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Epoxy Functionalized Hyberbranched Polymer/Epoxy Blends

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Epoxy Functionalized Hyberbranched Polymer/Epoxy Blends

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Abstract

In this preliminary study, two novel hyperbranched polymer (HBP)/epoxy blends were evaluated to determine their efficiency as blend modifiers and tougheners in a brittle epoxy resin. The HBP is miscible in the epoxy and phase separates as cure progresses to form a two-phase system with a dispersed secondary phase of HBP/epoxy compatibilizers in a rigid epoxy matrix. There is no significant increase in the viscosity of the blends when compared to the pure epoxy. This demonstrates an improved processibility over conventional tougheners. A modest increase in the fracture toughness was achieved in both systems but at different concentrations of HBP. Further improvements in the toughness may be realized in an epoxy system when these novel molecules are used in concert with chain extenders.

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1. Introduction

The next generation of Army ground combat vehicles, such as the composite armored vehicle, the composite infantry fighting vehicle, and future combat system, will rely on lightweight, damage-tolerant, impact-resistant toughened composites to achieve enhanced performance, improved survivability, and improved sustainability. Toughened, high-performance organic resin matrix/fiber-reinforced composites are a critical class of Army materials and essential to all next-generation ground vehicles.

Current high-performance resins are toughened by the addition of tough thermoplastic resins, liquid rubbers, or rubber particulates to the organic resin. During cure, these materials phase-separate to form microparticles in the cured matrix. These additions to the resin cause an increase in viscosity that prohibits the processing by advanced manufacturing techniques such as resin transfer molding (RTM). The limitations of processing techniques for rubber-toughened epoxy resins is preventing their widespread use in Army systems and presenting a technological barrier to the development of the lightweight, highly mobile systems being designed to reduce the logistics train of the Army 2010 and beyond.

Epoxy resins are commonly used in adhesives and fiber-reinforced composites and are popular for a variety of reasons. Epoxies adhere well to a variety of fillers and reinforcements. Their mechanical properties and processing characteristics can be tailored for a wide range of end-use applications. Their dimensional stability and good chemical resistance also make them attractive matrix materials [1]. Unfortunately, unfilled epoxies typically exhibit poor fracture toughness properties and fail in a brittle manner due to the lack of energy-absorbing mechanisms such as shear yielding, crazing, and cavitation [2, 3]. In a brittle epoxy resin system, an improvement in the fracture toughness is observed when low-modulus rubbery materials are added to a rigid matrix, where it is not uncommon for the strain energy release rate, G_{IC}, to increase 10–20 times [4].

Perstorp Polyols of Sweden has recently developed a new class of highly branched epoxy functional molecules. This new class of hyperbranched polymer molecules has the potential to not only increase the fracture toughness of the resin but also appear to improve the processing characteristics of the resin. Therefore, low-cost manufacturing techniques used to produce high-performance, integrated, thick-section composite parts needed for all future Army ground combat vehicles may be used. These improved resins will ultimately help in the production of high-performance, low-cost composites.

Ideally in the RTM process, a low-viscosity resin with a long pot life is needed to fill the mold and wet the reinforcing fibers before cure [5]. As mentioned earlier, when rubber or thermoplastic tougheners are added to improve the fracture toughness, the viscosity of the resin increases, which makes processing techniques such as RTM more difficult. Other difficulties arise when the reinforcing fibers act as filter and prevent the even distribution of tougheners throughout the composite, which results in a reduction in mechanical properties.

A low-viscosity, single-phase resin or blend is needed for infusion and wet out. The resin must also phase-separate and form a secondary rubber phase surrounded by a primary phase of epoxy for improved fracture toughness. The cure kinetics and processing variables can be adjusted to produce a morphology for optimum toughness for a particular resin system. However, the optimum size and distribution of these second-phase particles for a given system is ambiguous at best and must be determined via mechnical testing [2].

Novel hyperbranched polymer (HBP) molecules added to an epoxy system may improve the fracture toughness of the matrix as well as improve the processing characteristics [6]. The unique molecular architecture and end group functionality makes them attractive as blend modifiers [7]. The high number of branches and compact structure on these molecules will promote a low-viscosity behavior even at high-molecular weights due to the lack of restrictive chain entanglements found in linear analogues [8, 9, 10]. This low-viscosity behavior of the resin will aid in filling the mold and wetting out the reinforcing fibers.

The HBPs in this study possess a three-dimensional structure (Figure 1) with multiple short branches, each of which may be epoxy functionalized (R") or hydroxyl functionalized (R'). Since these materials may be functionalized to be compatible with the epoxy matrix, it is possible to have a single-phase, miscible blend of epoxy and HBP as the mold fills and the fibers are wet out. The system will phase-separate as cure begins and result in a two-phase system with a secondary phase of dispersed rubber particles in a rigid matrix [11]. The extent of phase separation and the point at which it occurs can be easily controlled by designing the surface functionality of the HBPs. This will influence the final particle size and resulting fracture toughness.

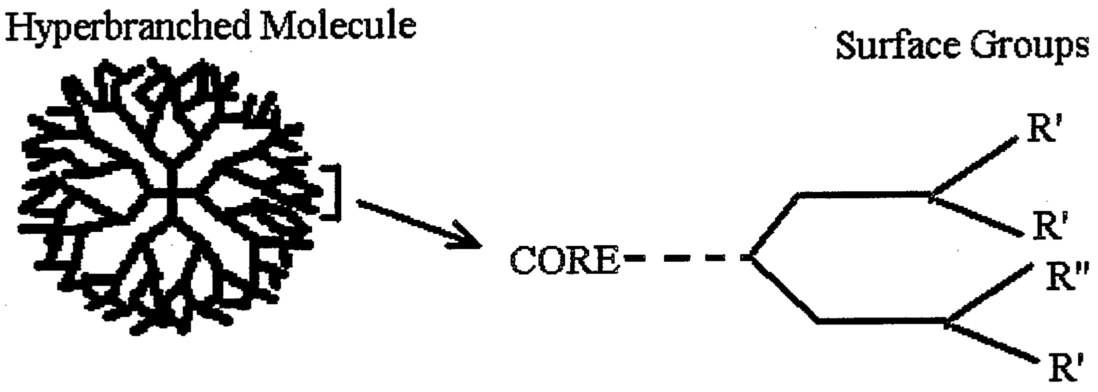

Figure 1. Hyperbranched Polymer Architecture and a Close-Up View of Surface Functional Groups.

Dendritic polymers are a natural for use as a blend additive in an epoxy system for the reasons mentioned previously. The unique, highly branched architecture promotes a low viscosity during processing, and an end-group chemistry that can be tailored to a specific reactivity is attractive for the formation of a two-phase toughened system.

2. Experimental

2.1 Materials. The epoxy that was modified in this study was Shell EPON 828, a Diglycedal Ether of Bisphenol A epoxy with an equivalent weight of 188 g/mol. Two types of experimental epoxy functional HBPs, E1 and E2, were blended with the epoxy in concentrations of 0, 4, 8, 12, 16, and 20% by weight epoxy (Table 1). The E1 dendritic molecules each have 11 epoxy functional groups and an equivalent weight of 830 g/mol. The E2 dendritic molecules each have 30 epoxy functional groups and an equivalent weight of 375 g/mol. An Air Products PACM aliphatic amine curing agent is used with an equivalent weight of 52.5 g/mol to cure all baseline epoxies and blends.

Table 1. Composition of Epoxy and Epoxy Blends

%828	%E1	%E2	Wt 828 (g)	Wt E1 (g)	Wt E2 (g)	Wt PACM (g)
100	0	0	300	0	0	84
96	4	0	285	15	0	81
92	8	0	270	30	0	78
88	12	0	255	45	0	74
84	16	0	240	60	0	71
80	20	0	225	75	0	68
100	0	0	300	0	0	84
96	0	4	285	0	15	81
92	0	8	270	0	30	79
88	0	12	255	0	45	77
84	0	16	240	0	60	75
80	0	20	225	0	75	72

The baseline epoxy and epoxy blends were all mixed in stoichiometric ratio to ensure complete reaction between the epoxide groups and the amine-terminated cross linkers. The resins were mixed in 400-g batches and cast into four molds, each of which could hold 100 g. The epoxies were cured at 80° C for 1 hr and post cured at 180° C for 2 hr.

2.2 Morphology. The fracture surface morphology of the epoxy blends was examined with the use of a Philips Electroscan 2020 environmental scanning electron microscope (ESEM) at a magnification of 2000× and 4000×.

2.3 Viscosity. The epoxy resins used in this study are typically used as base materials for RTM processing, and diluants are added to reduce the viscosity of the system. Diluants were not added to these blends since only the effects of the HBP molecules on the viscosity were under study, not the combined effects of diluents and HBP modifiers. RTM-type viscosities may be attained in these systems at elevated processing temperatures.

Separate batches of resin were prepared for viscosity measurements. The viscosity of the pure epoxy and HBP blends was measured at room temperature with a Rheology International Viscometer both with and without curing agent. The viscosity and cure temperature data for 0, 10, and 20% HBP by weight epoxy blends were collected as a function of time. Spindle 3 was used in all measurements, the rotational speed was adjusted to record data in the appropriate viscosity range, and these data were plotted on a strip chart recorder.

2.4 Fracture Toughness. In order to see the full effect of the HBP's improvement on the fracture toughness, a brittle epoxy system was chosen for study. Hence, any toughening observed would be due to energy-absorbing mechanisms such as rubber tearing in the secondary-phase particles and not shear yielding of the matrix.

The fracture toughness of the resins was determined according to ASTM D5045 with a Single Edge Notch Bending (SENB) geometry. All samples were approximately 76 mm × 6 mm × 12.5 mm with a 6-mm-deep notch, which ensures a state of plain strain ahead of the crack tip. The specimens were tested under standard conditions with a crosshead speed of 1 mm/min.

3. Results and Discussion

3.1 Processing. During resin infusion of an RTM composite, a single-phase resin is desired; this allows for the even distribution of low-modulus rubbery material throughout the composite part. All of the pure epoxies and epoxy/HBP blends were initially single-phase systems. When cured, the pure epoxies remained a single-phase system, while all of the epoxy/HBP blends formed two-phase systems.

The Gibbs free energy of mixing, ΔG_{mix}, governs the equilibrium phase behavior of a polymer blend:

$$\Delta G_{mix} = \Delta H_{mix} - T\,\Delta S_{mix}, \tag{1}$$

where ΔH_{mix} is the heat of mixing, ΔS_{mix} is the entropy of mixing, and T is the absolute temperature. The conditions for miscibility are:

$$\Delta G_{mix} < 0$$

and

$$(\partial^2 \Delta G_{mix} / \partial \phi_i^2)_{TP} > 0,$$

where ϕ_i is the volume fraction of component i in the mixture, T is absolute temperature, and P is pressure. A single-phase system is observed when ΔG_{mix} is negative, and a two-phase system is observed when ΔG_{mix} is positive.

When the epoxy and HBP are initially mixed, ΔS_{mix} is large and ΔH_{mix} is small but positive, this results in a negative value for ΔG_{mix}. As cure progresses and molecular weight increases, ΔS_{mix} approaches zero, and ΔH_{mix} is positive. This results in a positive value for ΔG_{mix}, and an immiscible multiphase morphology is observed in the final product [2, 3].

This behavior is due to the grafted epoxy functional groups on the surface of the HBP molecules, which promoted a miscible blend when mixed with the epoxy. The amine curing agent reacted with both the epoxy and HBP, the epoxy molecular weight increased, and HBP/epoxy copolymers were formed. As cure progresses, the buildup of molecular weight causes phase separation to occur, whereby a secondary phase of HBP/epoxy copolymers are surrounded by a continuous primary phase of epoxy.

3.2 Morphology. Although both epoxy/HBP blends depicted in Figures 2 and 3 have the same weight fraction of HBP, the fracture surfaces of the two blends exhibit dramatically different morphologies. The epoxy/12% E1 blend has an average second-phase particle size of over 1.0 µm in diameter, while the epoxy/12% E2 blend has an average second-phase particle size of less than 1.0 µm in diameter. The difference in the average second-phase particle size is primarily due to the number of reactive surface groups present on the HBP molecules since the processing conditions and curing agents were the same in all blends. Once the optimum second-phase particle size has been determined via mechanical testing, the processing variables or the HBP reactive groups may be adjusted to produce the desired blend morphology for improved toughness.

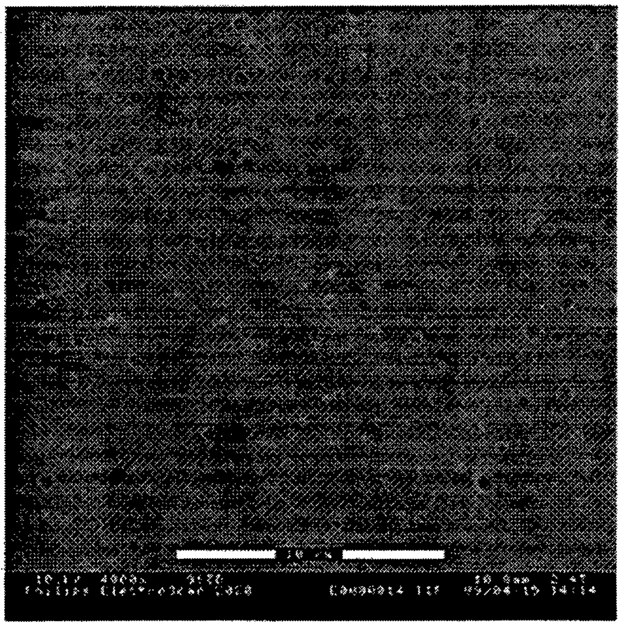

Figure 2. Fracture Surface of Epoxy/12% E1 Blend.

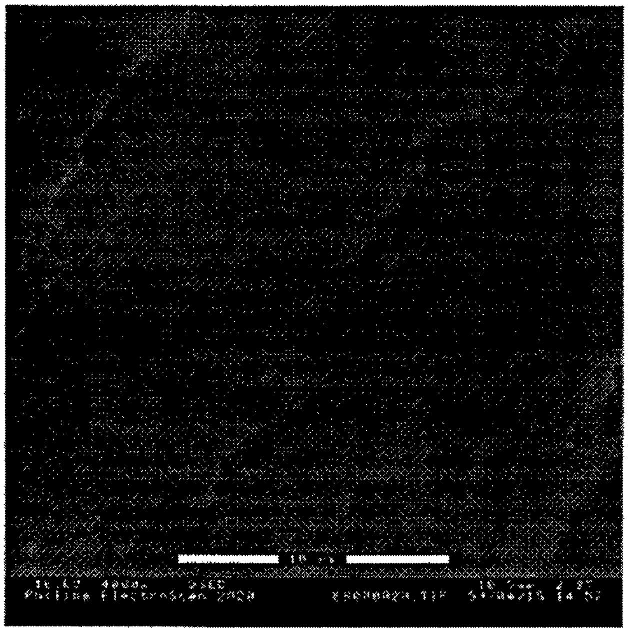

Figure 3. Fracture Surface of Epoxy/12% E2 Blend.

3.3 Viscosity. The addition of rubber particulates or traditional liquid rubbers increases the viscosity of the resin and makes a process such as RTM difficult. In this study, the addition of the HBP did not appear to dramatically affect the viscosity or the cure time relative to that of the pure epoxy in the initial stages of cure as seen in Figures 4 and 5. All of the resins and blends have essentially the same viscosity and temperature for the first 60 min, which, depending on the application, should be sufficient time to fill the mold and wet out the reinforcing fibers.

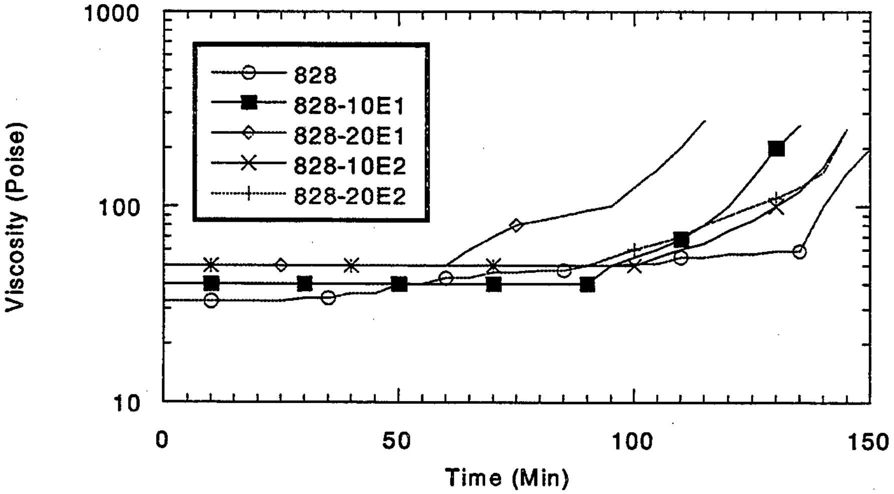

Figure 4. Viscosity Profile of Epoxy and Blends.

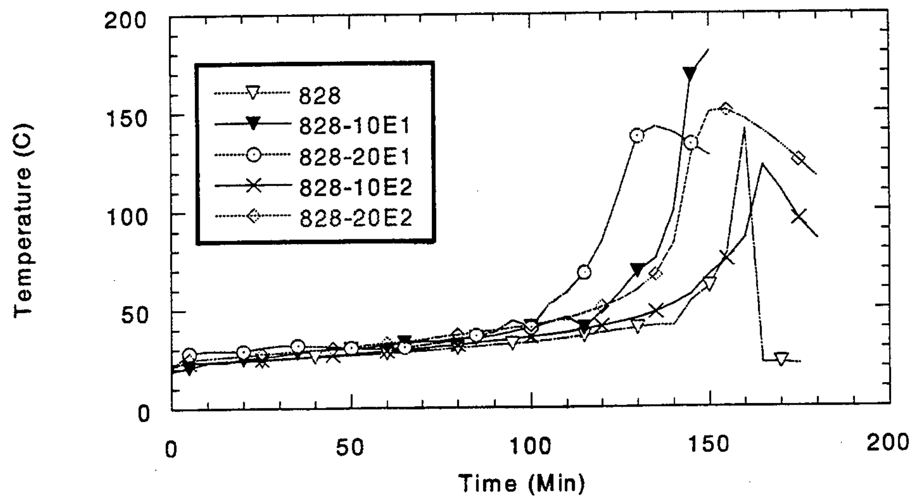

Figure 5. Cure Temperature of Epoxy and Epoxy Blends.

The HBP blends did increase in viscosity before the pure systems. This may be attributed to several factors. There may be an acceleration in the cure of the E1 and E2 blends due to the HBP molecular structure and the surface functional groups, whereby the presence of hydroxyl groups is known to speed up the reactions in an epoxy/amine curing resin system [12]. Minor variations in the stoichiometry of the system may have also caused this accelerated reaction, since the quality control of these experimental modifiers may not be reliable. This difference may also be due to the shear stresses induced by the rotating spindle of the viscometer.

The epoxies and blends started to react between 100 and 130 min and reached a peak exotherm temperature within a relatively short period of time. The HBP blends reacted before the pure epoxy system, which is indicated by the increase in temperature illustrated in Figure 5. Again, this may be due to some or all of the factors mentioned in the previous paragraph.

3.4 Fracture Toughness. Generally, little or no improvement in the toughness of an epoxy is observed without the presence of shear yielding prior to fracture. A brittle system was chosen to isolate the contribution of the HBP to the overall toughness. The strain energy release rate (G_{1C}) and plane strain fracture toughness (K_{1C}) of the epoxy and HBP/epoxy blends were measured as a function of HBP concentration. As seen in Figures 6–9, the addition of HBP to the epoxy matrix slightly improved the fracture toughness. Any improvement in the fracture toughness appears to depend on the concentration of HBP added as well as the type of HBP added.

In the E1 blends, the optimum loading of HBP appears to be less than 10% by weight epoxy. In the E2 blends, the optimum loading appears to be in approximately 12% by weight epoxy. This may be attributed to the cure kinetics and the resulting second-phase morphologies of the different blends. For an improvement in toughness to occur, this epoxy system and optimum second-phase particle size must be present. The different degrees of reactivity of the HBP molecules affect the second-phase morphology, particle size, and distribution. Therefore modest improvements in toughness were observed at different loadings of the different HBP additives.

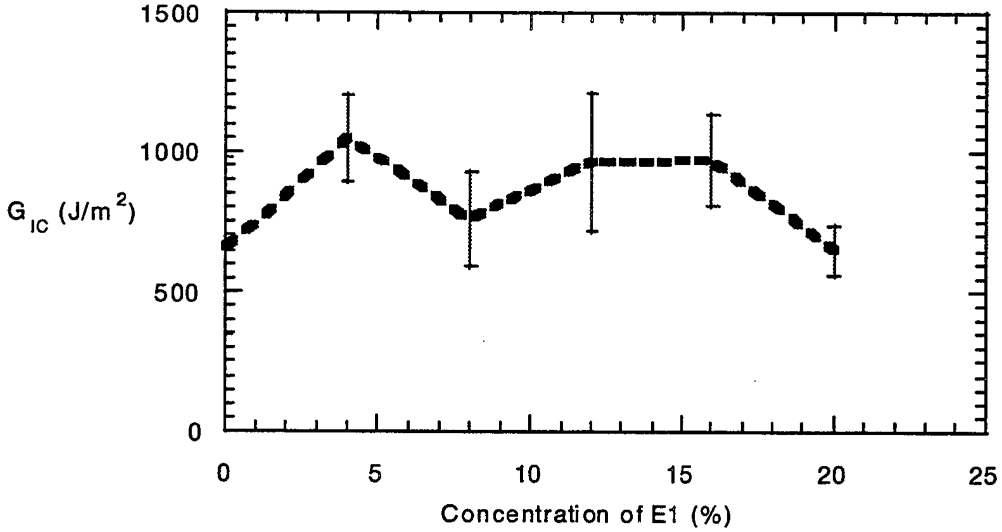

Figure 6. Strain Energy Release Rate of Epoxy/E1 Blends.

Dramatic improvements in the fracture toughness may be achieved in an epoxy system with a lower cross-link density and chain extenders, which improve the ductility of the matrix. An improvement in ductility allows for energy-absorbing mechanisms such as shear yielding and cavitation to occur, which complement the rubber tearing mechanisms.

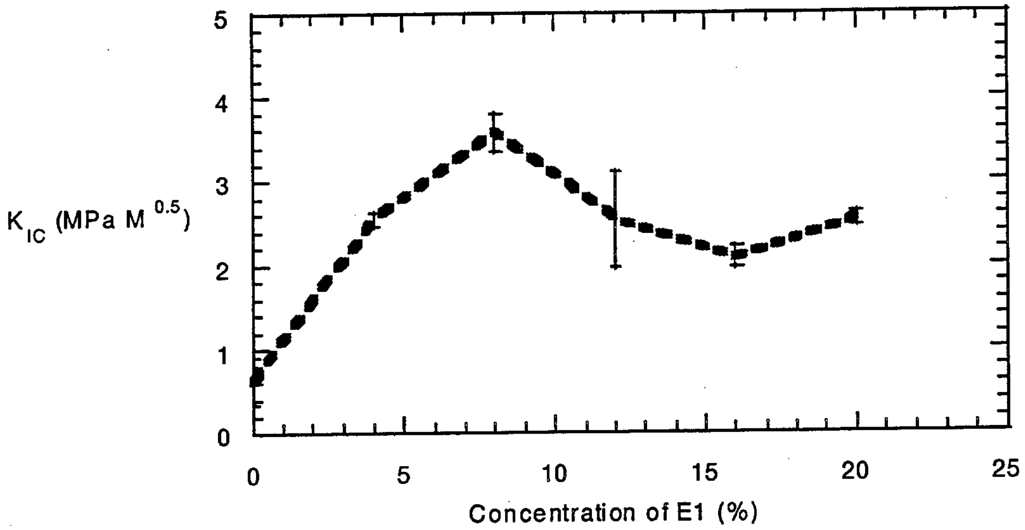

Figure 7. Plane Strain Fracture Toughness of Epoxy/E1 Blends.

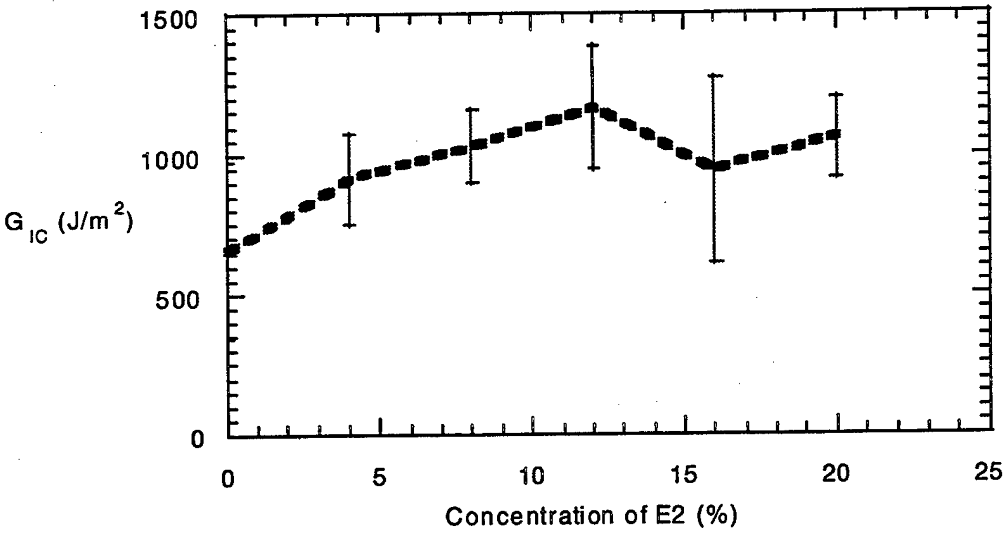

Figure 8. Strain Energy Release Rate of Epoxy/E2 Blends.

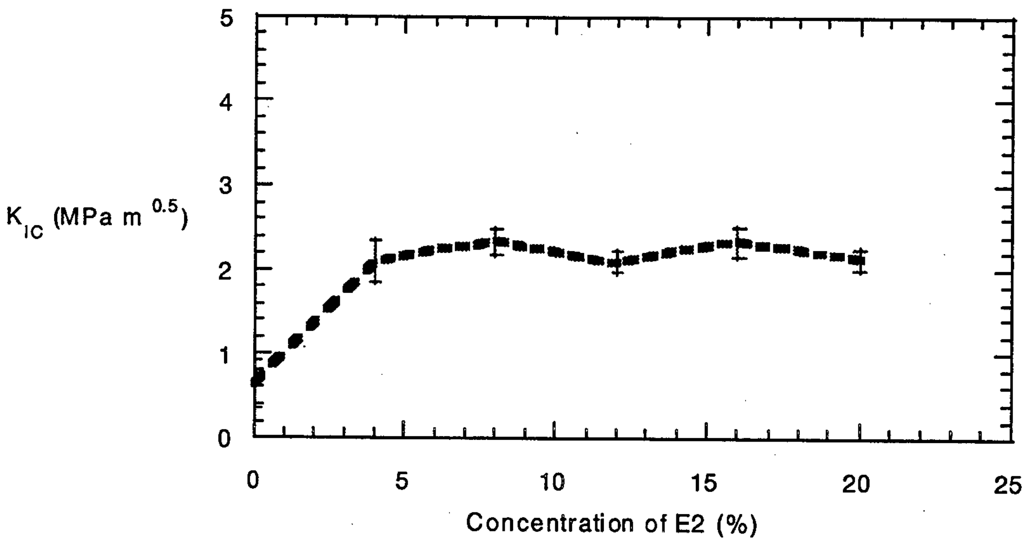

Figure 9. Plane Strain Fracture Toughness of Epoxy/E2 Blends.

4. Summary and Conclusions

An optimum balance between processibility and performance is desired in an RTM grade resin. The highly branched structure of the E1 and E2 molecules is attractive as a low-viscosity additive for improved RTM processing. There was no significant change in the viscosity of the blends during a 60-min processing window, which demonstrates the additive's ability to maintain the viscosity of the base epoxy.

The epoxy functionalized end groups on the HBP molecules formed a miscible single-phase blend with the epoxy during infusion and a two-phase system upon cure. This secondary phase of rubber particles slightly improved the energy-absorbing capability of the system, optimum results for each blend were achieved with different HBPs at different concentrations of HBP, and particle size varied as a function of HBP surface reactivity.

Based on these results, a better understanding of the structure property relationships must be determined in order to tailor the cure kinetics for an optimum second-phase morphology and energy absorption mechanisms. Epoxy functional HBP molecules do show promise as an effective viscosity modifier and rubber toughener, but more research needs to be carried out to realize the full benefit of these truly unique molecules. Once these materials are fully characterized, they may be used extensively in the low-cost processing of high-performance composite structures.

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