

Investigation of Readily Processable Thermoplastic-Toughened Thermosets. III. Toughening BMIs and Epoxy with a Comb-Shaped Imide Oligomer

A. GOPALA, H. WU, P. HEIDEN

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

Received 1 December 1997; accepted 7 March 1998

ABSTRACT: This is the third in a five-part series describing the preparation of tough, high-performance thermosets from low viscosity, autoclave-processable prepolymers. The first 2 articles described toughening of bismaleimides (BMI) and epoxy with linear imide thermoplastics of ~ 1000 g/mol. Highly processable prepolymers were obtained, which resulted in increases in fracture toughness for BMI of ~ 75 – 100% , while the fracture toughness of epoxy was increased by up to 220% . This article describes the preparation of a low-molecular-weight comb-shaped imide oligomer (~ 4100 g/mol) and the effect of the oligomer architecture and end-group on BMI and epoxy prepolymer viscosity and fracture toughness. When an unreactive comb-shaped oligomer was incorporated in a BMI prepolymer (10% thermoplastic loading in the thermoset), the fracture toughness increased by 67% over that of an untoughened control, while a reactive oligomer increased the fracture toughness by 150% over an untoughened control. At 55°C , the viscosity of the solution of the reactive comb-shaped imide in B was only 6.2 Pa \cdot S. When the oligomer was dissolved in epoxy resin, the viscosity was less than 0.2 Pa \cdot S at 90°C , and the fracture toughness increased by 110 and 133% (at $\sim 13\%$ loading in the thermoset), relative to an untoughened control, depending on the reactivity of the end group. The T_g and high-temperature modulus of BMI and epoxy remained approximately the same relative to the untoughened controls. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 943–951, 1998

Key words: autoclave processable; comb-shaped imide, low viscosity prepolymer; toughened thermoset

INTRODUCTION

Over the last 10 years, a significant quantity of research has been done on toughening of thermosets.^{1–24} Incorporation of high- T_g , high-performance thermoplastics into thermosets has been the most successful approach to date for toughening high-performance thermosets since this method successfully increases the fracture toughness with only minor decreases in other desired properties.^{15,17,23,24}

The disadvantage that has not yet been overcome with this approach has been that the incorporation of even small amounts of high-molecular-weight thermoplastic results in substantial increases in the prepolymer viscosity. This makes processing difficult, and autoclave processing, which is done under very low pressures, may not be possible. Much of the research on thermoplastic toughening has involved the use of oligomers, but probably most often, the oligomers studied have molecular weights close to $\sim 10,000$ g/mol. In those instances in which oligomers of ~ 3000 – 5000 g/mol have been studied,^{4,5} little or no increase in fracture toughness was found.

Correspondence to: P. Heiden

Journal of Applied Polymer Science, Vol. 70, 943–951 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/050943-09

Earlier research showed that low-molecular-weight linear imide thermoplastic (~ 1000 g/mol) could be incorporated into BMI and epoxy to give very low viscosity prepolymers, which could be cured to give tough epoxy and BMI thermosets.^{25,26} That research resulted in modest to good improvements in thermoset toughness ($\sim 75\%$ for BMI and up to 220% for epoxy). However, the reactive solvent approach employed resulted in decreasing the epoxy T_g , and the BMI toughness was less than desired. Use of higher-molecular-weight tougheners was not investigated because they cause significant increases in prepolymer viscosity, which compromise or prohibit low pressure processing.

In this article, epoxy and BMI are modified with a comb-shaped aromatic imide, and the effects on prepolymer viscosity and thermoset fracture toughness are described. The premise was that the total thermoplastic molecular weight might be increased without significant increases in viscosity if the thermoplastic architecture consisted of a short backbone grafted with short branches. It was thought that this would minimize entanglements due to the low molecular weight of the branches and steric hindrance around the backbone.

INSTRUMENTATION

Viscosity measurements were made on a Bohlin VOR rheometric system. Molecular weight measurements were made by size exclusion chromatography (SEC) with a Perkin–Elmer 601 equipped with Phenomenex phenogel columns and an ultraviolet–visible (UV-VIS) detector. Dynamic mechanical analyses (DMA) were performed on a Perkin–Elmer DMA 7 system in three-point bending mode. Compact tension tests were performed on an Instron Universal Testing Machine. ^1H nuclear magnetic resonance ($^1\text{H-NMR}$) and Fourier transform infrared (FTIR) were accomplished on a Varian 200 MHz instrument and a Mattson Galaxy Series 3000, respectively.

MATERIALS

The two-part BMI system (Matrimid® 5292A and Matrimid® 5292B; Fig. 1) purchased from Ciba Geigy (Hawthorne, New York) was employed as the thermoset matrix. The BMI, A, is a solid at

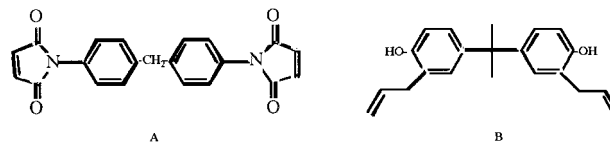


Figure 1 Two-part thermoset system consisting of BMI monomer (A) and bisallylphenol reactive diluent (B).

room temperature, while the reactive diluent, B, is a viscous liquid at room temperature (Fig. 1). The epoxy matrix employed was Epon 825®, which was purchased from Shell Chemical Co. (Houston, Texas).

The imide thermoplastics employed in this study were synthesized according to procedures described in the experimental section. The monomers employed were 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 1,3-bis(4-aminophenoxy)benzene (TPE-R), 3,5-diaminobenzoic acid (DABA), and 2,5-diaminopyridine (DAP). The end-groups were obtained from the monomers or by end-capping with *m*-aminophenol or phthalic anhydride. All dianhydrides and TPE-R diamine were purchased from Chriskev (Leeward, Kansas), while all other reagents were purchased from Aldrich Chemical Company (Milwaukee, WI). The monomer structures are shown in Figure 2.

EXPERIMENTAL PART

Preparation of Unreactive Comb-Shaped Thermoplastic

Unreactive comb-shaped thermoplastic imide toughener was prepared in 3 steps using NMP as a reaction solvent. The backbone was synthesized by adding 6FDA (1.33 g, 3.00 mmol) and DABA (0.300 g, 2.00 mmol) to NMP (20 mL) in a molar ratio of 3 : 2 and heating at 180°C for ~ 0.8 h under N_2 to give an anhydride-terminated backbone chain with a theoretical X_n of 5. DAP (0.218 g, 2.00 mmol) was then added. The solution was heated for another 0.8 h to give an amine-terminated backbone imide-containing pendant carboxylic acid groups. The amine groups were then capped by reacting with phthalic anhydride (0.0396 g, 2.00 mmol) at 180°C (0.5 h).

In a separate reaction kettle, the side-chain oligomer was prepared by reacting TPE-R diamine (0.585 g, 2.00 mmol) with 6FDA dianhydride (1.78 g, 4.00 mmol) in a 2 : 1 ratio in NMP (20 mL) at 180°C for 0.8 h to give the anhydride-

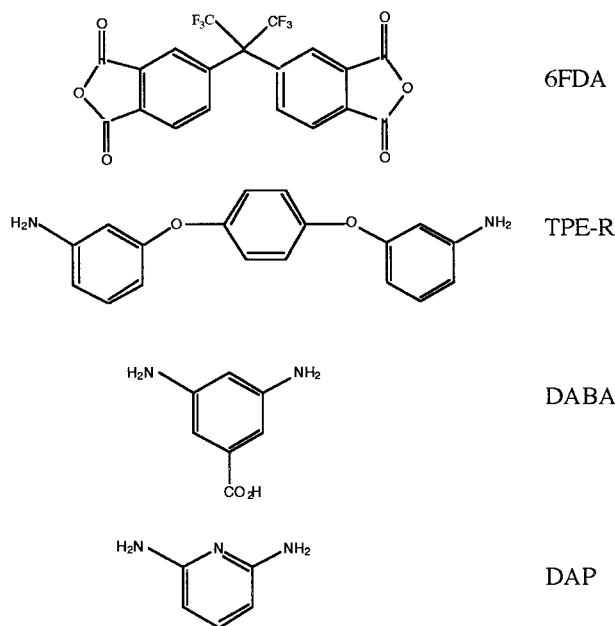


Figure 2 Structures of the monomers employed in the synthesis of the comb-shaped oligomer.

terminated graft (theoretical X_n of 5). *m*-Aminophenol (0.437 g, 4.00 mmol) was then added, and the solution was heated an additional 0.8 h to give chains with an average of one phenol per chain.

The reaction solutions containing the side-chain oligomer and the backbone oligomer were combined along with *p*-toluenesulfonic acid to catalyze the esterification grafting reaction between the backbone carboxyl groups and the graft chain phenol groups. The solution was heated at $\sim 200^\circ\text{C}$ for 4 h. The product was quantitatively recovered by pouring into water, followed by filtration. The molecular weight was 4100 g/mol (4550 theoretical).

The backbone and graft segments, as well as the final grafted oligomer product, were analyzed by FTIR and $^1\text{H-NMR}$. FTIR confirmed the presence of carboxylic acid in the backbone oligomer from the $-\text{OH}$ in the carboxylic acid ($\sim 3500\text{ cm}^{-1}$, broad) and the carbonyl of the acid ($\sim 1730\text{ cm}^{-1}$).

The final product showed the acid carbonyl ($\sim 1730\text{ cm}^{-1}$) was reduced relative to the imide carbonyl ($\sim 1870\text{ cm}^{-1}$), and the hydroxyl band was significantly reduced, but not eliminated. This indicated that the grafting was not 100% efficient.

$^1\text{H-NMR}$ analysis of the grafted chain product with and without D_2O showed the ratio of the protons in the range of 7.8–8.2 ppm to those in the 8.2–8.3 ppm range to be 9.8 and 9.7, respec-

tively, indicating that relatively few exchangeable protons remained, and no bands were observed above 8.3 ppm. Exchangeable protons were found in the spectrum between ~ 6.6 and ~ 8.3 ppm, which might be due to amine and phenolic protons from uncapped DAP amines and unreacted phenolic sidechain. Therefore, the oligomer employed as a toughener was a mixture of species and was not entirely unreactive with the matrix but was far less reactive than the “reactive” comb-shaped oligomer.

Preparation of Reactive Comb-Shaped Thermoplastic

The backbone segment was prepared by dissolving 6FDA (9.477 g, 21.33 mmol) and DABA (2.165 g, 14.20 mmol) in NMP (100 mL) and heating at 190°C for 45 min. DAP (1.553 g, 14.20 mmol) was then added, and the reaction was heated at 190°C for an additional 45 min. This gave a segment with a 3 : 2 : 2 molar ratio of 6FDA–DABA–DAP, which was theoretically terminated with DAP amine groups and had a theoretical X_n of 7.

In a separate reactor, the side-chain segment was prepared by adding 6FDA (12.636 g, 28.440 mmol) and TPE-R (4.157 g, 14.22 mmol) to NMP (100 mL) and heating at 190°C for 0.8 h, followed by the addition of *m*-aminophenol (3.104 g, 28.44 mmol) and heating at that temperature for an additional 0.8 h. The molar ratio of reactants was 2 : 1 : 2 of 6FDA–TPE-R–*m*-aminophenol to give a segment with phenol end groups and a theoretical X_n of 5.

The grafted oligomer was prepared by combining the 2 reaction solutions along with *p*-toluenesulfonic acid (0.20 g, 1.1 mmol) and heating at 200°C for 4 h. The product was collected by filtration after pouring into water to precipitate the oligomer (97% yield). Analysis (SEC) showed the product had an M_n of ~ 4100 g/mol (4476 g/mol theoretical).

Thermoplastic Molecular Weight Determination

Thermoplastic was isolated from solution by precipitation in water or ethanol, collected by filtration, and dried under reduced pressure. End-groups were identified by $^1\text{H-NMR}$ and FTIR. Estimates of the average thermoplastic molecular weight were determined by $^1\text{H-NMR}$ (end-group analysis) and SEC. The average number of grafts per chain was estimated by comparison of theoretical with measured molecular mass.

Preparation of Unmodified BMI Prepolymer

Control specimens without thermoplastic were prepared and degassed according to procedures described elsewhere.²⁵

Preparation of Unmodified Epoxy Prepolymer

Epoxy control specimens were prepared (100 parts epoxy to 30 parts of DDS) and degassed according to procedures described elsewhere.²⁶

Preparation of BMI Prepolymer Containing Comb-Shaped Thermoplastic

Comb-shaped oligomer (3.6 g) was dissolved by heating at 180°C in B (18.0 g) until a clear solution was obtained. A (21.1 g) was then added, and the mixture was further stirred and heated until a homogenous prepolymer solution was obtained. The prepolymer was degassed at 180°C.

Preparation of Epoxy Prepolymer Containing Comb-Shaped Thermoplastic

Comb-shaped oligomer (6.0 or 9.0 g) was dissolved in acetone (100 mL) to yield an homogenous solution. Epoxy (30.0 g) was added, and the acetone was removed by heating the solution up to 100°C over a 5 h period. The solution was subjected to reduced pressure to ensure complete removal of the acetone (2 h). The solution was then restored to atmospheric pressure, and the temperature was increased to 140°C. DDS (9.0 g) was added, the solution was stirred at 180°C until an homogenous prepolymer solution was obtained (~ 0.3–0.5 h), and degassed.

Molding Procedure for BMI Prepolymers

The clear prepolymer solution was further degassed in a preheated oven (180°C) for 0.5 h under reduced pressure and then poured into a preheated vertical mold treated with a thermally stable release agent. The prepolymer was cured at 180°C for 5.5 h, followed by 3.5 h at 200°C. Following demolding samples were post-cured for 6.5 h at 250°C.

Molding Procedure for Epoxy Prepolymers

The clear prepolymer was poured into a preheated vertical mold, which was treated with a thermally stable release agent. The mold was placed in a preheated oven, and the prepolymer

was cured according to the following cycle: 140°C for 8 h, followed by 200°C for 1 h. Heating was discontinued, and the cured specimen was allowed to slowly return to room temperature.

Specimen Preparation and Mechanical Testing by Compact Tension

The procedure for specimen preparation and mechanical testing using compact tension specimens is described elsewhere.²⁵

Storage Modulus (E') and Glass Transition Temperature (T_g s)

E' was found from DMA in a three-point bend mode. Thermoset T_g s were determined as the onset of loss of E' for BMI specimens and as the inflection point of the E' for epoxy specimens.

RESULTS AND DISCUSSION

Preparation of Comb-Shaped Oligomer and Prepolymers with the Oligomer

BMI and epoxy thermosets were toughened with a low-molecular-weight comb-shaped imide oligomer (~ 4100 g/mol). The comb-shaped oligomer was initially prepared by grafting an amine-terminated imide oligomer to the carboxylic-acid-containing backbone, which yielded amide graft units. However, this oligomer could not be solvated in B. A more soluble ester-linked oligomer was prepared by grafting an hydroxyl-terminated imide oligomer onto the pendant carboxylic acid groups of the imide backbone. The ester comb-shaped oligomer could be solvated directly in B to yield an homogenous BMI prepolymer. No attempt was made to prepare these oligomers directly in B, using the one-pot reactive solvent method described for the linear imide oligomers^{25,26} since individual components were isolated for analysis. Also, the final product was to be used in epoxy without the reactive solvent, since B causes a decrease in the epoxy T_g . However, the reactive solvent approach would be advantageous for the BMI but would require the use of an ester of diaminobenzoic acid due to the low solubility of DABA in B.

The comb-shaped oligomer was introduced into the epoxy with the aid of acetone to facilitate the solution process; however, the reactive oligomer

Table I Effect of Loading of Comb-Shaped Oligomer on Viscosity

Solvent	Oligomer	% Thermoplastic ^c (w/w)	M_n Theoretical (g/mol)	M_n Measured (g/mol)	Viscosity ^b (Pa · S)	Δ Viscosity (%)
B	—	0	—	—	0.60	—
	2a ^a	20	700	858	6.0	1000
	2d ^a	20	2200	5849	31	5167
	2d ^a	30	2200	5849	33	5400
B	Comb ^b	20	4550	4100	6.2	1000
	(unreactive)	30	—	—	10.5	1650
			4550	4100	70	11,700
B	Comb ^b	20	—	—	58	9567
	(reactive)	30	4476	4100	2.3	283
			—	—	6.0	900
Epoxy	—	0	—	—	4.0	567
			—	—	12.2	1933
Epoxy	Comb ^b	20	4550	4100	0.15	650
	(unreactive)	30	4550	4100	0.53	2550
Epoxy	Comb ^b	20	4476	4100	0.14	600
	(reactive)	30	4476	4100	2.0	9900

^a Linear imides from Gopala et al.²⁵

^b Viscosity measurements were made at 55°C in B and 90°C in epoxy.

^c Weight of thermoplastic to weight of B or weight of epoxy.

possessed high solubility and might be directly soluble in the epoxy.

Effect of Comb-Shaped Oligomer on Viscosity

The viscosity of solutions of comb-shaped oligomer (~ 4100 g/mol) was measured in B (20 and 30% w/w in B) without the thermoset monomer A, to avoid risk of cure during the measurement. At 55°C and 20% thermoplastic loading, the viscosity of the nonreactive comb-shaped oligomer was 6 Pa · S. This is the same value measured for B containing 20% of linear imide oligomer of ~ 1000 g/mol and significantly lower than the 31 Pa · S measured for B containing 20% of a ~ 5800-g/mol linear imide.²⁵ The reactive comb-shaped oligomer possessed a viscosity of only 2.3 Pa · S at 20% loading.

At 30% loading (w/w in B), the nonreactive comb-shaped thermoplastic possessed a viscosity of 70 Pa · S, compared with a viscosity of only 31 Pa · S for the linear thermoplastic of ~ 1000 g/mol at that loading. Interestingly, the reactive comb-shaped oligomer at 30% loading increased the solution viscosity to only 4.0 Pa · S under these same conditions. The reactive oligomer was more soluble in the B, and the viscosity difference was

noticeable to the eye. This significant difference must be attributed to end groups, since the molecular weights are virtually identical. To confirm these results, new batches of comb-shaped oligomer were synthesized, and fresh solutions in B were prepared. The viscosity of the new solutions was measured immediately after running a series of viscosity standards (Brookfield Engineering Laboratories, Inc., Stoughton, MA). The viscosity measured for the standards was slightly higher than the reported viscosity, but the error was systematic. The new thermoplastic solutions were also measured at values slightly higher than the original solutions, which could be due to either differences in the molar mass of the new thermoplastic, or to instrument error, but still confirmed the earlier trends for the viscosity. The viscosity of the new samples of unreactive comb-shaped imide was 10.5 Pa · S at 20% loading and 58 Pa · S at 30% loading (55°C). The viscosity of the new samples of reactive comb-shaped oligomer was measured at 6.0 Pa · S at 20% loading and 12.2 Pa · S at 30% loading (55°C). The results are shown in Table I.

The original hypothesis for preparing the comb-shaped thermoplastic was that low-molecular-weight grafted chains might not entangle ef-

Table II Effect of Comb-Shaped Oligomer on Thermoset K_{Ic}

Thermoset Matrix	Oligomer End Groups	% Thermoplastic (w/w) ^a	% Thermoplastic (Total) ^b	K_{Ic} MPa · m ^{1/2}	ΔK_{Ic} (%)
BMI	—	0	0	0.42 +/- 0.10	—
	Unreactive	20	10	0.75 +/- 0.05	67
	Unreactive	30	15	0.75 +/- 0.05	67
	Reactive	20	10	1.05 +/- 0.18	150
Epoxy	Reactive	30	15	0.65 +/- 0.06	55
	—	0	0	0.48 +/- 0.10	—
	Unreactive	20	13	0.64 +/- 0.12	33
	Unreactive	30	19	1.01 +/- 0.38	110
	Reactive	20	13	0.85 +/- 0.26	77
	Reactive	30	19	1.12 +/- 0.17	133

^a For BMI specimens, this is the loading in the B component, while for the epoxy specimens, this is the loading in the epoxy monomer.

^b For BMI specimens, this is the percentage of thermoplastic per total mass (thermoplastic, A and B components), while for epoxy specimens, this is the percentage of thermoplastic per total mass (thermoplastic, epoxy, and DDS).

fectively, allowing the molecular weight to be further increased and so potentially increase the fracture toughness without significantly increasing the viscosity. This appears to have been a successful approach at 20% loading since the molecular weight of the thermoplastic was approximately 4 times higher than the linear thermoplastic, and yet the viscosity at 55°C was the same. At 30% loading, however, the unreactive comb-shaped oligomer performed differently than the reactive oligomer. The fact that the viscosity increased significantly with loading suggested that a critical loading factor was involved but does not explain the difference in viscosity based on end groups.

The viscosity of the thermoplastic was also measured in epoxy, without DDS, at 90°C. All the solutions possessed a viscosity of less than 1 Pa · S except the solution with the reactive oligomer at 30% loading, which was still only 2 Pa · S. The oligomer possessed both amine and phenolic groups, so, despite the absence of the DDS cure agent, this increase may have been due to some reaction between the oligomer and epoxy. However, the viscosity of all the prepolymers was well within the range for autoclave processing. The results are shown in Table I.

EFFECT OF COMB-SHAPED OLIGOMER ON FRACTURE TOUGHNESS

The fracture toughness of BMI toughened with the unreactive comb-shaped oligomer was 0.75

MPa · m^{1/2} at both 20% (w/w B, ~ 10% overall) and 30% (w/w B, or ~ 15% overall) thermoplastic loading (Table II). This is essentially the same result as was obtained with the linear thermoplastic with a similar molecular weight (measured at 4100 g/mol for the comb-shaped oligomer versus ~ 5000 g/mol for the linear imide), which yielded a fracture toughness of 0.8 MPa · m^{1/2}.²⁵ However, when the comb-shaped oligomer possessed reactive end groups (amine and phenol), the fracture toughness at 20% loading (w/w B) increased to 1.05 MPa · m^{1/2}. This is a 150% increase in fracture toughness relative to the untoughened control and 50% greater than that for the linear thermoplastic of similar molecular weight. At 30% loading (w/w B), the fracture toughness was only 0.65 MPa · m^{1/2}, which is lower than that for the unreactive oligomer. The reactive oligomer was more soluble than the unreactive oligomer, and this may have affected the morphology in a way that was detrimental to the toughness. Therefore, optimizing systems using comb-shaped oligomers may require controlling the competing effects of end groups, which promote solubility, and may decrease toughness by changing morphology, but which also more effectively lock the thermoplastic into the matrix and may enhance toughness by increasing the required work to create new surface area.

The fracture toughness of epoxy modified with comb-shaped oligomer increased with thermoplastic loading for both unreactive and reactive thermoplastic. The unreactive comb-shaped ther-

Table III Effect of Comb-Shaped Oligomer on Thermoset T_g and E'

Matrix	Oligomer End Groups	Weight % Thermoplastic (Total w %)	T_g (°C)	E'^a (Pa $\times 10^9$)	E'^b (Pa $\times 10^9$)
BMI	—	0 (0)	265	0.55	0.53
	Unreactive	20 (11)	240	0.76	0.74
	Unreactive	30 (17)	255	0.74	0.69
	Reactive	20 (11)	265	0.64	0.62
	Reactive	30 (17)	260	0.73	0.68
Epoxy	—	—	157	2.3	1.9
	Unreactive	20 (13)	159	2.5	1.9
	Unreactive	30 (19)	157	2.4	1.9
	Reactive	20 (13)	165	2.4	1.9
	Reactive	30 (19)	158	2.0	1.6

^a At 30°C for BMI specimens and at 25°C for epoxy specimens.

^b At 200°C for BMI specimens and at 100°C for epoxy specimens.

moplastic-modified epoxy yielded fracture toughness values of 0.64 and 1.01 MPa \cdot m^{1/2} at a thermoplastic loading of 20 and 30%, respectively, in epoxy (\sim 13 and 19% overall). As expected, the reactive oligomer resulted in tougher specimens than the unreactive thermoplastic, yielding fracture toughness values of 0.85 and 1.12 MPa \cdot m^{1/2} at 20 and 30% thermoplastic loading in the epoxy (13 and 19% overall). The results are shown in Table II. The highest value obtained in epoxy, 1.12 MPa \cdot m^{1/2} for 30% reactive comb-shaped oligomer, is a 133% increase in fracture toughness relative to the untoughened control. This is a lesser improvement than the 220% increase reported in an earlier article using linear low-molecular-weight imide oligomer,²⁶ but the comb-shaped oligomer could be introduced without the aid of the reactive solvent B and so did not compromise the T_g or E' . The toughness difference may be due to the fact that the comb-shaped oligomer possessed some phenolic groups, which would be expected to promote greater solubility in the epoxy.

Effect of Comb-Shaped Oligomer and End-Groups on T_g and E'

Both the room temperature and high-temperature storage modulus (E') of the thermoplastic-modified BMI was increased relative to that of the control, irrespective of the reactivity of the comb-shaped thermoplastic. The T_g of the BMI modified with unreactive comb-shaped thermoplastic decreased by \sim 10–20°C relative to the control, but

the T_g of the BMI modified with the reactive comb-shaped oligomer was unaffected (Table III).

The T_g and E' of epoxy modified with comb-shaped oligomer were essentially the same as the epoxy control, \sim 157°C T_g and 1.9×10^9 Pa for E' at 100°C, except for the reactive comb-shaped oligomer at 30% loading in epoxy, where a slight decrease was measured (Table III).

Effect of Oligomer Architecture and End Groups on Solubility

The comb-shaped oligomers were miscible with the epoxy and the BMI prepolymer. Consequently, unlike the linear imide thermoplastics reported earlier,²⁶ the comb-shaped imide could be dissolved in the epoxy without the use of the reactive solvent B, so neither T_g nor E' of the thermoset were compromised. The reactive comb-shaped oligomer was more soluble, as evidenced by the greater ease with which it was solvated in the prepolymer, presumably due to the amine and phenol end groups. The results, to date, show that the choice and number of end groups strongly influence the solubility and therefore affect the phase separation process of these oligomers. Since the graft oligomers have more end groups than do linear oligomers, the solubility of the thermoplastic and final morphology of the thermoset are strongly influenced. Prior research has shown that morphology is one of the most critical factors for control of toughness.²⁷

CONCLUSIONS

Comb-shaped aromatic imide oligomers were studied as high-performance thermoplastic tougheners for BMI and epoxy resins. These oligomers were selected for investigation in this work for 2 reasons. It was thought that they would cause a lesser increase in prepolymer viscosity relative to prepolymer modified with linear imide of similar molecular weight. It was also thought that the increased number of functional groups would lock the branched thermoplastic into the matrix more effectively than linear thermoplastic and so further enhance the toughness of the thermoset relative to linear thermoplastics with similar structures.

Good increases in fracture toughness were obtained for both the BMI and epoxy modified with reactive comb-shaped thermoplastic (150% increase for the BMI and 133% increase for the epoxy), and excellent processability was maintained. At $\sim 20\%$ thermoplastic loading in B, the viscosity of the resin using comb-shaped imide oligomers was significantly lower than that of the resin with linear imide oligomers of similar molecular weight studied previously.²⁵ At 30% loading in B the measured viscosity was much higher, suggesting a critical loading. However, a 30% loading of comb-shaped thermoplastic in epoxy did not significantly increase viscosity, which does not support a critical loading theory. We do not have an explanation for this phenomenon, although it may be linked to a difference in solubility of the oligomer in the epoxy resin, coupled with the fact that the viscosity of the epoxy was measured at 90°C versus only 55°C for the oligomer in B.

Because no precedents were found for comb-shaped thermoplastics as tougheners, an attempt was made to separate the affect of architecture and the multiple functional groups by first preparing a nonfunctional graft thermoplastic and then preparing a similar reactive graft thermoplastic. However, in this preliminary work, no definitive conclusions could be drawn. The reactive comb-shaped oligomer did result in a tough thermoset, but it cannot be concluded that this was solely the result of reactivity because the presence of the amine and phenol end groups also altered the miscibility and the morphology of the thermoplastic-modified thermosets. The results reported here, coupled with the differences found between the measured viscosity of epoxy and BMI prepolymers as a function of comb-shaped oligomer loading, indicate that additional work is

required using oligomer in which end groups, molecular weight, and grafting efficiency is more thoroughly characterized.

The reactive comb-shaped oligomers caused no decrease in the T_g and E' of the BMI and epoxy thermosets when the thermoplastic was incorporated at a level of $\sim 10\%$ (20% w/w B) in BMI and 13% (20% w/w epoxy) in the epoxy thermoset.

Overall, the results of this work were very promising. Low-molecular-weight comb-shaped oligomers did result in a lesser viscosity increase than did linear thermoplastics of similar molecular weight. Toughness might be further enhanced by altering the backbone structure to make it somewhat less compatible with the matrix or possibly increasing the number of branches off the backbone and controlling the end-group identity in such a way as to provide sufficient numbers of amine or phenol end groups to lock the thermoplastic into the backbone while introducing some phenyl end groups to decrease miscibility.

In the case of the epoxy, the toughness increase (133%) was less than that obtained with the linear imide tougheners (220%²⁶). Nevertheless, there were 2 features of the epoxy work that are highly promising. First, the graft oligomer possessed sufficient solubility such that it could be introduced into the epoxy without the use of B. The earlier work showed that the use of B decreased the T_g from 157 to 90°C. The T_g is not compromised by this approach since B was not required to introduce the oligomer into the epoxy prepolymer. Secondly, these oligomers possessed some phenol end groups, which are highly miscible with epoxy. By altering the oligomer structure to an all amine-terminated thermoplastic, sufficient solubility could be maintained so that B is not required for solubility, yet the thermoplastic miscibility might be decreased sufficiently to cause a more complete phase separation and so further increase toughness.

At lower levels of loading, comb-shaped oligomers appear to have the potential to toughen more effectively than linear oligomers with a similar structure and molecular weight without causing the significant increase in viscosity associated with linear oligomers. The rheology is not as well controlled as with hyperbranched materials, however, the synthesis is simpler, and the structures can be more easily varied and controlled. Therefore, comb-shaped oligomers may offer a reasonable compromise between ease of toughener preparation, prepolymer processing, and thermoset properties.

REFERENCES

1. C. B. Bucknall and I. K. Partridge, *Polymer*, **24**, 639 (1983).
2. R. S. Raghava, *Proceedings of the 29th National Symposium and Exhibition*, Society for the Advancement of Material and Processing Engineering, Reno, NV, April 3–5, 1984, pp. 1384–1394.
3. C. B. Bucknall and A. H. Gilbert, *Polymer*, **30**, 213 (1989).
4. J. A. Cecere and J. E. McGrath, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **27**, 299 (1986).
5. J. L. Hedrick, I. Yilgor, G. L. Wilkes, and J. E. McGrath, *Polym. Bull.*, **13**, 201 (1985).
6. C. B. Bucknall and I. K. Partridge, *Polym. Eng. Sci.*, **26**, 54 (1986).
7. R. A. Pearson and A. F. Yee, *Polym. Mater. Sci. Eng.*, **63**, 311 (1990).
8. H. Jabloner, B. J. Swetlin, and S. G. Chu, U.S. Pat. 4,656,207 (1987).
9. S. G. Chu, B. J. Swetlin, and H. Jabloner, U.S. Pat. 4,656,208 (1987).
10. R. S. Raghava, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 65 (1988).
11. Z. Fu and Y. Sun, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **29**, 177 (1988).
12. J. C. Amazigo and B. Budiansky, *J. Mech. Phys. Solids*, **36**, 581 (1988).
13. H. D. Stenzenberger, *Brit. Polym. J.*, **20**, 383 (1989).
14. B. H. Lee, M. A. Chaudhari, and Y. Blyakhman, *Polym. News*, **13**, 297 (1988).
15. J. Kim and R. Robertson, *Polym. Mater. Sci. Eng.*, **63**, 301 (1990).
16. R. J. Morgan, R. Jurek, and D. E. Larive, *Polym. Mater. Sci. Eng.*, **63**, 681 (1990).
17. S. P. Wilkinson, T. C. Ward, and J. E. McGrath, *Polymer*, **34**, 870 (1993).
18. C. K. Riew and R. W. Smith, *Rubber Toughened Plastics*, C. K. Riew, Ed., ACS Advances in Chemistry Series 222, American Chemical Society, Washington, DC, 1989.
19. F. F. Lange and K. C. Radford, *J. Mater. Sci.*, **6**, 1197 (1971).
20. Y. Huang, D. L. Hunston, A. J. Kinloch, and C. K. Riew, in *Toughened Plastics I*, C. K. Riew and A. J. Kinloch, Eds., ACS Advances in Chemistry Series 233, American Chemical Society, Washington, DC, 1993.
21. H. D. Stenzenberger, P. Konig, M. Herzog, and W. Romer, *Proceedings of the 18th International SAMPE Technical Conference*, Society for the Advancement of Material and Process Engineering, Washington, DC, Oct. 7–9, 1986, pp. 500–509.
22. H. D. Stenzenberger, *Compos. Struct.*, **24**, 219 (1993).
23. C.-R. Lin, W.-L. Liu, and J.-T. Hu, *Proceedings of the 34th International SAMPE Symposium*, Society for the Advancement of Material and Process Engineering, Reno, NV, May 8–11, 1989, pp. 1803–1813.
24. D. Rakutt, E. Fitzer, and H. D. Stenzenberger, *High Perform. Polym.*, **2**, 133 (1990).
25. A. Gopala, H. Wu, F. Harris, and P. Heiden, *J. Appl. Polym. Sci.*, to appear.
26. H. Wu, A. Gopala, F. Harris, and P. Heiden, *J. Appl. Polym. Sci.*, to appear.
27. G. R. Almen, R. M. Byrens, P. D. MacKenzie, R. K. Maskell, P. T. McGrail, and M. S. Sefton, *Proceedings of the 34th International SAMPE Symposium*, May 8–11, 1989, pp. 259–265.