A Morphological Investigation of Thermosets Toughened with Novel Thermoplastics. I. Bismaleimide Modified with Hyperbranched Polyester

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ABSTRACT: The morphology of a bismaleimide (BMI) toughened with a thermoplastic hyperbranched aliphatic polyester (HBP) was studied by scanning electron microscopy (SEM). The effect of thermoplastic architecture, molecular weight, and end group on the size and arrangement of the dispersed phase was investigated and compared with the thermoset fracture toughness. SEM micrographs showed that higher molecular weight HBP formed roughly spherical dispersed domains of up to $\sim 60~\mu$m, which contained BMI inclusions. Lower molecular weight HBP formed spherical dispersed thermoplastic domains, with diameters up to $\sim 10~\mu$m with no BMI inclusions. A low molecular weight linear polyester with a repeat unit structure, which was similar to that of the HBP, was prepared and used as a control. Within error, BMI toughened with the linear control yielded the same fracture toughness as the best values obtained with HBP-modified BMI, but the morphology differed. The linear polyester phase separated into particles with a larger average diameter and also possessed some phase-inverted regions. End group effects were studied by modifying the hydroxy-terminated HBP to unreactive nitrophenyl, phenyl, and acetyl end groups. The nitrophenyl-terminated HBP did not phase separate from the thermoset, whereas the nonpolar phenyl- and acetyl-terminated HBP phase separated to form small ($\leq 1~\mu$m and $\sim 2~\mu$m, respectively) spherical domains. Some comparisons were made to other results with HBP thermoplastics in BMI and epoxy thermosets. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1065–1076, 1999

Key words: hyperbranched polymer; toughened thermoset; BMI; morphology

INTRODUCTION

Hyperbranched polymers are of interest for many applications because they are easier to synthesize than dendrimers and yet possess a highly branched architecture, giving them properties similar to dendrimers. In particular, hyperbranched polymers are often more soluble and possess a lower viscosity than linear polymers with a similar molar mass and repeat unit structure, so these materials have potential as thermoplastic tougheners for thermosets.[1–6] Boogh and colleagues[2] were the first researchers to investigate hyperbranched polymers as thermoset tougheners when they investigated a hyperbranched aliphatic polyester (HBP) as a toughener in epoxy composites.[2–4] Our group also investigated HBPs as tougheners for bis-

a)

b)

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

maleimide (BMI) and epoxy. Mechanical and rheological properties, along with preliminary morphological results, were reported.[5,6] Those results showed that a low molar mass linear polyester (LPE), prepared as a control, yielded a prepolymer with similar viscosity and toughened as well as the HBPs, causing similar decreases in the T_g of the final thermoset. This suggests there is no advantage to selecting more expensive hyperbranched thermoplastics over low molar mass linear thermoplastics, especially considering the fact that there are few commercially available monomers that are suitable for the preparation of hyperbranched polymers.

This article reports the results of a more detailed morphological study of HBP-modified BMI with the objective of identifying those structural

features of hyperbranched polymers that most affect morphology and toughness. If those factors can be identified and are specific to the hyperbranched architecture, then that would indicate that there may be some inherent advantages to the use of hyperbranched polymers for toughening thermosets. If no factors can be found for enhancing toughness that are specific to the hyperbranched architecture, then the added cost and difficulty associated with the preparation of hyperbranched thermoplastics may not be warranted.

The term generation, or G, used for dendrimers, is adapted in this work for hyperbranched thermoplastics for the sake of simplicity. That is, irrespective of branching efficiency, if two "layers" of monomer are attached to the central core, the HBP is termed G2; three "layers" of monomer

Figure 2 Two-part thermoset system consisting of BMI monomer (A) and bisallyl-phenol reactive dilutent (B).

bonded around the central core is termed a G3 HBP, etc. A representation of a G3 HBP and the LPE control is shown in Figure 1.

MATERIALS

The BMI (Matrimid 5292; Figure 2) was from Ciba Geigy (Hawthorne, New York). HBP thermoplastic (G 2-5) was purchased from Aldrich Chemical Co. (Milwaukee, WI). Viscosity standard solutions were from Brookfield Engineering (Stoughton, MA). All other reagents were purchased from Aldrich.

INSTRUMENTATION

Scanning electron microscopy (SEM) was done using a JEOL 35C SEM (at 15 kV) or an AMR 1000 SEM (at 20 kV). SEM specimens were gold coated using an E5000 Sputter Coater. Molar mass was determined by size exclusion chromatography (SEC) using a Perkin–Elmer model 610 equipped with Phenomenex columns (Phenogel) and a UV-VIS detector. Dynamic mechanical analyses (DMAs) were performed on a Perkin–Elmer DMA 7 system in 3-point bending mode. Differential scanning calorimetry (DSC) was done with a Shimadzu DSC 50.

EXPERIMENTAL

Preparation of Thermoplastic Modifiers

HBP (hydroxy-terminated) was used as received. The G5 HBP was modified to possess acetyl, nitro, and phenyl end groups, which were introduced by reacting the hydroxy functionalized G5 HBP with the appropriate acid chloride according to procedures reported elsewhere.[1] Preparation of a LPE was described elsewhere.[5]

Preparation of BMI Prepolymer Blends

BMI prepolymer blends were prepared by adding thermoplastic directly to B, with heat and stirring, to yield a clear solution. "A" was then added. The homogenous prepolymer was obtained by heating and stirring an additional 0.3 h at ~ 190°C. DSC analysis was performed on a blend of HBP (G4, 0.9 mg) with A (5.3 mg) and heating at 5°C min^{-1} from 25°C to 250°C.

Thermoset Cure Cycle

The thermoplastic containing BMI was cured according to the cycle—Cure Cycle 1: 150°C (3.5 h), then 200°C (5.5 h), and then 250°C (6 h).

SEM Specimen Preparation

Surfaces were obtained from compact tension test specimens that were fractured in an Instron. Details of the testing are reported elsewhere.[5] Excess material was removed from other faces of the specimens by saw and razor blade.

RESULTS AND DISCUSSION

Hyperbranched polymers have potential as tougheners for thermosets. This is because the hyperbranched architecture minimizes chain entanglements and so these polymers can be blended into a thermoset prepolymer with little increase in prepolymer viscosity. This was first demonstrated by Boogh and coworkers in epoxy,[2,4] later by Gopala and Heiden with BMIs,[5] and Wu and colleagues who investigated epoxy resins.[6] Gopala[5] and Wu[6] compared the prepolymer viscosity and the thermoset fracture toughness of BMI and epoxy modified with HBP with the results for those same thermosets modified with a low molar mass LPE with a similar repeat unit and a molar mass similar to G4 HBP. They found that the LPE gave essentially as low a

Table I Properties[a] of HBP Thermoplastics

HBP (G)	Molar Mass (M_n) (g mol^{-1})	Functionality (—OH Equivalents)	Viscosity (Pa · S at 100°C)	T_g (°C)
2	1,750	16	2.6	64
3	3,600	32	19	—
4	7,300	64	67	—
5	14,000	128	93	—

[a] Data reported by Aldrich Chemical Company.

prepolymer viscosity and as high a fracture toughness as the best values with the HBPs.

Those results were unexpected and not well understood. The objective of this work was to undertake a more thorough morphological investigation of the LPE and HBP-modified BMIs to identify which HBP variables influence morphology to determine if HBPs afford any inherent advantages over an LPE. The effect of thermoplastic architecture on thermoset morphology was investigated by comparison of the morphology of G4 HBP-modified BMI with the LPE-modified BMI, because the molar mass of the thermoplastics was similar. The effect of increasing HBP molar mass was studied by using HBPs of G2–G5. End group polarity and reactivity effects were studied by converting the reactive hydroxyl end groups of G5 HBP to unreactive acetyl, phenyl, and nitro groups.

Understanding how the structural variables of HBPs affect morphology is important because a considerable body of research exists showing toughness is related to the morphology of a thermoset.[7–9] HBPs themselves are not ideal tougheners for use in high-performance thermosets due to the insufficient thermal stability and low modulus, which are characteristic of aliphatic polyesters. Hyperbranched high-performance materials would preferably be used as tougheners in high-performance thermosets. However, such materials were not available, and their synthesis was beyond the scope of these studies. The commercially available HBPs were both convenient and also were suitable for a fundamental study. The properties of the HBPs used are given in Table I. HBP data reported herein is cited from Aldrich. The M_n and functionality are the theoretical values assuming 100% branching efficiency. The reported molar mass for the lower generations is probably close to the true molar mass, but branching efficiency decreases at higher generations, so the true molar mass for the G4 and G5 HBPs are probably lower than the nominal value.

Effect of Thermoplastic Architecture on BMI Morphology

A linear aliphatic polyester was prepared, which possessed a repeat unit structure and a molecular weight ($\sim$ 5,400 g mol^{-1}) that was similar to that of G4 HBP (theoretical 7,300 g mol^{-1}; but, at 90% branching efficiency, the molar mass would be $\sim$ 6,000 g mol^{-1}). Although the repeat units themselves are similar, a critical distinction between linear and hyperbranched thermoplastics is the fact that the hyperbranched architecture results in a large number of end groups. The HBP end groups are hydroxyl, so the thermoplastics have a different solubility. Therefore, although this difference arises as a direct consequence of the HBP architecture, it could also be argued that the solubility/polarity difference prohibits a complete separation of the effect of modifier architecture on thermoset morphology.

Homogenous BMI prepolymers containing LPE and G4 HBP (10% w/w thermoset) were prepared and cured. The LPE-modified BMI possessed a mixed morphology (Figure 3). A continuous thermoset phase dominated that contained dispersed thermoplastic domains of $\sim$ 1–40 μm, but regions were seen where a continuous thermoplastic phase existed. Adhesion between the dispersed LPE phase and the BMI matrix appeared less effective than with HBP, because it appeared that a higher percentage of particles had cavitated. SEM micrographs of the fracture surface of G4 HBP-modified BMI (Figure 3) showed large, irregularly shaped HBP domains dispersed within a continuous BMI phase. The dispersed domains had diameters that were mostly in the range of $\sim$ 5–15 μm, but varied from $\sim$ 1 to 30 μm. The HBP domains contained BMI inclusions and adhered well to the BMI matrix, presumably due to a Michael-type addition reaction between the BMI and the hydroxyl groups of the HBP. Some particles had undergone cavitation; and, in

Figure 3 Fracture surfaces of BMI modified with (9% w/w) of (a) LPE, (b) G2 HBP, (c) G3 HBP, (d) G4 HBP, and (e) G5 HBP.

some instances, there was evidence of matrix deformation around the some of the cavitated HBP domains.

Hydroxyl groups can react with the maleimide of the BMI, so a multifunctional HBP presumably would adhere more effectively to the matrix than the difunctional LPE. The reactivity of hydroxy-terminated HBP with BMI was confirmed using DSC analysis. DSC thermograms of the BMI monomer, A, blended with the G2 HBP and G4

Figure 4 DSC thermograms of (a) A only, (b) G2 HBP, (c) G4 HBP, (d) G2 HBP with A, and (e) G4 HBP with A.

HBP, were compared with control thermograms of A only and HBP only (Figure 4). Pure HBP showed no transitions, but distinct reaction exotherms were seen for the A and the HBP/A blends. The thermogram of the pure A shows a melting temperature onset of ~ 145°C, with a homopolymerization onset at ~ 175°C (possibly somewhat lower, because a second melt may be obscuring the exotherm onset). Blending the A in the HBP lowers the melting temperature of A. The onset of melting is ~ 155°C in G4 HBP and ~ 118°C in G2 HBP, indicating the A is more soluble in the G2 HBP than in the G4 HBP. Both HBP/A blends show a reaction exotherm that is below the melting temperature of the pure A. This exotherm is thought to be the result of a Michael-type addition between HBP hydroxy groups and the maleimide bonds of the A. The exotherm for the A/G2 HBP began at 75°C, peaked at 88°C, and was complete at 107°C. The exotherm was followed immediately by melting of additional, unsolvated A, which itself was followed immediately by a second reaction exotherm that may be the result of homopolymerization of the A and/or further Michael-type addition. This second reaction exotherm was less vigorous in the G4 HBP than with A/G2 HBP, and was still incomplete at 250°C. The thermograms were not carried beyond 250°C, because this was the maximum temperature used in the cure. This may suggest that the G4 HBP reacts with the A more slowly, possibly due to steric hindrance, or, if the second exotherm is due only to homopolymerization of A, then the slow exotherm suggests the G4 HBP hinders the homopolymerization, possibly by entrapping some of the A or hindering the reaction in some similar manner.

The morphological differences between the HBP and LPE-modified BMIs were attributed to solubility differences between the HBP and LPE modifier. This hypothesis was made because continuous thermoplastic domains were observed in the sample toughened with LPE, despite the fact that the total LPE content in the thermoset was only 10% (w/w). Theoretical calculations show that phase inversion should be expected at a minimum volume fraction of ~ 26%.[8] The presence of phase-inverted LPE domains at only 10% (w) loading suggested that, despite the transparent appearance of the prepolymer, the linear thermoplastic was not uniformly dispersed in the prepolymer, and the system began to cure before the LPE became homogeneously dispersed within the prepolymer. Therefore, the LPE formed an irregular continuous phase in regions in the BMI where it was present in a volume fraction in excess of 26%. The thermoplastic formed large (1–40 μm) dispersed, spherical domains in regions where the LPE volume fraction was below that required for phase inversion. The HBP was presumably sufficiently compatible with the BMI prepolymer under the conditions used to be homogeneously dispersed, because there was no evidence of phase inversion, but the BMI inclusions in the dispersed phase also suggest sufficiently rapid phase separation during the cure that trapped BMI within the domain. The high reactivity of the hydroxyl groups with the BMI matrix is demonstrated not only by the small extent of cavitation, but also by the BMI inclusions in the HBP domains.

The morphology indicated the HBP was more soluble in the BMI than the LPE, which would also suggest that the volume fraction of the phase separated LPE could be greater than the HBP. This could not be confirmed due to the BMI inclusions in the G4 HBP dispersed phase, and phase-inverted regions in the LPE-modified BMI that would also have resulted in a substantial error in the calculations. However, the thermoset mechanical properties, such as T_g and E' (Table II) give some support to this conclusion, although incomplete reaction of the large number of end groups would also be expected to result in some plasticization, regardless of phase separation.

Effect of HBP Generation on BMI Morphology

HBP molecular weight and functionality increase with the generation, "G," of the HBP. To study the

Table II   Effect of Hyperbranched Polymer (10% w/w) on Mechanical Properties of BMI[a,b]

Thermoplastic	M_n (g mol^{-1})	K_{Ic} (MPa $\cdot$ m$^{1/2}$)	ΔK_{Ic} (%)	T_g (°C)	E' Pa $\times$ 10^9 30°C	E' Pa $\times$ 10^9 200°C
None	—	0.42 ± 0.10	—	265	3	2
LPE	5,400[c]	0.92 ± 0.04	119	256	0.8	0.7
G4	7,300[d]	0.90 ± 0.05	114	230	0.7	0.6

[a] Data cited from ref. 5.
[b] BMI specimens cured using cure cycle 1.
[c] Measured by SEC in tetrahydrofuran against polystyrene standards.
[d] Theoretical molecular weight, reported by Aldrich Chemical Company.

effect of HBP generation on morphology and toughness, BMI was modified with HBP (10% w/w) with generations from G2 to G5. The morphological results are summarized in Table III, and the fracture toughness is reported in Table IV. SEM micrographs of the fracture surfaces are shown in Figure 3. The BMI modified with G5 HBP possessed large, irregularly shaped HBP particles containing BMI inclusions. The particle diameters ranged from 1 to 60 μm, but most of the particles were $\sim$ 15 μm. Particle adhesion to the matrix was strong, and relatively few particles had undergone cavitation. There was evidence of matrix deformation around some particles that had undergone cavitation. The matrix plasticization suggests incomplete phase separation, but the volume fraction of the dispersed phase was not calculated due to BMI inclusions in the dispersed HBP phase. The morphology of the G4-modified BMI was similar, except that the range of particle sizes and average domain size was smaller ($\sim$ 10 μm). Some BMI inclusions were present in the larger particles, and interfacial adhesion was strong, although a few of the smaller particles had cavitated and some matrix deformation was also evident herein.

The morphology of BMI modified with G2 and G3 HBP was somewhat different from that of the higher generations. The HBP particles were smaller and more uniformly spherical, with no evidence of BMI inclusions. The particles appeared to adhere less well to the BMI matrix, as evidenced by a greater tendency to undergo cavitation.

A relationship between the HBP generation, morphological features, and fracture toughness is evident. As HBP generation increases, both the fracture toughness of the thermoset and the average particle diameter of the dispersed HBP phase increase. The increases in toughness are not outside the error range for the test method, but the toughness also increased slightly with each generation when the HBPs were used to toughen epoxy,[6] which suggests the order of toughness is correct. The toughness and morphology of the LPE-modified BMI (Figure 3) was closest to that of the G4 HBP-modified BMI, although the particle diameter ranged to higher values, and the average particle diameter was also greater.

To maximize toughness with HBPs, it is important to understand why the toughness increased

Table III   Morphology[a] of BMI Thermoset Modified with HBP (10% w/w)

Generation	M_n[a] (g mol^{-1})	Particle Diameter and Shape Range (μm)	Particle Diameter and Shape Average (μm)	Particle Shape
LPE	5,400[b]	1–40	~20	Spherical, some phase inverted
2	1,750	0.2–1	$\sim$ 0.2	Spherical
3	3,600	0.2–10	$\sim$ 5	Spherical
4	7,300	1–30	~10	Irregular sphere
5	14,000	1–60	~15	Irregular sphere

[a] HBP data cited from Aldrich Chemical Company.
[b] Measured in tetrahydrofuran by SEC against polystyrene standards.

**Table IV   Mechanical Properties[a] of BMI
Modified with HBP (10% w/w)**

Generation	OH Functionality[a] (Equivalents)	K_{Ic} (MPa · m$^{1/2}$)	ΔK_{Ic} (%)	T_g (°C)
None[b]		0.42 ± 0.10	—	265
LPE	2	0.92 ± 0.04	119	256
2	16	0.75 ± 0.05	79	250
3	32	0.8 ± 0.1	90	260
4	64	0.90 ± 0.05	114	230
5	128	1.0 ± 0.1	138	225

[a] Data cited from ref. 5. This is a theoretical functionality.
[b] Unmodified BMI.

with the generation. As HBP generation increases, both the molar mass and the functionality increase. The molar mass of the HBPs is thought to be only a minor contributor to toughness, because the increased toughness in going from G4 HBP to G5 HBP is small, despite the molar mass roughly doubling. A doubling of the molar mass with linear thermoplastics would be expected to cause a substantial increase in toughness, yet the increase from doubling the mass of the HBP is not beyond the error range for the test method. It is possible that the molar mass does make some contribution to toughness; but, if it exists, the contribution is sufficiently small that it would not warrant the added cost of trying to further increase the molar mass.

The number of hydroxyl functional groups also increases with HBP generation, and the DSC results confirmed that the hydroxyl groups do react with the BMI. Chemical reaction between the thermoplastic and the matrix promotes interfacial adhesion. Many studies compared linear thermoplastics with reactive and unreactive end groups, and found higher toughness resulted when the thermoplastic possessed reactive end groups (e.g., refs. 10 and 11), but it is unclear what degree of reaction is required. The toughening results from this study suggest that interfacial adhesion may not be a critical factor, because the difunctional LPE, which should not adhere as well to the matrix as multifunctional HBPs, toughened as effectively as the G4 and G5 HBPs. This result was not anticipated. There is insufficient data to make any conclusions, but the evidence from this study suggests that either interfacial adhesion is not a factor in toughening with HBPs, or that only some minimal degree of adhesion is needed, which is met by the difunctional

LPE, and beyond that minimal degree of adhesion, little additional toughness is gained by further locking the thermoplastic to the matrix.

An alternative explanation for the apparent lack of significant effect of interfacial adhesion may be that the BMIs require a high cure temperature, yet the HBPs have low T_gs ($\sim$ 64°C). Wilkinson and colleagues[12] and Riew and colleagues[13] investigated the effect of temperature on the triaxial stress of particles dispersed in a matrix and determined that high cure temperatures left low T_g thermoplastics in a state of high triaxial stress. If the high cure temperature of the BMI, coupled with the mismatch in the T_gs of the thermoplastic and thermoset phases, resulted in the particles existing in a high state of triaxial stress, this may have counteracted any beneficial effect increased interfacial adhesion might have provided. However, if triaxial stress is the reason why interfacial adhesion did not result in a significant difference in the toughness of the thermoset with the functionality of the thermoplastic, then HBPs will only be applicable in low temperature cure systems. Thus, other hyperbranched thermoplastics must be carefully designed for the thermoset system to avoid thermal mismatch.

The other parameter that varied with the thermoset toughness was the average particle size and the range in particle size of the HBP phase. The volume fraction of the dispersed phase may also have varied. In this work, it was not possible to determine the volume fraction of the dispersed phase, because some of the G4 and G5 HBP particles contained BMI inclusions that would prevent accurate measurement. The average particle size of the dispersed G2 HBP phase was $\sim$ 0.2 μm, and increased $\sim$ 5 μm with each generation (i.e., $\sim$ 5 μm for the G3 HBP, $\sim$ 10 μm for the G4 HBP, and $\sim$ 15 μm for the G5 HBP). The range of particle diameters also increased with each generation, and reached a maximum range of 1–60 μm for the G5 HBP. The LPE formed the largest particles, with a median diameter of $\sim$ 20 μm, but the range was only from $\sim$ 1 to 40 μm. Particle size has been shown to be important for toughening in studies of rubber-toughened epoxies, although there is still disagreement about what particle size is most effective for toughening. Some studies have shown that different particle sizes toughen by different mechanisms, and not all mechanisms are equally effective.[13] However, in those studies, the volume fraction of the phase-separated material was not determined and may have varied. Other studies held a constant vol-

ume fraction and found particle size was not a factor in toughening,[13] but the particle diameter studied ranged only from ~ 0.5 to 5 μm. There does not seem to be a consensus about what is required in terms of volume fraction or particle size for toughening a thermoset.

Again, data are not conclusive, but it is proposed that the toughness correlates best with particle size. The greatest fracture toughness measured was with the G5 HBP-modified BMI in which the particle size ranged from ~ 1 μm up to 60 μm, with an average particle size of ~ 15 μm. The next highest measured fracture toughness was found with LPE-modified and G4 HBP-modified BMIs, which possessed nearly identical fracture toughness values. The average particle diameter for the LPE was larger, ~ 20 μm *versus* ~ 10 μm for the G4 HBP, and the LPE had a greater range in particle size. Therefore, larger particles toughen more effectively than smaller particles, and the correlation between average particle size and fracture toughness is strong, but it is not exact, because the LPE toughened slightly less well than the G5 HBP.

Therefore, average particle size is important, but an additional factor is playing a role in fracture toughness. This factor presumably contributed a component to toughness that allowed the G4 and G5 HBP-modified BMIs to have a higher toughness than particle size alone would account for, because the G4 had the same fracture toughness as the LPE-modified BMI and the G5 was tougher, but the average particle diameters were smaller. It is possible that the additional toughening factor still lay in the particle size, because the G5 HBP did possess some very large particles up to 60 μm. To determine the effect of particle size and distribution more precisely, the particle sizes would be better recorded as a histogram to determine if toughness correlated most accurately with the volume fraction of the dispersed phase above some critical particle size. This was not done herein because of the inclusions in the G4 and G5 HBP particles and the phase-inverted regions of the LPE. A more precise investigation of particle size and distribution could be conducted with an unreactive HBP to avoid the BMI inclusions, and might be more revealing.

If the additional G5 HBP toughness "component" is not due to the distribution of the particles, then there is a second, minor toughening mechanism at work. The possible minor contributor may be some minor energy dissipation mechanism available to the higher molar mass HBP, which is not available to the lower molecular weight thermoplastics. Additionally, it is quite possible that the added adhesion of the HBPs is affording an additional minor toughening component. For example, it is possible that the larger LPE particles toughen better than the smaller G4 and G5 HBP particles, but their smaller size is compensated for by the added interfacial adhesion of the multifunctional HBPs.

The evidence is insufficient to determine if the reason the toughening does not correlate exactly with the average particle size is a result of the distribution of particle sizes or if a second minor factor is affecting the toughening results. If the answer lies in a minor toughening mechanism, this mechanism likely involves molar mass or functionality. Only a small increase in toughness was obtained in going from G4 to G5 HBP, with approximately twice the molar mass and number of functional groups. Therefore, it does not appear that a second toughening mechanism could be realistically exploited. If the answer lies in the distribution of particle sizes, then the toughness of LPE-modified and HBP-modified BMIs could be enhanced by better control of the cure conditions.

HBPs are inherently more difficult and costly to prepare than linear thermoplastics. The two features that distinguish HBPs from linear thermoplastics are the fact that high molecular weight HBP can be introduced into a thermoset prepolymer without unduly increasing prepolymer viscosity, whereas only lower molecular weight linear thermoplastics can be introduced while maintaining a low prepolymer viscosity, and HBPs possess a large number of functional groups. Data from this work suggests neither of these features affords any inherent advantage for thermoplastic toughening of thermosets.

Effect of HBP End Groups on BMI Morphology

Hydroxy-terminated G5 HBP was modified with acetyl chloride, benzoyl chloride, and 4-nitrophenyl acetyl chloride to study the effect of end groups on morphology. Acetyl and phenyl end groups were unreactive and less polar than hydroxyl groups. Nitrophenyl end groups were unreactive, but were polar. The fracture surfaces of the BMIs modified with the different HBPs (10% w/w) are shown in Figure 5, and the morphological results are presented in Table V.

The hydroxy-functionalized G5 HBP showed a high degree of adhesion to the BMI, as evidenced

Figure 5   Fracture surfaces of BMI modified with 9% (w/w) of: (a) G5$_{Ac}$ HBP, (b) G5$_{Ph}$ HBP, and (c) G5$_{PhNO2}$ HBP.

by large spherical domains that contained some BMI inclusions and that underwent little cavitation. The BMI modified with HBP G5$_{Ac}$ showed smaller spherical domains (most in the range of $\sim$ 2–3 μm) with no BMI inclusions and that were subject to more extensive cavitation. The phenyl-terminated HBP yielded even smaller spherical domains ($\leq$1 μm) that also underwent extensive cavitation. The nitrophenyl end groups were sufficiently compatible with the BMI matrix that either no phase separation occurred or the domain size was below SEM detection limits. Therefore, the effect of changing the identity of the end groups was primarily to affect the size and adhesion of the particles; but, in both cases, where phase separation occurred, the HBP phase was present as spherical domains within a continuous thermoset phase.

The fracture toughness of the BMI toughened with the modified HBPs was not measured; but, if the hypothesis regarding particle size is correct, then the BMI modified with the hydroxy-termi-

nated HBP would give the greatest toughness, followed by the acetyl-terminated HBP, then the phenyl-terminated HBP, and finally the nitrophenyl-terminated HBP.

CONCLUSIONS

Structural features of a hyperbranched polymer that influence the morphology and toughness of a BMI modified with HBP were investigated with the objective of determining if the hyperbranched architecture affords any inherent advantage over a similar linear thermoplastic in toughening a thermoset. The effect of molar mass, architecture, and end group was investigated.

Both toughness and average particle size increased with HBP molar mass. The increased toughness appeared to correlate most closely with the particle size of the dispersed phase, but it was apparent that average particle size was not the only factor contributing to toughness, because the

Table V   Effect of G5 HBP[a] End Groups on Modified BMI Morphology

HBP End Group	Volume Fraction (%)	Particle Diameter Range (μm)	Average Diameter (μm)
—OH	—	1–60	$\sim$30
—COCH$_3$	15	1–3	$\sim$ 2
—C$_6$H$_5$	15	0.2–1	$\sim$ 0.8
—C$_6$H$_5$—NO$_2$	15	None	None

[a] HBP 10% (w/w thermoset).

LPE produced particles with an average diameter of ~ 20 μm, but was slightly less tough than G5 HBP-modified BMI, which yielded particles with a average diameter of ~ 15 μm. Therefore, it was proposed that the toughness was also affected by either the distribution of particle sizes or one or more additional, minor toughening mechanisms associated with the increased molar mass.

Interfacial adhesion did not seem to play a significant role in toughening, because a difunctional LPE possessed essentially the same fracture toughness as the G4 and G5 HBPs, with a hydroxy functionality of 64 and 128, respectively. The greater number of end groups was initially thought to be the key architectural difference that might allow HBPs to toughen more effectively than a linear thermoplastic, because it would promote interfacial adhesion, which is widely accepted as promoting toughness. Possibly the high cure temperature required with BMIs left the relatively low T_g thermoplastics in a state of high triaxial stress, making cavitation a low toughening mechanism and obscuring the effects of interfacial adhesion. If this is the case, then the HBP architecture may, by virtue of their multifunctional architecture, outperform a similar linear thermoplastic toughener cured at a lower temperature. An alternative explanation for the lack of a significant effect of interfacial adhesion was that reactive end groups did promote toughness, but only up to a "threshold" level that was also met by difunctional thermoplastics, so the greater adhesion of multifunctional HBPs is not advantageous.

The overall morphology of the thermoset did not vary with the thermoplastic architecture. With the exception of a few small phase inverted regions, the morphology of the LPE-modified BMI resembled the HBP-modified BMI. The strongest effect on morphology was obtained when the HBP end groups of a G5 HBP were modified. When the HBP was modified to 4-nitrophenyl end groups, the HBP was either not phase-separated or separated into domains below the detection limit of the SEM. When the HBP end groups were converted to nonpolar acetyl and phenyl end groups, the HBP formed small, spherical domains, with the average diameter being reduced from ~ 15 μm for the hydroxyl end groups, down to only ~ 2 μm for the acetyl end groups, and to less than ~ 1 μm for the phenyl end groups.

No inherent advantage was found for the hyperbranched architecture over a linear low molecular weight thermoplastic with a similar repeat unit structure. Fracture toughness seemed to be most dependent on particle size, with cavitation as the dominant toughening mechanism.

Data are insufficient to conclude that no conditions exist where the hyperbranched architecture is inherently advantageous. Data do suggest that one key advantage of hyperbranched thermoplastics could offer, the ability to introduce higher molecular weight species with relatively little increase in prepolymer viscosity, is not advantageous. Higher molar mass did not significantly increase toughness. Data are insufficient to determine if the second potential advantage of the hyperbranched architecture, the large number of end groups, can afford sufficient toughness improvements to warrant the added cost of producing the architecture. If the only contributor to toughness is the particle size, then a low-cost linear thermoplastic can perform as well as a hyperbranched thermoplastic if the cure conditions are controlled. If the potential advantage of greater interfacial adhesion was obscured in this work through the high cure temperature, which may have left the relatively low T_g HBP particles in a state of high triaxial stress, then the architecture may afford an advantage if the T_gs of thermoplastic and thermoset matrix are more closely matched.

The hyperbranched architecture is inherently more expensive to prepare than a linear thermoplastic, and the most likely application would be for high-performance thermosets. The difficulties in preparing a suitable monomer and controlling the reaction conditions to obtain a high-performance hyperbranched thermoplastic are considerable. Data are insufficient to conclude there are no conditions where the hyperbranched architecture cannot provide higher toughness than a linear low molar mass thermoplastic, but the HBPs did not outperform a linear low molecular weight thermoplastic under these cure conditions.

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