### Investigation of Readily Processable Thermoplastic-Toughened Thermosets. V. Epoxy Resin Toughened with Hyperbranched Polyester

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ABSTRACT: This article describes the use of hyperbranched polyester oligomers (HBPs) as modifiers for epoxy thermosets. The effect of HBP molar mass, end group, and loading on prepolymer viscosity, thermoset fracture toughness,  $T_{\sigma}$ , and high-temperature dynamic storage modulus (E') were measured. The HBP molar mass was systematically increased from nominal values of  $\sim 1750$  g mol (Generation 2, or G2) up to  $\sim$  14,000 g mol (Generation 5, or G5), which corresponds from a low of two layers of monomer up to a maximum of five layers of monomer around the central core. Toughness increased only modestly with the molar mass of the HBP. At 7% loading in the epoxy thermoset, the G5 HBP increased toughness by  $\sim 60\%$  over the untoughened control. Toughness increased to 82% above the untoughened control at a loading of 19% G5 HBP, but the toughness decreased at 28% HBP loading. The  $T_g$  and E' were influenced by the HBP modifier, but the effect was not systematic and may have been due to competing effects of HBP molar mass and end group. The effect of the architecture of the thermoplastic modifier was investigated by introducing a linear aliphatic polyester ( $\sim 5400$  g mol) with a repeat unit structure, which was similar to that of the HBP. At the molecular weight range investigated, neither the prepolymer viscosity nor the thermoset toughness of the HBP-epoxy was significantly different from that of the linear polyester in epoxy. Preliminary results are presented showing the effect of thermoplastic molecular weight and architecture on morphology. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 151-163, 1999

**Key words:** hyperbranched polymer; thermoplastic toughening; autoclave processable; thermoset morphology

#### INTRODUCTION

Hyperbranched polymers have a lower branching efficiency than dendrimers but possess many of the same useful properties. The highly branched architecture minimizes chain-chain entanglements and so imparts both high solubility and low melt viscosity to these polymers. These properties, coupled with the fact that their synthesis is less costly than dendrimer synthesis,<sup>1</sup> could make such materials useful tougheners for thermosets.

The hyperbranched thermoplastics are not true geneological species, that is, each layer of monomers is not built up in a separate reaction step around the central core, but in this work, the hyperbranched polyesters (HBPs) are described using that type of terminology. That is, if two or

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three monomer layers exist around the core, the species is termed G2 and G3 HBP, respectively.

HBPs<sup>1,2</sup> were first studied as tougheners for thermosets by Boogh and coworkers.<sup>3-5</sup> That research was done with the same motivation that inspired this work, that is, to toughen a brittle thermoset matrix while maintaining prepolymer processability. Boogh and coworkers reported that with the appropriate choice of end groups, an HBP loading of 5% increased the fracture toughness of an epoxy composite by  $\sim 140\%$  with no effect on  $T_{\sigma}$  or E'. That work focused on epoxy composite properties and the phase separation process. The work reported here was done with the objective of identifying structural variables of hyperbranched polymers, which affect processability and fracture toughness. Ideally, high-performance thermosets would be toughened with high-performance thermoplastics, such as aromatic polyimides or polyamides. However, the synthesis of a high-performance hyperbranched material was beyond the scope of this work, so commercially available HBPs were used here. Although aliphatic polyesters possess low thermal stability and modulus, and so are not suitable for toughening thermosets intended to be used in high-performance applications, they are suitable for identifying variables that should be controlled when hyperbranched polymers of any type are employed as thermoset tougheners. Some morphological results are presented, but a more detailed morphological study of these thermosets is the subject of a separate article.<sup>6</sup>

### MATERIALS

Epoxy (Epon® 825) was purchased from Shell (Houston, TX). All other chemicals, including HBP (hydroxy-terminated) and 4,4'-diaminodiphenylsulfone (DDS) were purchased from Aldrich Chemical Company (Milwaukee, WI). A representation of a G3 HBP is given in Figure 1(a). Linear polyester [Fig. 1(b)] and modified HBPs were prepared as described below.

### **INSTRUMENTATION**

Viscosity measurements were made on a Bohlin VOR rheometer. Differential scanning calorimetry (DSC) was performed using a Shimadzu DSC 50. Molecular weight measurements were made on a Perkin–Elmer 601 SEC equipped with Phenomenex phenogel columns and a ultraviolet–visible (UV–VIS) detector. Dynamic mechanical analyses were performed on a Perkin–Elmer DMA 7 system in the three-point bending mode. Compact tension tests were performed on an Instron Universal Testing Machine. Scanning electron microscopy (SEM) was done using an AMR 1000 SEM (at 20 kV). SEM specimens were gold coated using an E5000 Sputter Coater.

#### **EXPERIMENTAL**

## Procedure for the Preparation of Linear Polyester (LPE)

Glutaric acid (10.000 g/75.068 mmol), 2,2-diethyl-1,3-propanediol (10.510 g/79.501 mmol), and ptoluenesulfonic acid (p-TSA, 0.0700 g/3.68 × 10<sup>-4</sup> 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. The reaction solution was 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 size exclusion chromatography (SEC) (theoretical  $M_n$ , 5419 g/mol;  $M_n$  found, 5400 g/mol).

### Procedure for the Preparation of Acetyl-Terminated HBP (HBP<sub>Ac</sub>)

HBP was reacted with acetyl chloride to convert hydroxyl end groups to acetyl end groups. The reaction was carried out by dissolving HBP (G5, 3.0 g) in acetone (40 mL) in a three-neck, roundbottom 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 maintained 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 volatiles under reduced pressure. The solid product was dried at 50°C. The hydroxyl band [Fourier transform infrared, (FT-IR) 3000-3700 cm<sup>-1</sup>] was significantly reduced but not eliminated. Residual hydroxyl groups were not quantified.



**Figure 1** Structure of the (a) hydroxy-terminated G3 HBP and (b) linear polyester (LPE).

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

Epoxy and DDS were combined (9 parts DDS to 30 parts epoxy) and heated with rapid stirring to 190°C until the DDS dissolved. The homogenous solution was degassed.

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

Thermoplastic polyester was dissolved in acetone, and the solution was added to epoxy. The mixture was stirred and heated until an homogenous solution was obtained. The acetone was then removed under reduced pressure. The temperature was raised to  $180-190^{\circ}$ C, and DDS cure agent (9 parts for each 30 parts of epoxy) was added while the mixture was rapidly stirred. Once an homogenous solution was obtained, the solution was degassed. Thermoplastic was dissolved in epoxy at 10, 20, 30, and 50% w thermoplastic/w epoxy, which corresponded to 7, 13, 19, and 28% w thermoplastic/w thermoset (epoxy, DDS, and thermoplastic).

#### Molding Procedure

The degassed solution containing thermoplastic was poured into a preheated mold and degassed again. The prepolymer was cured at  $140^{\circ}$ C for 8 h and then post-cured at  $200^{\circ}$ C for 1 h.

#### **Thermal Analysis of Prepolymer**

HBP (G2, G4) was blended with epoxy (9% w/w) and heated at 5°C/min from 25 to 200°C.

Thermoplastic	$M_n^{\rm b}$ (g/mol)	Viscosity (Pa s)	$\Delta$ Viscosity (%)	Appearance (30°C)
None	_	2.1	_	Transparent
LPE	$5400^{\circ}$	3.9	86	Transparent
G2	1750	—	—	Opaque
G3	3600	_	_	Opaque
G4	7300	_	_	Opaque
G5	14,000	_	_	Opaque
$G5_{Ac}$		5.0	138	Transparent

Table I Effect of Thermoplastic Molar Mass on Prepolymer Viscosity<sup>a</sup>

 $^a$  Measured at 10% (w/w epoxy) at 30°C. At 30°C, only  $\rm G5_{Ac}$  HBP and LPE dissolved completely for a reliable viscosity.

<sup>b</sup> Molecular weight reported by Aldrich Chemical Company.

<sup>c</sup> Measured in tetrahydrofuran (THF) by SEC against polystyrene standards.

#### **Mechanical Properties**

Cured test specimens were cut and tested by compact tension according to a procedure previously described.<sup>7</sup> All  $K_{\rm IC}$  values reported are the averages from numerous measured values with multiple test specimens.

#### Rheology

The viscosity of degassed thermoplastic-containing epoxy solutions was measured at 30 and 90°C on a cone and plate set up with a 25-mm cone diameter at a 5.4° angle to determine zero shear viscosity. The measurements were reproducible, but the calibration curve, using standard fluids (Brookfield Engineering Standards, Stoughton, MA), showed a systematic error, so the viscosity data are adjusted for this error.

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

Cured specimens were analyzed in three-point bending mode by dynamic mechanical analysis (DMA) to determine E'. Thermoset  $T_g$ s were determined as the temperature at which the E' began to decrease.

### **RESULTS AND DISCUSSION**

Hydroxy-terminated HBPs and a linear polyester (LPE) with a repeat unit structure, which was similar to that of the HBP, were introduced into epoxy. Prepolymer viscosity was measured at dif-

ferent thermoplastic loadings and temperatures. The toughness  $(K_{\rm Ic})$  of cured neat resin plaques was measured by compact tension. The  $T_g$  and E' of cured plaques was determined by DMA in the three-point bending mode. Properties were correlated with thermoplastic architecture, molar mass, and loading. Fracture surfaces were evaluated by SEM to determine the effect of thermoplastic architecture on morphology and to study the relationship between architecture and toughness.

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

The effect of thermoplastic architecture and molar mass on viscosity was measured at 10% loading in epoxy resin (equivalent to 7% in the thermoset). The viscosity was measured at 30°C (Table I). The viscosity of pure epoxy resin was 2.1 Pa S at 30°C. Incorporation of the thermoplastic increased the viscosity to  $\sim 3-5$  Pa s. At this temperature and concentration, the viscosity of the LPE-modified epoxy was lower than that of the acetylated G5 HBP (G5<sub>Ac</sub>). The hydroxy-terminated HBPs did not form transparent solutions at this temperature.

## Effect of Thermoplastic Loading, End Group, and Temperature on Prepolymer Viscosity

The effect of thermoplastic loading, end group, and solution temperature on the viscosity of epoxy containing LPE and HBP was investigated. The viscosity was measured using solutions of 10,

TP Loading <sup>a</sup> (%)	TP Identity	LPE Control	G2	G5	G5 <sub>Ac</sub>
10	(30°C)	3.9	_	_	5.0
	(90°C)	0.1	0.03	0.04	0.04
30	(30°C)	7.4	_	_	5.2
	(90°C)	0.12	0.09	0.09	0.07
50	(30°C)	10.9			—
	(90°C)	0.17	0.18	0.30	0.17

Table IIEffect of Thermoplastic Loading andTemperature on Viscosity (Pa s)

 $^{\rm a}$  10, 30, and 50% in epoxy correspond respectively to 7, 19, and 28% w/w thermoset.

30, and 50% thermoplastic (w/w epoxy) at 30 and 90°C. The effect of HBP end groups on viscosity was studied by converting the hydroxyl groups of G5 HBP to acetyl groups. The results are given in Table II. At 90°C, all the thermoplastics yielded transparent solutions and had very low viscosity. but the percentage difference between the viscosity of the LPE-modified epoxy and the G5 HBPmodified viscosity was significant. DSC analysis (Fig. 2) of epoxy-HBP blends (no DDS) showed no exotherm, so the viscosity difference was not due to a reaction between the hydroxy end groups and the epoxide ring. The viscosity difference may be an end group effect due to hydrogen bonding since the HBP  $G5_{Ac}$  had a lower viscosity than the G5 HBP or may simply be due to entanglements since branching decreases with increased generation. While the G5 HBP certainly had a lower viscosity than would an LPE with the same molar mass, this result is significant since the mechanical properties of the G5 HBP-modified epoxy were not significantly better than those of the low-molar-mass LPE-modified epoxy (7% w/w thermoset; Table III). If neither the rheological properties of the prepolymer (Table II) nor the mechanical properties of the modified thermoset (Table III) are better than those obtained from a low-molecular-weight linear thermoplastic, then there is no advantage to employing a more costly and difficult to prepare HBP over a lower cost linear thermoplastic.

## Effect of Thermoplastic Architecture and Molar Mass on Fracture Toughness

#### Background

The mechanism(s) by which thermoplastics increase the toughness of thermosets is an area

that has been extensively researched, and yet, is still under debate. It is, however, generally believed that phase separation is essential<sup>7-14</sup> and that the nature of the dispersed phase, that is, domain size and dispersity of size,<sup>10-14</sup> arrangement of the phases,<sup>15,16</sup> and volume fraction of the dispersed phase,<sup>10,14</sup> all play a critical role in toughening. Adhesion of the thermoplastic to the matrix is also widely thought to be essential.<sup>17</sup> Thermoplastic molar mass also plays a role in toughness but probably does so by influencing the phase separation process and degree of phase separation, and, therefore, the morphology, rather than being a result of the molar mass and toughness of the thermoplastic modifier itself since increases in toughness have been observed even with very low molar mass tougheners.<sup>7–9,18</sup>

The objective of this part of the research was to determine the following. (1) In what ways does the hyperbranched architecture affect thermoset toughness, and why? (2) Given the fact that a hyperbranched thermoplastic is more difficult and costly to prepare than linear thermoplastic, does the hyperbranched architecture offer any inherent advantage for the toughness of the thermoset? To accomplish these objectives, the toughness and morphology of epoxy was studied after modification with LPE and HBP at different loadings.

## Effect of Thermoplastic Architecture on Fracture Toughness

The effect of thermoplastic architecture on toughness was studied by incorporating LPE (5400 g



Figure 2 DSC thermograms of (a) G2 HBP, (b) G4 HBP, (c) G2 HBP–epoxy blend, and (d) G4 HBP–epoxy blend.

Theoretical Generation	$M_n^{\ \mathrm{b}}$ (g/mol)	Functionality <sup>b</sup> (—OH Equivalents)	$K_{\rm Ic}$ MPa m $^{1/2}$	${\Delta K_{ m Ic} \over (\%)}$
Nono			$05 \pm - 01$	
LDE	 E 400			
LPL	5400	Z	0.63 + - 0.05	20
2	1750	16	0.42 +/- $0.05$	
3	3600	32	0.6 + / - 0.1	20
4	7300	64	0.7 + / - 0.1	40
5	14,000	128	0.8 + / - 0.1	60

Table III Effect of Thermoplastic Molar Mass and Architecture on Fracture Toughness  $(K_{Ic})^a$ 

<sup>a</sup> Thermoplastic loading of 7% (w/w thermoset)

<sup>b</sup> HBP data was reported by Aldrich Chemical Co.; LPE molar mass was measured by SEC (polystyrene standards).

mol) and HBP (G4, theoretical  $M_n$  7300 g mol) into epoxy. The theoretical molar mass of the HBP assumes 100% branching efficiency. The true molar mass was unknown, but assuming 90% branching efficiency, the molar mass of the G4 HBP would be ~ 6000 g mol.

The fracture toughness of the LPE and G4 HBP-modified epoxy (7% w/w thermoset) was measured at 0.63 and 0.7 MPa m<sup>1/2</sup>, respectively (Table III), so, within error, the thermoplastic architecture resulted in no difference in the toughness.

The fracture surfaces were observed by SEM, and the morphology of the G4 HBP-modified epoxy [Fig. 3(c)] was essentially identical to the LPE-modified epoxy (Fig. 4). Both thermoplastics formed spherical domains dispersed within the continuous epoxy phase. The average domain size was  $\sim 2-3 \ \mu m$  for the G4 HBP-modified epoxy and  $\sim 3 \ \mu m$  for the LPE-modified epoxy. The thermoplastic domains in both thermosets underwent extensive cavitation, suggesting poor adhesion between the thermoplastic and the epoxy.

Alcohols could potentially react with an epoxide ring, but if reaction occurred, the G4 HBP, with 64 hydroxy groups (Table III), should have been more effectively locked to the matrix than the difunctional LPE, which should have resulted in a higher fracture toughness. The lack of a significant difference in toughness or cavitation between the LPE and HBP-modified epoxy suggested that no reaction had occurred between the hydroxy groups and the epoxy matrix. This was confirmed by DSC analysis. The HBP was blended with the epoxy, without DDS cure agent, and the blend was heated (5°C/min) from 25 to 200°C, which was the maximum temperature reached during the cure. There was no evidence of any reaction exotherm (Fig. 2).

#### Effect of HBP Molar Mass on Fracture Toughness

The fracture toughness of epoxy was measured with HBP thermoplastic modifiers with a different molar mass but at constant thermoplastic loading (7% w/w thermoset). The results are given in Table III. Increasing the HBP molar mass appeared to increase fracture toughness steadily but slightly. In fact, within error, the LPE and the G3 and G4 HBPs gave the same fracture toughness  $(0.6-0.7 \text{ MPa m}^{1/2}, \text{ or a} \sim 20-40\%$  increase over the control value). The G5 HBP, with a nominal molar mass of  $\sim$  14,000 g/mol (the true molar mass was likely to have been somewhat lower than the 14,000 g mol reported by Aldrich, due to a branching efficiency below 100%), yielded only a 60% increase in toughness above the unmodified control (0.8 MPa  $m^{1/2}$ ). Considering the error range, this toughness increase was not significantly greater than the other HBPs. The G2 HBP  $(\sim 1,750 \text{ g mol})$  gave no increase in toughness.

The morphology of the modified thermosets did not vary significantly with either the thermoplastic architecture or molar mass of the HBP, except in the case of the G2 HBP-modified epoxy. In all cases, the thermoplastic formed spherical domains within a continuous epoxy phase. The domains underwent extensive cavitation, which indicated that there was no significant interfacial adhesion between thermoplastic and matrix. The G2 HBP modified epoxy differed from the other thermosets only in that the domain size was smaller than the higher molar mass HBPs. The dispersed HBP domains of the G2 HBP-modified



**Figure 3** SEM micrographs of the fracture surfaces of HBP-modified epoxy (7% w/w): (a) G2 HBP; (b) G3 HBP; (c) G4 HBP; (d) G5 HBP.

epoxy had an average diameter below 1  $\mu$ m [Fig. 3(a)] and gave no increase in toughness. The G3–G5 HBP-modified epoxy thermosets possessed dispersed HBP domains with average diameters of ~ 2–3  $\mu$ m [Fig. 3(b)–(d)] and gave fracture toughness increases of ~ 20–60%. The average diameter of the LPE domains in the LPE-modified epoxy was also ~ 3  $\mu$ m (Fig. 4) and yielded a fracture toughness increase of ~ 30%. These results suggest the toughness in hydroxy functionalized HBPs was dependent on particle diameter, with a requirement that the particles be at least 1  $\mu$ m to enhance toughness, but otherwise were largely, although possibly not completely, independent of molar mass.

The toughness of the G5 HBP-modified epoxy was only slightly greater than the value mea-

sured for the G4 HBP and LPE-modified thermosets, and the difference was sufficiently small so that it may not be significant. If the toughness difference was real, the difference does not appear to be due to the morphology itself, which was very similar for these thermosets. It is possible that the higher molar mass of the G5 HBP allowed some energy dissipation mechanism to occur within the G5 HBP domains themselves prior to cavitation that was not available to the lower molar mass thermoplastics, and this resulted in the slightly higher degree of toughness. The relationship between increased thermoplastic molar mass and increased toughness has been well established with linear thermoplastics,<sup>8,9</sup> but has not been studied with HBPs. Higher molar mass normally promotes phase separation, and the phase separation, in turn, typically enhances toughness. The G4 and G5 HBPs differ from each other in molar mass (7300 g/mol versus 14,000 g/ mol) but also in the number of functional end groups. This is a critical distinction between linear and HBP thermoplastics. The G5 HBP possesses 128 OH end groups, or 64 more hydroxyl end groups than the G4 HBP, and 126 more than the difunctional LPE. The large number of HBP end groups must influence the HBP compatibility with the uncured epoxy and/or the cured matrix. Therefore, the simple correlation between increased molar mass and increased phase separation that holds with linear thermoplastics may not hold with hyperbranched thermoplastics. The correlation between molar mass and phase separation was not studied in this work, but it is suspected that the phase separation process of hyperbranched thermoplastics, in general, and HBPs specifically, is dominated the type and number of end groups. It is speculated here that if the higher toughness found for the G5 HBP is real, and there is no difference in the degree of phase separation, that the slightly higher difference in toughness most likely arises from a difference in the particle size and distribution of sizes, or possibly slightly higher interfacial adhesion between the HBP and the epoxy matrix due since hydrogen bonding could occur between the phases.

The toughness of the G5 HBP was not sufficiently larger than that of the LPE-modified epoxy to justify the added cost. However, it must be pointed out that even though the LPE toughened as effectively as high molar mass HBPs, the high



Figure 4 SEM micrograph of the fracture surface of LPE-modified epoxy (7% w/w).

Table IV Effect of HBP Molar Mass on  $T_g$  and E' at 7% Loading

			$E'~(\mathrm{Pa} imes10^8)$	
Thermoplastic	$\begin{array}{c} M_n{}^{\rm a} \\ ({\rm g/mol}) \end{array}$	$T_g$ (°C)	30°C	125°C
None	_	157	2.3	1.8
LPE	5400	142	2.1	1.4
G2	1750	180	2.2	1.5
G3	3600	140	2.0	1.4
G4	7300	152	2.5	1.7
G5	14,000	160	2.4	1.6

<sup>a</sup> HBP molar mass was reported by Aldrich Chemical Co.; LPE mass was measured by SEC (polystyrene standards).

functionality of HBPs ought to be able to offer two inherent advantages over linear thermoplastics, which are the use of end groups to "fine tune" the phase separation process, and the use of appropriate end groups to react with the matrix to effectively lock the domains to the matrix. Consequently, end group modification of HBPs ought to be able to result in a more effective thermoplastic toughener. This was already illustrated in the reports of Boogh and coworkers.<sup>3-5</sup> Those researchers used an HBP with end groups, which could react with the epoxy matrix, and they measured higher toughness values than those found here, but they did not make a linear control with reactive end groups. The work here showed no advantage for an HBP architecture over a linear low molar mass thermoplastic, but if the architecture can afford an advantage, this data suggests reaction between the matrix and the dispersed HBP phase is essential to take advantage of the increased number of end groups to promote interfacial adhesion.

# Effect of HBP Architecture and Molar Mass on $T_{\rm g}$ and $E^\prime$

The  $T_g$  and dynamic storage modulus (E') of the thermoplastic-modified epoxy resins cured at high temperature are reported in Table IV. It is clear that the HBP and LPE have an effect on the  $T_g$  and on the high-temperature E', but there was no obvious trend. The  $T_g$  of the G2 HBP-modified epoxy actually increased over that of the unmodified control, but when the G3 HBP was used, there was a 17°C decrease below the  $T_g$  of the unmodified epoxy. Each subsequent generation on the HBP increased the  $T_g$  by  $\sim 10°$ C so that

				E' (Pa × 10 <sup>8</sup> )	
Thermoplastic (%)	$K_{\rm Ic}$ MPa m $^{1/2}$	$\Delta K_{ m Ic} \ (\%)$	$\begin{array}{c} T_g \\ (^{\circ}\mathrm{C}) \end{array}$	30°C	125°C
0	0.5 + / - 0.1	_	157	2.3	1.8
7	0.8 + / - 0.1	60	160	2.4	1.6
13	0.74 + / - 0.09	48	140	2.0	1.3
19	0.91 + / - 0.09	82	128	1.6	1.0
28	0.84 + / - 0.08	68	125	1.6	0.7

Table V Effect of Loading of HBP (G5) on Fracture Toughness and E'

the  $T_g$  of the G5 HBP-modified epoxy recovered to nearly the same value as the unmodified epoxy. The high-temperature E' also decreased but did not recover fully. The LPE caused a larger decrease in  $T_g$  and E' than did the G4 HBP.

The inconsistent data may be the result of competing effects. One possibility is that the increased hydroxy functionality promotes compatibility with the matrix, while higher molar mass decreases compatibility with the matrix. If this is the case, then the hydroxyl groups promote compatibility with the matrix and decrease  $T_g$ ; but as the molar mass increases, it overcomes the end group effects and then dominates the properties. However, this hypothesis does not explain the increase in the  $T_g$  of the G2 HBP-modified epoxy. If the hydroxyl groups of the G2 HBP were reactive with the epoxy, then it might function as an additional crosslinking agent, but the DSC evidence confirmed no reaction between hydroxyterminated HBPs and the epoxy matrix. The high number of hydroxyl groups might also allow some moisture uptake. This would decrease the  $T_g$  by plasticization and, possibly, despite the plasticization by moisture uptake, the  $T_g$  recovered to some extent with higher G solely due to increased molar mass of the HBP. However, this explanation would not explain why the LPE also had a very low  $T_g$ . Again, the contradictory data support competing effects obscuring the analysis, and further data is needed before definite conclusions can be drawn.

#### Effect of Thermoplastic Loading on Fracture Toughness

The effect of increased HBP loading on fracture toughness was studied by varying the loading of G5 HBP in epoxy from 7 up to 28% (w/w thermoset). The mechanical properties are presented in Table V, and the fracture surfaces of the HBP-

modified epoxy are shown in Figure 5. At 7 and 13% HBP loading, the toughness was  $\sim 50-60\%$  greater than the unmodified control epoxy, while at 19% HBP loading, the fracture toughness increased by 82%. When the HBP loading was increased to 28%, the toughness decreased slightly to 68% above the control.

The  $T_g$  of the thermoset showed a steady decrease as HBP loading increased. Therefore, increased HBP loading promoted plasticization of the matrix. This might have been expected to increase the toughness by facilitating matrix deformation during fracture. However, although some matrix deformation was observed at 28% loading, the thermoset was less tough than the epoxy modified with only 19% G5 HBP. At 28% loading, the HBP particles were very close together, and some had merged, indicating that the system was on the verge of becoming co-continuous. The operative toughening mechanism may have been undergoing a change with the impending morphological change.<sup>10,11</sup>

#### **Related Work with HBPs**

The hyperbranched architecture appeared to offer no inherent advantage in toughening epoxy when compared to a similar low molar mass LPE-toughened epoxy. However, it is useful to compare the results of this work with the earlier work of Boogh and coworkers who used HBPs to toughen epoxy composites.<sup>3–5</sup> In that work, they obtained a fracture toughness increase of  $\sim 140\%$  at 5% HBP loading in epoxy. The structure of the HBP employed by those researchers was not described beyond stating that it was a G3 based on a tetrafunctional core and that the end groups were hydroxyl and secondary epoxy. They also did not prepare a linear thermoplastic control to determine if it toughened as effectively as the HBP; but even so, comparison of their results with the re-



**Figure 5** SEM micrographs of the fracture surfaces of G5 HBP-modified epoxy (w/w): (a) 7% G5 HBP; (b) 13% G5 HBP; (c) 19% G5 HBP; (d) 28% G5 HBP.

sults found here yield interesting clues to potential advantages HBP tougheners may offer over linear thermoplastics.

The two key differences between the study done by Boogh et al. and the work done here was the cure temperature and the HBP end groups. Boogh et al. employed an HBP that had been modified to possess secondary epoxy groups. Secondary epoxy groups would react with the epoxy matrix, even with a room temperature cure. The HBPs employed here were commercially available hydroxy-terminated HBPs, and the hydroxyl groups were unreactive with epoxy, even at 200°C, which was the maximum temperature reached during cure. Chemical reaction between the HBP and the epoxy matrix would promote much stronger interfacial adhesion then hydrogen bonding, and interfacial adhesion is considered to be important to promote toughness.<sup>17</sup> It is possible that this interfacial adhesion is why Boogh et al. obtained an increase in fracture toughness of ~ 140%, while toughness increases of only ~ 30–60% were found here.

However, since an epoxide functionalized linear control was not evaluated under similar circumstances, the results of Boogh et al. do not prove that HBPs will necessarily toughen more effectively than similar linear thermoplastics. An earlier article in this series<sup>19</sup> studied these same hydroxy-terminated HBPs as tougheners for bismaleimides (BMIs). Hydroxy groups can react with the maleimide bonds of a BMI in a Michaeltype addition. The HBPs and LPE yielded fracture toughness values as high as 138% (with the G5 HBP). Also, within error, the LPE, G4 HBP, and G5 HBP yielded the same fracture toughness (0.92, 0.90, and 1.0 MPa m<sup>1/2</sup>). Therefore, while interfacial adhesion may explain why these HBPs toughen BMI more effectively than epoxy, the evidence does not suggest that the increased functionality of HBPs, even when the end groups can react with the matrix, affords an inherent advantage over a linear thermoplastic. Also, in that work, it is interesting to note that the LPE caused no significant decrease in the  $T_g$  of the BMI, while the G4 and G5 HBPs cause a 35–45°C decrease in thermoset  $T_g$ . That suggests that the HBPs were more compatible than the LPE with the matrix, while the opposite results were found here.

Boogh also reported that the toughness depended on the cure temperature and also concluded that interparticle distance played an important role in toughness. Maximum toughness occurred with a 20°C cure temperature, then decreased as cure temperature increased, until at 60°C, the toughness slightly rose again and then leveled off. The maximum cure temperature investigated in that work was 120°C. The authors reported that the dissolution temperature of their HBP was 50°C, so their best results were obtained with a prepolymer which was never homogenous. Therefore, the 20°C cure temperature ensured complete phase separation and did not prevent reaction between the thermoset and thermoplastic, since their HBP had secondary epoxide end groups. As stated before, phase separation, like interfacial adhesion, is known to enhance toughness. The authors did not report matrix shear yielding, but that too might have contributed to the higher toughness since shear yielding would be more likely to occur with a thermoset with a lower crosslink density, which might result with low-temperature cures, than a system with a higher crosslink density.<sup>20</sup> Complete phase separation of the dispersed phase is also advantageous since it does not result in depressing the  $T_g$  of the thermoset, which occurred to a significant extent in the BMI work.

The cure temperature employed here was 140°C, followed by 200°C. This cure temperature was required because the DDS cure agent, which is commonly used in high-performance epoxy resins, does not dissolve in epoxy below 100°C. The high cure temperature used yielded an initially homogenous prepolymer for all the HBP–epoxy prepolymers employed, so all HBP phase separation occurred during the cure. The possibility ex-

ists that the high-temperature cure did not result in complete phase separation. Many studies have correlated the volume fraction of the dispersed phase with toughness.<sup>10,14</sup> However, the thermoset  $T_g$ s (Table IV) suggest that the phase separation was nearly complete. The unmodified epoxy control possessed a  $T_g$  of 157°C, while the G4 and G5 HBP-modified epoxy had  $T_{\sigma}s$  of 152 and 160°C, respectively. The  $T_g$  was determined by DMA, which has an error of +/-5°C, so the differences were not significant. However, the  $T_g$  of the G2 HBP-modified epoxy was  $\sim 20^{\circ}$ C higher than the unmodified epoxy, while the G3 HBPmodified epoxy was  $\sim 20^{\circ}$ C lower. The  $T_g$  data was not understood but seemed to indicate that HBP compatibility with the matrix was not the only factor controlling it.

Different cure temperatures can affect not only the extent of phase separation (the volume fraction of the dispersed phase) but can also affect the morphology by changing the particle sizes of the dispersed phase. Boogh et al. did not measure the volume fraction but thought the HBP phase separated quantitatively because the  $T_{g}$  was not depressed. Although the effect of HBP on  $T_{\sigma}$  appears complex, since the cure was done below the dissolution temperature of the HBP, no HBP would be expected to be in solution in the epoxy so the dispersed HBP phase should quantitatively contain all the added HBP. They reported that the lower cure temperatures yielded bimodal particles with the largest particles having a diameter of  $\sim 4.5 \ \mu m$ . Riew et al.<sup>21</sup> reported a CTBNtoughened epoxy with a bimodal particle distribution, and it was claimed that bimodal distributions were advantageous because both sizes of particles toughened the thermoset, although they did so by different mechanisms. The toughening mechanism evident in this work, by SEM analysis, was particle cavitation, with propagating cracks being deflected around the particles. If the difference in the toughening of HBP-modified epoxy from the prior work of Boogh with that done here was not due to interfacial adhesion, then the difference must arise from the difference in the cure temperature. Riew, Wai, and coworkers<sup>22</sup> postulated that rubbery thermoplastic modifiers cured at elevated temperatures yielded dispersed particles, which were in a high state of triaxial stress and that, in such a case, cavitation would be a low-energy process. In many respects, HBPs are similar to rubber modifiers, so triaxial stress is a possible explanation; however, when these

same HBPs were used as modifiers for BMI<sup>19</sup> and cured at 200°C, the HBPs adhered strongly, through covalent bonding, to the BMI matrix, and good improvements in toughness resulted. However, the BMI did show evidence of some matrix shear yielding, which is considered a high-energy process,<sup>10,11</sup> and may have accounted for some of the toughness increase. Therefore, the possibility that triaxial stress is causing cavitation to be a lower energy toughening process for HBP particles from a high cure temperature than in a lower temperature cure cannot be excluded, but it seems more likely that the low toughness in hydroxy-terminated HBP-modified epoxy was a result of poor adhesion between the matrix and the HBP. If that is the case, then the fact that the toughness of the LPE-modified was so close to that of the HBP-modified BMI is critical, because it suggests that adhesion is important up to some critical value but is not enhanced by the added adhesion possible with a multifunctional HBP.

The combined results from this work and the prior research on the use of HBPs as tougheners for  $BMI^7$  and epoxy,<sup>3–5</sup> collectively indicate the following:

- 1. the hyperbranched architecture does not afford an advantage in viscosity or toughness over a linear low molecular weight thermoplastic;
- 2. cavitation was the observed toughening mechanism, with matrix deformation being observed only at very high loading with high-molecular-weight HBP;
- 3. particles below 1  $\mu$ m gave no increase in toughness, while particles of ~ 2–3  $\mu$ m gave nearly the same fracture toughness irrespective of molar mass or thermoplastic architecture;
- 4. HBP end groups are a significant factor for control of prepolymer viscosity, phase separation during cure, and matrix adhesion;
- 5. cure temperature influences toughness in the vicinity of the dissolution temperature of the HBP, which may be due to either the degree of phase separation and/or triaxial stress; and
- 6. HBP compatibility with the matrix is dominated by end groups, not molar mass, and increasing the molar mass of a hyperbranched modifier has little effect on compatibility.

Hyperbranched polymers are more difficult and expensive to prepare than are linear thermoplastics, and there are relatively few commercially available monomers that are suitable for the synthesis of hyperbranched polymers. This research used only HBPs, and the data is insufficient to conclude definitively that there are no circumstances under which any class of hyperbranched thermoplastics will fail to significantly outperform similar linear low molar mass thermoplastics. However, the data, with both BMIs and epoxy matrices, show that the LPE performed essentially as well as the G4 and G5 HBPs, which suggests that toughness is not significantly improved by using a high molar mass HBP (for example, changing from a G4 HBP to G5 HBP), over a lower molar mass HBP. Therefore, since the primary advantage of this type of architecture is that a higher molar mass thermoplastic can be used without significant increases in architecture, the data suggests a real possibility that the hyperbranched architecture is not advantageous in a toughening application. If a real advantage is to be found for this architecture, it appears that the advantage must be found by optimize toughness through careful control of end groups to optimize morphology and adhesion.

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