### Investigation of Readily Processable Thermoplastic-Toughened Thermosets: IV. BMIs Toughened with Hyperbranched Polyester

#### A. GOPALA, H. WU, J. XU, P. HEIDEN

Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931, USA

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ABSTRACT: This is the fourth article in a series describing efforts to produce tough, high-performance thermosets from very low viscosity prepolymers which are autoclave processable. Hydroxy-terminated hyperbranched polyester (HBP) with a systematically increased molar mass was used to toughen bismaleimide (BMI). HBP was dissolved in the allyl phenol component, B, of a two-part BMI, to yield homogeneous solutions. The BMI monomer, A, was dissolved in the solution of HBP in B to give homogeneous prepolymers. The fracture toughness  $(K_{Ic})$  of neat resin plaques was measured by compact tension, while the  $T_{g}$  and storage moduli (E', at 55 and 200°C) were determined by DMA. At 9% loading, the  $K_{\rm Ic}$  of the BMI increased steadily with HBP molecular weight up to 138% over the control with G5 HBP ( $M_n \sim 14,000$  g/mol); however, significant decreases in both the  $T_{g}$  and E' resulted, indicating incomplete phase separation of the thermoplastic. A linear hydroxy-terminated polyester  $(M_n)$ 5400 g/mol) with a repeat unit structure which was similar to the HBP's was prepared and used as a control. The linear polyester (LPE) toughened the BMI nearly as effectively as did the HBP and caused a smaller decrease in the  $T_{\sigma}$  and E'. The viscosity of solutions of HBP and LPE in B were essentially the same at lower loadings in B, but at higher loadings, the HBP viscosity increased faster than did that of the LPE. The viscosity increase was end group-dependent. Preliminary morphological results are presented to show the effect of the thermoplastic architecture, loading, and end group on the cured thermoset. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1809-1817, 1999

Key words: hyperbranched polyester; toughening; BMI; bismaleimide

#### **INTRODUCTION**

Commercially available hydroxy-terminated (HBPs) were investigated as thermoplastic tougheners for bismaleimide (BMI). The branching efficiency of hyperbranched polymers is usually less than that of dendrimers (generally below  $\sim 80\%$ ), but they still possess many of the desirable properties for which dendrimers are noted. Furthermore, hyperbranched polymers are easier to synthesize than are dendrimers,<sup>1</sup> so they are comparatively inexpensive. Hyperbranched polymers could be desirable materials for toughening thermosets because such materials tend to be more soluble than similar linear polymers. Therefore, they are easier to introduce into thermoset prepolymers. Also, the highly branched structure minimizes entanglements, which should result in only minor increases in prepolymer viscosity,

Correspondence to: P. Heiden.

*Present address:* J. Xu, Department of Engineering, University of Minnesota, Minneapolis, MN.

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**Figure 1** Two-part thermoset system consisting of (A) BMI monomer and (B) bisallylphenol reactive diluent.

which would facilitate processing with low-pressure methods such as autoclave processing.

Hyperbranched polymers have not been studied before as tougheners in BMIs, although a team of investigators, in the first reported use of hyperbranched thermoplastics as thermoset tougheners, published a series of  $\operatorname{articles}^{2-4}$  using HBPs to toughen epoxy composites. This work was inspired by the same objectives as those which motivated that earlier work, that is, to toughen a brittle thermoset matrix while maintaining prepolymer processability. Those first investigators found that, with appropriate end groups, the fracture toughness of carbon fiberreinforced epoxy composites could be increased by  $\sim$  140% using only 5% HBP, without compromising either the thermoset  $T_g$  or the modulus. When the HBP content was increased to 10%, the epoxy toughness increased by 180%, although at that loading, a decrease in  $T_g$  and modulus was reported. The HBP employed was described only as a G3 polyester with a tetrafunctional core.<sup>3</sup>

In this article, the effects of the incorporation of commercially available HBP modifiers into BMI neat resins are described. Aliphatic polyesters possess low thermal stability and low modulus, and so are not ideal tougheners for highperformance composites. Ideally, BMI would be toughened with a hyperbranched thermoplastic based on a high-performance material, such as an aromatic polyimide or polyamide. This preliminary work sought to identify the key hyperbranched thermoplastic variables which control toughness and how the hyperbranched architecture alters the fracture toughness. For this purpose, commercial HBPs were suitable.

#### **EXPERIMENTAL**

#### Instrumentation

Viscosity measurements were made on a Bohlin VOR rheometric system. Molecular weight measurements were made on a Perkin–Elmer 601 SEC equipped with Phenomenex phenogel columns and a UV-vis detector. Dynamic mechanical analyses were performed on a Perkin–Elmer DMA 7 system in a three-point bending mode. Compact tension tests were performed on an Instron universal testing machine. Scanning electron microscopy (SEM) was done using a JEOL 35C SEM (at 15 or 20 kV) and an AMR 1000 SEM (at 20 kV). SEM specimens were gold-coated using an E5000 sputter coater.

#### Materials

A two-part BMI system (Matrimid<sup>®</sup> 5292A and Matrimid<sup>®</sup> (Hawthorne, NY) 5292B, Fig. 1) was purchased from Ciba Geigy. HBP was provided by Midland Molecular Institute (Midland, MI) or purchased from Aldrich Chemical Co. (Milwaukee, WI).

# Procedure for the Preparation of Linear Polyester (LPE)

Glutaric acid (10.000 g, 75.0680 mmol), 2,2-diethyl-1,3-propanediol (10.5100 g, 0.0795 mol), and *p*-toluenesulfonic acid (*p*-TSA, 0.0700 g,  $3.68 \times 10^{-4}$  mol) were added into a three-neck round-bottom flask equipped with a nitrogen inlet–outlet and a mechanical stirrer. The reaction was stirred and heated to 140°C for 4 h and then subjected to reduced pressure for 0.5 h to further advance the reaction by removal of residual water. The linear oligomer was characterized by SEC. (Theoretical  $M_n$ : 5419 g/mol,  $M_n$  found: 5400 g/mol.)

## Procedure for the Preparation of Acetyl-terminated HBP

To obtain HBP which would be unreactive with the BMI matrix, commercial hydroxy-terminated HBP was reacted with acetyl chloride. The reaction was carried out by dissolving HBP (G5, 3.0 g,  $7.0 \times 10^{-4}$  mol) in acetone (40 mL) in a three-neck

round-bottom flask equipped with a condenser and a pressure-equalizing addition funnel. Acetyl chloride (20.0 mL, 0.28 mol) was added to the solution over a period of 1 h while the system was flushed with nitrogen to facilitate removal of the HCl by-product. The reaction solution was heated at reflux by the reaction exotherm. When the exotherm had subsided, the reaction was stirred an additional 10 h at room temperature. The product was collected by removal of the acetone and excess acetyl chloride under reduced pressure at 50°C. FTIR of the product showed that the hydroxy band (3000-3700 cm<sup>-1</sup>) was substantially reduced but not eliminated. Therefore, the reactivity of the HBP with BMI was decreased but not eliminated. HBP recovery was quantitative but the acetylation was not quantified.

#### Procedure for the Preparation of Untoughened BMI Prepolymer

Prepolymer solutions without thermoplastic were prepared by adding B (35 g) to a reaction kettle equipped with a mechanical stir assembly and a nitrogen inlet/outlet. A (41 g) was added and the mixture was heated and stirred at 145  $\pm$  5°C until a clear solution was obtained (~ 0.3 h). Heat was discontinued and the solution was degassed under reduced pressure.

#### General Procedure for the Preparation of Thermoplastic Containing Prepolymer

B (35 g) was weighed into a reaction kettle equipped with a mechanical stir assembly and with a nitrogen inlet/outlet. The required mass of HBP or linear polyester (LPE) was added to B and heated and stirred until a clear solution was obtained. The temperature of the solution was raised or lowered as necessary to  $145 \pm 5^{\circ}$ C and A (41 g) was added. The mixture was stirred until a clear solution was obtained. Heat was discontinued and the solution was degassed.

#### **Molding Procedure**

Degassed solutions of thermoplastic were poured into a preheated mold, degassed again, and cured according to the following cycle:  $150^{\circ}C$  (5 h), then  $200^{\circ}C$  (3 h), and next  $250^{\circ}C$  (3 h).

#### **Mechanical Properties**

The fracture toughness was measured by compact tension. Specimen preparation and testing meth-

ods were previously described.<sup>5</sup> All  $K_{\rm IC}$  values are averages from multiple measurements from at least three test specimens.

#### Rheology

Viscosity measurements were made on solutions of HBP or LPE in B and measured on a cone and plate set up with a 25-mm cone diameter at a 5.4° angle to determine the zero shear viscosity. In selected cases, a second series of measurements were made on solutions containing newly prepared or newly purchased thermoplastics to confirm the reproducibility of the measurements.

### Determination of E' and Glass Transition Temperatures $(T_g's)$

Cured specimens were analyzed in a three-point bending mode by DMA to determine E'. The  $T_g$ 's were reported as the inflection points of the loss modulus (E'') from the DMA results.

#### **SEM Specimen Preparation**

Fracture surfaces from compact tension specimens were prepared by removing excess material from other faces by a saw and razor blade. The thickness of the specimens was kept below 3 mm to minimize electron charge accumulation on the surface. Samples were mounted to aluminum studs with epoxy glue and then coated with gold to a depth of 200-250 Å.

#### **RESULTS AND DISCUSSION**

Boogh and co-workers reported the first use of hyperbranched thermoplastics as thermoset tougheners in 1995 when they employed HBP to toughen an epoxy composite.<sup>2</sup> That team has con-tinued that research,<sup>3,4</sup> but little additional work has been undertaken with this approach to thermoset toughening. This article reports the first use of HBPs as tougheners for BMI resins. HBPs are not ideal tougheners for high-performance thermosets, due to the low modulus and thermal stability associated with aliphatic polyesters. However, the hyperbranched architecture is advantageous because, like dendrimers, hyperbranched materials are not prone to entanglements and so yield low-viscosity solutions.<sup>6</sup> Therefore, prepolymers modified with hyperbranched thermoplastic tougheners should be sufficiently low in viscosity to be processable by

autoclave techniques. Autoclave processing is often limited to processing pressures of 100-200 psi, so low prepolymer viscosity is essential. Hyperbranched high-performance materials (e.g., aromatic polyimides or polyamides) are more suitable thermoplastic modifiers, but the synthesis and characterization of hyperbranched polymers is difficult and costly. This preliminary research was intended to determine the effect of hyperbranched architecture, molecular weight, and loading on prepolymer viscosity and thermoset morphology and toughness. For these preliminary studies, the commercially available HBPs were suitable and convenient. Rheological and mechanical results of HBP modification of BMI are reported here, while the results of a similar study in epoxy are reported in a subsequent article.<sup>7</sup> Some morphological results are also presented, but a more detailed analysis of the effect of thermoplastic architecture, molecular weight, end group, and cure cycle on morphology are reported elsewhere.<sup>8,9</sup>

### Effect of Thermoplastic Architecture, Molar Mass, and Loading on Prepolymer Viscosity

Hydroxy-terminated HBPs (G2, 3, 4, and 5) with nominal  $M_n$ 's ranging from  $\sim 1,750$  g/mol (G2) to  $\sim 14,000$  g/mol (G5) were dissolved in B at 20% (w/w B). At higher G's, the branching efficiency decreases so the true  $M_n$ 's of the higher molecular weight HBPs are probably somewhat lower than the values reported. An hydroxy-terminated LPE ( $\sim 5400$  g/mol) with a repeat unit structure which was similar to the HBP was prepared and dissolved in B at 20% (w/w B) to study the effect of thermoplastic architecture on the viscosity. A representation of the structures of HBP and LPE is shown in Figure 2.

The viscosity of a series of solutions of HBP and LPE (in B) was measured at  $55^{\circ}$ C (Table I). The viscosity of unmodified B was measured at 0.6 Pa s at  $55^{\circ}$ C. When HBP was dissolved in B at 20% w/w (equivalent to ~ 9% w/w in the cured BMI), the viscosity of the solution was between ~ 2 and 3 Pa s, depending on the HBP molecular weight. It is interesting to note that under the same conditions the viscosity of the LPE control was measured at only 1.3 Pa s. To ensure the accuracy of these results, the viscosity of a series of viscosity standards was measured (Brookfield Engineering Laboratories) and then the viscosity of freshly prepared HBP prepolymer (from newly purchased samples) were measured immediately afterward.

In the lower viscosity range, the viscosity of the standards was measured at somewhat greater values ( $\sim 5-10\%$ ) than the true viscosity, but deviated in a systematic manner from the true values. The newly prepared HBP samples gave somewhat higher values than did the first samples, but the relative relationships in the viscosity measurements remained the same. Therefore, the specific numbers measured for the viscosity were subject to some error, but the error was systematic.

Hyperbranched polymers are more easily prepared than are dendrimers; nevertheless, their synthesis is more difficult than that of linear thermoplastic, and few suitable monomers are commercially available. The reason that difficult-toprepare hyperbranched thermoplastic would be selected over a similar but easy to prepare linear thermoplastic would be the presumption that the HBP architecture would afford a less viscous prepolymer. In the case of these aliphatic polyesters, there does not appear to be a viscosity advantage to selecting the hyperbranched architecture over a linear, low molecular weight oligomer. However, earlier,<sup>5</sup> it was found that the viscosity of a linear aromatic imide of  $\sim 5000$  g/mol, measured under identical conditions of concentration and temperature, was 31 Pa s, which is considerably higher than the LPE viscosity. Therefore, a hyperbranched polyimide might afford a viscosity advantage over linear imide oligomers.

# Effect of Thermoplastic Loading and End-group on Viscosity

The effect of thermoplastic loading on prepolymer viscosity was measured using the lowest and highest molecular weight HBPs (G2 and G5) and the LPE control (Table II). The effect of the end group was also studied using G5 HBP which had been modified to possess acetyl end groups rather than hydroxyl groups. The viscosity of the LPE showed relatively little increase when the loading increased from 20 to 50% loading in B, while the G2 and G5 HBP showed significant viscosity increases in going to the higher loading. However, while the G2 HBP is reported to have a molar mass of only  $\sim 1750$  g/mol, which is much lower than the 5400 g/mol of LPE, the viscosity of the HBP was an order of magnitude greater. Furthermore, the viscosity of the G5 HBP was close to that of the G2 HBP (32 Pa s versus nearly 25 Pa s) despite the fact that its molar mass is reported at nearly 14,000 g/mol. However, when the G5



Figure 2 Representation of (a) hydroxy-terminated HBP (G3) and (b) LPE.

HBP was acetylated, the viscosity at 50% loading only increased to 6.2 Pa s. Therefore, it appears that the viscosity of the HBPs in B is more dependent on the number and identity of end groups than on molar mass.

# Effect of Thermoplastic Architecture and Molecular Weight on Mechanical Properties

HBP (G2, 3, 4, and 5) and LPE were incorporated into BMI at 9% (w/w thermoset). The fracture toughness was measured by compact tension. The

 $T_g$  and dynamic storage modulus (E') were measured by DMA. The fracture toughness increased steadily with HBP molecular weight. The lowest molecular weight HBP (G2) increased the fracture toughness ( $K_{\rm Ic}$ ) by 80% to 0.75 MPa m<sup>1/2</sup>, up from a value of only 0.42 MPa m<sup>1/2</sup> for the untoughened control. The G3 and G4 HBP gave slightly higher increases, 90 and 114%, respectively, over the untoughened control. The highest value was obtained with the G5 HBP which increased the  $K_{\rm Ic}$  by 138% over the control. However, the BMI modified with LPE gave a 119%

Thermoplastic	${M_n}^{ m a}$ g/mol	Viscosity <sup>b</sup> (Pa s)	$\Delta \ { m Viscosity} \ (\%)$	
None	_	0.6	_	
LPE	$5400^{\circ}$	1.3	117	
G2	1750	2.1(4.3)	233(617)	
G3	3600	2.6(4.9)	333 (717)	
G4	7300	3.4(5.4)	450 (800)	
G5	14,000	3.1(5.1)	400 (750)	

Table IEffect of Thermoplastic Molar Massand Architecture on Viscosity

Viscosity was measured at 20% (w/w in B) at 55°C.

<sup>a</sup> Molecular weight reported by Aldrich Chemical Co. <sup>b</sup> The second set of measurements were made immediately

following measurement of viscosity standards.

<sup>c</sup> Molecular weight measured in THF by SEC against polystyrene standards.

increase in fracture toughness, which is, within error, essentially the same value as was obtained for the HBP G4 and G5.

All the HBPs caused a significant decrease in the E' as well as decreases in the thermoset  $T_g$ , but the greatest decreases occurred with the G4 and G5. The LPE caused a small decrease in the  $T_g$ . The results indicate that neither the LPE nor the HBPs fully phase-separated from the BMI matrix, but the smaller decrease resulting from the LPE indicates that it was less miscible with the matrix than was the HBP. The results are presented in Table III.

# Effect of Thermoplastic Architecture and Molecular Weight on Morphology

SEM analysis of the fracture surfaces of the thermoplastic-modified BMIs suggest possible reasons for the differences in toughness and thermomechanical properties with thermoplastic architecture and molar mass. A more detailed morphological study of HBP-modified BMIs is the subject of a separate article,<sup>8</sup> but the effect of the HBP molar mass (9% w/w thermoset) can be seen in the SEMs below along with the SEM of the LPE-modified BMI for comparison (Fig. 3). In all cases, the HBP phase-separated into spherical domains, but the size of the dispersed phase and adhesion between the phases was dependent on the HBP molecular weight. Lower molecular weight HBP (G2 and G3) formed smaller ( $\sim 5-10$  $\mu$ m) and more uniform spherical-shaped domains. Also, a large number of particles underwent cavitation and there was no evidence of matrix deformation around the cavities.

By contrast, the G4 and G5 HBP formed large, irregularly shaped domains within the BMI continuous phase. The domain size was polydisperse and varied from 1 to 60  $\mu$ m, with the largest particles possessing BMI inclusions in the HBP dispersed phase. The G4 and G5 HBP domains show greater adhesion to the BMI matrix than do the G2 and G3 HBPs, as evidenced by the lesser number of particles which underwent cavitation. When the smaller particles of G4 and G5 HBP did undergo cavitation, there was some evidence of matrix deformation around the cavity.

There are some claims in the literature that smaller particles are more effective at toughening than are larger particles (e.g., ref. 10). Those authors suggested that this might be the case since only a small area around the particles is subject to plastic deformation and small particles which undergo cavitation facilitate shear yielding and so toughen the thermoset. In this work, the G4 and G5 HBPs formed larger particles and also toughened more effectively. This may be because particles from G4 and G5 HBP appeared to adhere more effectively to the matrix than did the G2 and G3 HBP, but when the G4 and G5 HBP particles did undergo cavitation, the matrix around the cavity underwent some deformation. This was not observed with the G2- and G3-modified systems. Therefore, the G4 and G5 HBP possessed more compatibility with the matrix than did the G2 and G3 HBP, which facilitated matrix yielding. This added compatibility and greater adhesion to the matrix are presumably due to the greater number of reactive end groups on the higher molecular weight HBP. Usually, greater molecular weight facilitates phase separation from the matrix rather than promoting compatibility. However, with the HBP architecture, the compatibility with

Table IIEffect of Temperature and HBPLoading on Solution Viscosity

		TP Identity			
TP Loading (w/w B)	LPE (Pa s)	G = 2 (Pa s)	G = 5 (Pa s)	$\begin{array}{l} \mathrm{G} = 5_{\mathrm{Ac}}{}^{\mathrm{a}}\\ (\mathrm{Pa} \ \mathrm{s}) \end{array}$	
20% 50%	$\begin{array}{c} 1.3\\ 2.7\end{array}$	$\begin{array}{c} 2.0\\ 24.7\end{array}$	$\begin{array}{c} 3.0\\ 32.0\end{array}$	$\begin{array}{c} 2.1 \\ 6.2 \end{array}$	

Viscosity was measured at 55°C in B.

<sup>a</sup> Acetyl-terminated HBP.

Thermoplastic	$M_n^{\mathbf{a}}$ (g/mol)	$\begin{matrix} K_{\rm Ic} \ ({\rm MPa} \\ {\rm m}^{1/2}) \end{matrix}$	$\Delta K_{ m Ic} \ (\%)$	$T_g$ (°C)	$E'~{ m Pa} imes 10^9$	
					30°C	200°C
None	_	$0.42\pm0.10$	_	265	3	2
LPE	$5400^{ m b}$	$0.92\pm0.04$	119	256	0.8	0.7
G = 2	1750	$0.75\pm0.05$	79	250	0.6	0.6
G = 3	3600	$0.8 \pm 0.1$	90	260	0.7	0.6
G = 4	7300	$0.90\pm0.05$	114	230	0.7	0.6
G = 5	14,000	$1.0 \pm 0.1$	138	225	0.7	0.6

Table III Effect of Hyperbranched Polymer (9% w) on Mechanical Properties of BMI

All BMI specimens were cured using the same cure cycle.

<sup>a</sup> Molecular weight reported by Aldrich Chemical Co.

<sup>b</sup> Measured by SEC in THF against polystyrene standards.

the matrix will be controlled by the end groups, and clearly as molecular weight increases, the importance of the end groups will dominate the effects of the modifier on the matrix. The greater compatibility of the G4 and G5 HBP with the BMI is corroborated by the fact that these thermoplastics caused significant decreases in the thermoset  $T_g,$  while far lesser  $T_g$  decreases resulted with the G2 and G3 HBPs.

The volume fractions of the phase-separated material may also play a significant role in the differences in toughness, but were not calculated because the BMI inclusions in the G4 and G5 HBP-dispersed phases would make the error too



Figure 3 SEMs of BMI modified with 9% (w/w thermoset) of (a) G2 HBP; (b) G3 HBP; (c) G4 HBP; (d) G5 HBP; (e) LPE.

large for useful comparison. By contrast, the BMI modified with LPE showed a mixed morphology on the fracture surface. The dominant morphology was a continuous thermoset phase which contained dispersed thermoplastic domains of  $\sim 1-40$  $\mu$ m, but regions of thermoplastic continuous phase were also evident. The morphological differences between the HBP and LPE-modified BMI are thought to be due to a solubility difference between the HBP and LPE modifier. The fact that continuous linear thermoplastic domains existed in the sample at such a low loading level  $(\sim 9\% \text{ w/w})$  suggests that the linear thermoplastic is not as compatible with the BMI as is the HBP. even in the uncured prepolymer. It is suspected that, despite the transparent appearance of the prepolymer solution, the linear thermoplastic was not uniformly dispersed in the prepolymer. On heating, the system cured before the linear thermoplastic ever became truly homogeneously dispersed within the prepolymer. Consequently, the thermoplastic formed an irregular continuous phase in those regions where it was present in a sufficiently large volume fraction. This hypothesis is suggested based on the theoretical calculations of Rakutt and co-workers<sup>11</sup> who found that phase inversion should occur at approximately 26% (w) of the thermoplastic. Therefore, the phase-inverted domains probably occurred in areas where, at the onset of phase separation, the local thermoplastic concentration was in the range of 26%, rather than the theoretical concentration of 9% assumed for an homogeneous prepolymer solution. In regions where the thermoplastic volume fraction was below the critical value for phase inversion, the LPE formed large  $(1-40 \ \mu m)$ , spherical dispersed domains. It is also evident that the linear thermoplastic particles had undergone more cavitation during fracture, suggesting that these domains did not adhere as well to the BMI matrix as did the HBP. This is not surprising since hydroxy end groups are very reactive with BMI and the functionality of the HBP is greater than for a linear hydroxy-terminated polyester.

It is interesting to note that the LPE-modified BMI was nearly as tough as was the G5 HBPmodified BMI. The SEMs show that, like the G5 HBP, the toughening mechanism is cavitation, but very little matrix deformation was observed around the cavitated sites. It was suggested by Riew and Smith,<sup>12</sup> on studying rubber-toughened epoxy, that cavitation is a minor toughening mechanism because the rubber particles which bonded to the matrix expand during cure and shrink on cooling. Therefore, they exist in a state of triaxial stress and little energy is required to cavitate the particles.

HBP-modified thermosets resemble rubbermodified thermosets in several ways, including morphological features and by virtue of the fact that HBP is a low  $T_g$  material. However, the HBP phase-separated particles may not exist in the state of triaxial stress described by Riew and Smith because of their architecture. If the branching efficiency is sufficiently high, unlike typical rubber molecules, the densely packed spherelike molecule may not have a sufficient degree of freedom to allow it to undergo significant expansion or contraction. If this is the case, cavitation would be expected to be a higher-energy process for HBPs than for other particles. However, this argument would not explain why the LPE toughened approximately as effectively as did the G4 and G5 HBP-modified BMIs unless the low molecular weight of the LPE allowed it to phase separate in domains which were also relatively free of triaxial stress.

Based on the fracture surfaces observed, cavitation (with some matrix deformation for G4 and G5 HBP) appears to be the primary energy-absorbing processes. The measured values for fracture toughness show that the energy required to cavitate the G4 and G5 HBP particles is essentially the same. Although more cavitation was observed with the G2- and G3-modified BMIs, less energy was reguired to cavitate these particles. The logical explanation would be that less adhesion existed between the matrix and the particles due to the lower functionality. However, the LPE toughened as effectively as did the G4 and G5 HBP, and the functionality for the LPE was only 2. The LPE particles did undergo considerable cavitation and they were larger particles than were those of the G2 and G3 HBP and, also, phase-inverted domains were present. Therefore, it is possible that the larger LPE particle size required additional energy to cause cavitation despite the lesser matrix adhesion. Also, the inverted LPE domains may have provided pathways for energy dissipation not available to the HBP-modified BMIs.

### CONCLUSIONS

HBP modifiers with systematically varied molar masses were introduced into BMI (9% w/w ther-

moset). The viscosity,  $T_g$ , and fracture toughness were measured as a function of the HBP molar mass and compared to those of an LPE control  $(\sim 5400 \text{ g/mol})$ . The fracture toughness was found to increase with HBP molecular weight up to a maximum increase of 138%, which is similar to the results found by earlier researchers with HBP-modified epoxy. However, unlike the results found with epoxy, the HBP modifiers possessed compatibility with the BMI matrix, resulting in significant decreases in both the  $T_g$  and E'. It was also found that an LPE oligomer toughened the BMI as effectively as did the HBPs and compromised the  $T_{\sigma}$  to a lesser extent than did the HBPs. The viscosity of the LPE control was similar to the HBPs at lower loadings, and at higher loadings in B, the viscosity was substantially lower. The viscosity of the HBPs appeared to be more dependent on the number and identity of the end group than on the molar mass itself. The results show that the hyperbranched architecture does not always afford an advantage in toughness or viscosity over lower molar mass thermoplastic modifiers.

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