-18-2-0304. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein.

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