

# Investigation of Readily Processable Thermoplastic-Toughened Thermosets. II. Epoxy Toughened Using a Reactive Solvent Approach

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**ABSTRACT:** The fracture toughness of epoxy thermosets was increased by up to 220% using very low-molecular-weight ( $\sim 1000$  g/mol) imide thermoplastic. The objective was to produce a low-viscosity prepolymer that could be easily autoclave-processed to give a tough thermoset. Here, an homogenous epoxy prepolymer was prepared by first synthesizing very low-molecular-weight linear aromatic imide ( $\sim 1000$  g/mol) directly in a liquid allyl phenol reactive solvent, followed by dissolution of the epoxy (Epon® 825) and the cure agent (DDS) directly in the thermoplastic solution. The allyl phenol both cures into the epoxy network, through phenol functional groups, and accelerates the cure. The viscosity of the pure epoxy was  $1.4 \text{ Pa} \cdot \text{S}$  at  $30^\circ\text{C}$ . The prepolymer formulations ranged from  $\sim 5\text{--}33 \text{ Pa} \cdot \text{S}$  at  $30^\circ\text{C}$ , but all reduced to less than  $1 \text{ Pa} \cdot \text{S}$  at  $90^\circ\text{C}$ . The onset of cure is well above  $90^\circ\text{C}$  so the prepolymer viscosity is within the range for autoclave processing. The cured resin plaques were not transparent, but phase-separated domains were not found by scanning electron microscopy, indicating that the domain size is below the detection limit of the instrument. The reactive solvent causes a decrease in both the  $T_g$  and the high temperature modulus of the thermoset. Introduction of the thermoplastic results in partial recovery of the  $T_g$  and modulus. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 935–942, 1998

**Key words:** autoclave-processable; reactive solvent; low-viscosity prepolymer; toughened epoxy; imide oligomer

## INTRODUCTION

Thermoplastic-toughening of thermosets is an area that has been extensively investigated in the last 15 years, and a great deal of excellent research has been published in this area.<sup>1–19</sup> Toughening thermosets with high performance, high- $T_g$  thermoplastics is advantageous because increases in fracture toughness are obtained with little or no decrease in other desired properties,

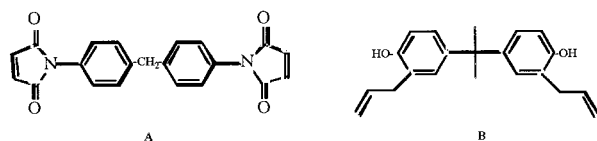
for example, modulus and  $T_g$ , which is not the case with rubber toughening. It is well known that a higher molecular weight thermoplastic toughens more effectively than a lower molecular weight thermoplastic,<sup>4,20</sup> and for that reason, toughening with extremely low-molecular-weight thermoplastic has been of little interest. However, incorporation of even a small amount of thermoplastic polymer causes exponential increases in prepolymer viscosity. Oligomeric thermoplastics also cause significant increases in prepolymer viscosity.<sup>21</sup> Autoclave processing is often a preferred method for processing high-performance thermoset composites; and since autoclave

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**Figure 1** Two-part BMI system: (A) is a high melting solid, and (B) is a liquid reactive diluent.

pressures are limited to  $\sim 100$ – $200$  psi, prepolymer viscosity is preferably kept below  $\sim 5$  Pa  $\cdot$  S in the early stages of a processing cycle to ensure adequate resin flow.<sup>22</sup> Therefore, autoclave processing of a prepolymer that contains thermoplastic is often difficult or may not be possible. Therefore, while toughening with thermoplastic offers the best performance, it comes at the expense of processability.

The overall objective of this work is to produce tough, easily autoclave-processable thermosets. The first article in this series<sup>21</sup> reported on toughening of a two-part BMI (Fig. 1) with very low-molecular-weight imide thermoplastic ( $\sim 1000$  g/mol) to yield readily autoclave processable BMIs. Modest increases in fracture toughness (50–100%) were obtained. Our group was simultaneously exploring these oligomers as tougheners for epoxy matrices with the same intent. In an epoxy matrix, fracture toughness increases with the imide thermoplastics investigated ranged from an 11% increase up to an increase of 220%.

The imide thermoplastics employed in this study (Fig. 2) were only  $\sim 1000$  g/mol but were nevertheless unable to be dissolved in the epoxy monomer directly or with the aid of any suitable solvent that could be distilled out of the solution. We therefore used the one-pot reactive solvent approach for prepolymer synthesis previously described.<sup>21</sup> In this approach, the allyl phenol, B (Fig. 1), is initially employed as a reaction solvent for the thermoplastic and then used as a reactive diluent for the epoxy. Therefore, fracture toughness values for modified epoxy were compared with both formulated (epoxy and B) and unformulated epoxy (without B) controls.

## MATERIALS

Epoxy resin (Epon® 825) was purchased from Shell Chemical Co (Houston, TX). All monomers were purchased from Chriskev (Leeward, Kansas), except 1,3-bis(4-aminophenoxy)benzene (APB), which was purchased from National

Starch (Woodruff, S. Carolina), and 2,6-diaminopyridine (DAP), which was purchased from Aldrich (Milwaukee, WI). B was purchased from Ciba Geigy (Hawthorne, New York). All other materials were purchased from Aldrich.

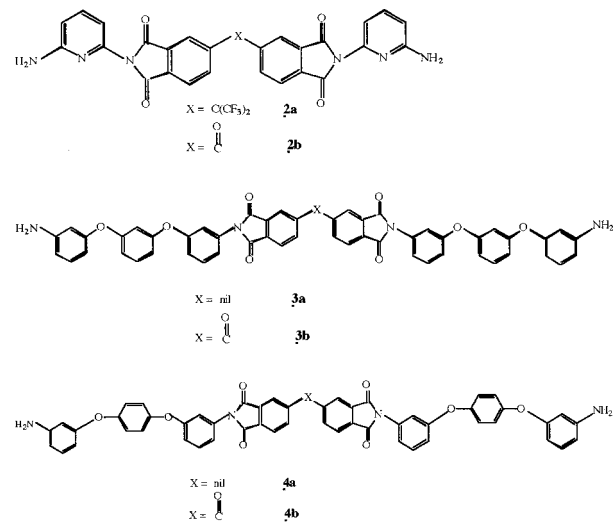
## INSTRUMENTATION

Viscosity measurements were made on a Bohlin VOR rheometric system. Molecular weight measurements were made by size exclusion chromatography (SEC) on a Perkin–Elmer 601 instrument equipped with Phenomenex columns packed with Phenogel, an ultraviolet–visible (UV–VIS) detector, and calibrated against polystyrene standards. Differential scanning calorimetry (DSC) was done on a Shimadzu DSC-50. Dynamic mechanical analyses (DMA) were performed on a Perkin–Elmer DMA 7 system in 3-point bending mode. Compact tension tests were performed on an Instron Universal Testing Machine. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR) and Fourier transform infrared (FTIR) were done on a Varian 200 MHz instrument and a Mattson Galaxy Series 3000 instrument, respectively.

## EXPERIMENTAL PART

### Prepolymer Synthesis

The diamine and dianhydride monomers (2 : 1, respectively) are added to B, (20–100% w/w B), in



**Figure 2** Amine-terminated thermoplastics employed to toughen epoxy.

a polymer reaction kettle and heated to 190°C  $\pm$  5°C for  $\sim$  0.5–1 h under a nitrogen purge. The 2 : 1 diamine to dianhydride ratio yields thermoplastic with a theoretical  $X_n$  of  $\sim$  3, which is a molecular weight in the range of  $\sim$  1000 g/mol. The cure agent, 4,4'-diaminodiphenylsulfone (DDS, 30 parts per 100 parts epoxy), is added, and heating is continued at 190°C until the cure agent is solvated. The temperature is then lowered to 110°C, and the solution of B, DDS, and thermoplastic, is degassed under reduced pressure. In a separate beaker, epoxy (Epon® 825) is heated to 110°C and degassed under reduced pressure. Epoxy is then blended with the thermoplastic solution at 110°C with high-speed mixing.

Untoughened control prepolymers were prepared as formulated and unformulated controls. The unformulated control contained epoxy and cure agent only, while for comparison, the formulated control prepolymer was prepared containing epoxy, cure agent, and B in the same ratio as in the toughened specimens. The epoxy–DDS unformulated control was prepared by blending together epoxy (100 parts) and DDS (30 parts), with mixing and degassing procedures identical to those described for the thermoplastic toughened specimens. Epoxy–DDS–B formulated controls were prepared by blending B (33.3 parts) and DDS (30.0 parts) at 190°C until a clear solution is obtained. The solution temperature is lowered to 110°C and degassed according to the procedure described above. Simultaneously, epoxy (100 parts) is heated to 110°C and degassed. The degassed epoxy is blended with the degassed B–DDS solution and mixed at high speed.

### Prepolymer Cure

Gel times for the prepolymers were measured according to ASTM D2471-94. The prepolymer cure characteristics were evaluated by DSC on a Shimadzu DSC-50 at 20°C/min.

### Molding Procedure

The clear prepolymers are degassed a final time at room temperature under reduced pressure for 40 min and then poured into a preheated vertical mold. The prepolymer is then cured at 140°C for 3 h. The specimen is allowed to cool to room temperature, demolded, and then postcured at 200°C for an additional 1 h.

Formulated epoxy control specimens were molded, cured, and postcured according to the

same procedure. Unformulated epoxy control specimens were cured for 8 h at 140°C, followed by 1 h at 200°C.

### Mechanical Properties

The compact tension testing procedure employed here was previously described.<sup>21</sup> All  $K_{Ic}$  values reported are the averages from multiple test specimens with multiple measured values from each specimen.

### Thermoplastic Characterization

Thermoplastic was obtained from B by precipitation in ethanol, collected by filtration, and dried under reduced pressure. Molecular weight was determined by SEC. Amine end-groups were confirmed by FTIR and <sup>1</sup>H-NMR. By <sup>1</sup>H-NMR, it was estimated that  $\sim$  95% of the end-groups were amine terminated.

### Rheology

The viscosity of the thermoplastic solutions in B 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.

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

Cured specimens were analyzed by DMA in the three-point bending mode to determine  $E'$ . Thermoset  $T_g$ s were determined as the inflection point on the  $E'$  curve.

## RESULTS AND DISCUSSION

### Effect of B on Epoxy Cure

The formulated epoxy employed in this work contains a significant amount of the phenolic compound B (1 part B for every 3 parts epoxy). The effect of B and the thermoplastic amine end-groups on gel time and cure onset is shown in Table I. Comparison of the gel time of the formulated control resin with the unformulated epoxy shows that B accelerates the cure. Although B did not form a thermoset with the epoxy at 140°C without DDS, it is thought that the B does react with the epoxy and is chemically incorporated into the network at high temperatures. Chemical reaction was not confirmed spectroscopically, but was postulated because the molded thermoset

**Table I** Effect of B and Thermoplastic on Epoxy Cure Characteristics

Sample	Gel Time <sup>a</sup> (min)	Peak Onset <sup>b</sup> (°C)	Peak Maximum <sup>b</sup> (°C)	Peak End <sup>b</sup> (°C)
Epoxy-DDS (3 : 0.9)	69	199	250	313
Epoxy-DDS-B (3 : 0.9 : 1)	48	152	222	303
Epoxy-DDS-B- <b>2a</b> (3 : 0.9 : 1 : 0.2)	33	153	187	217
Epoxy-B- <b>2b</b> (3 : 1 : 0.2)	>3000	—	—	—

<sup>a</sup> At 140°C.<sup>b</sup> By DSC at 20°C/min.

plaques obtained in the presence of DDS were hard, tack-free surfaces.

It was found that the amine hydrogens of DAP terminated thermoplastics (**2a** and **2b**), are largely unreactive at 90°C since no gelation was observed for the epoxy-B-**2b** system, and the onset of cure by DSC is the same in DAP thermoplastic systems as in the formulated control systems (~ 153°C). At higher cure temperatures, it was evident that the DAP amines enter the cure since both the maximum and the end of the cure exotherm occur at lower temperatures for formulations with the imide than without the imide.

#### Effect of B and Low-Molecular-Weight Thermoplastic on Viscosity

The effect of B and thermoplastic loading on the prepolymer viscosity was measured at 30 and 90°C (Table II). The reactive diluent, B, is more viscous than the epoxy, so at 30°C, pure epoxy has a viscosity of only 1.4 Pa · S, while the formulated epoxy control (3 : 1 epoxy : B) has a viscosity of 3.5 Pa · S. When thermoplastic **2a** (~ 850 g/mol) is

incorporated into the prepolymer, the viscosity increases rapidly with loading, giving a nearly 800% increase in viscosity relative to the untoughened, formulated epoxy control. Nevertheless, although the viscosity, at 30°C, is 32 Pa · S at 10% loading and is off the instrument scale at 15% loading, at 90°C, the viscosity for all the samples is well below 1 Pa · S, and the prepolymer should be readily autoclave-processable. Thermoplastic **3b** (~ 1200 g/mol) possessed a higher viscosity than **2b** but showed a similar viscosity trend, and, like **2a**, the viscosity was well below 1 Pa · S at 90°C.

#### Effect of B and Low-Molecular-Weight Thermoplastic on Fracture Toughness

Fracture toughness was measured by compact tension. The reported  $K_{Ic}$  values (Table III) are the averages of numerous measurements taken from multiple specimens. At 5% loading (w/w thermoset), moderate fracture toughness increases were found. Thermoplastic **3a** yielded the lowest increase (11%), while **2b** gave the largest

**Table II** Effect of Temperature and Thermoplastic Loading on Prepolymer Viscosity

Thermoplastic	% Thermoplastic (w/w B)	% Thermoplastic (w/w)	Viscosity (Pa · S)		$\Delta$ Viscosity <sup>c</sup> (%)	
			30°C	90°C	30°C	90°C
None <sup>a</sup>	0	0	1.4	0.02	—	—
None <sup>b</sup>	0	0	3.5	0.02	—	—
<b>2a</b>	10	3	5.0	0.02	43	0
	20	5	12	0.04	243	100
	40	10	32	0.05	814	15
	60	15	—	0.18	—	800
<b>3b</b>	20	5	33	0.09	843	350
	60	15	—	0.23	—	—

<sup>a</sup> Unformulated epoxy control with epoxy-DDS (3 : 0.9).<sup>b</sup> Formulated control with epoxy-B-DDS (3 : 1 : 0.9).<sup>c</sup> Values compared with formulated control.

**Table III** Effect of Low-Molecular-Weight Linear Thermoplastic on Toughness

Thermoplastic ( $M_n$ )	% Thermoplastic (w/w B)	% Thermoplastic (w % overall)	$K_{Ic}$ (MPa · m <sup>1/2</sup> )	$\Delta K_{Ic}$ <sup>c</sup> (%)
None <sup>a</sup>	0	0	0.48 ± 0.10	—
None <sup>b</sup>	0	0	0.35 ± 0.09	—
<b>2a</b> (858 g/mol)	20	5	0.62 ± 0.16	77
	40	10	0.66 ± 0.10	89
	60	15	0.90 ± 0.33	157
	100	25	0.79 ± 0.18	126
<b>2b</b> (720 g/mol)	20	5	0.66 ± 0.28	89
<b>3a</b> (1300 g/mol)	20	5	0.39 ± 0.15	11
	60	15	0.52 ± 0.11	49
	100	25	0.62 ± 0.22	77
<b>3b</b> (1200 g/mol)	20	5	0.60 ± 0.17	71
	60	15	1.12 ± 0.43	220
<b>4a</b>	20	5	1.05 ± 0.32	200 <sup>d</sup>
	40	15	0.52 ± 0.14	49
	60	15	0.56 ± 0.10	60
<b>4b</b> (1020 g/mol)	20	5	0.57 ± 0.16	63

<sup>a</sup> Epoxy–DDS (3 : 0.9).<sup>b</sup> Formulated control with epoxy–B–DDS (3 : 1 : 0.9).<sup>c</sup> Values compared with formulated control.<sup>d</sup> Value measured after preparation of new thermoplastic and new molded specimens.

increase (89%). When the loading was increased to 15%, the fracture toughness increased modestly for epoxy modified with **3a** and **4a** (50–60%), but epoxy modified with **2a** and **3b** yielded significant increases of 157 and 220%, respectively. The fracture toughness obtained with **3b** was confirmed by synthesis of a second batch of thermoplastic in B and molding an additional specimen from the new resin. The large increase in toughness was also found with the second resin batch. These increases are attributed to thermoplastic incompatibility with the epoxy matrix since, although thermoplastics **3a** and **3b** gave a 49 and 220% increases in toughness in an epoxy matrix (15% w/w), these same resins gave only a 25 and 75% increase in toughness in a BMI (bismaleimide) matrix (20% w/w).<sup>21</sup> The data is not conclusive but suggests that imide thermoplastic will, in general, afford better improvements in fracture toughness in epoxy than in BMI. Because the imides appear to be less compatible with epoxy matrices than BMI matrices, this would suggest that the thermoplastic phase separated at an earlier point during the cure, possibly yielding a morphology that toughens more effectively than the resulting BMI morphology. However, as with the BMI, SEM of the fracture surfaces showed no obvious phase-separated domains.

### Effect of B and Low-Molecular-Weight Thermoplastic on $T_g$ and $E'$

The molded specimens were analyzed in three-point bending mode by DMA to obtain  $T_g$  and  $E'$  (Table IV). The epoxy control which was unformulated (no B) possessed a  $T_g$  of 157°C and an  $E'$  of  $1.9 \times 10^9$  Pa (at 100°C), while the epoxy control that contained B possessed a much lower  $T_g$  and  $E'$  (90°C and  $0.7 \times 10^9$  Pa, respectively). The  $E'$  at 25°C was essentially the same for both the formulated epoxy control and the unformulated control. When an imide thermoplastic was incorporated into the formulation, the  $T_g$  recovered to some extent, (~ 105–110°C) as did the high temperature modulus; however, the presence of the B did compromise the high temperature properties of the thermoset. Epoxy modified with **3b**, which afforded the highest increase in fracture toughness, also provided the greatest degree of recovery with a fairly high  $T_g$  of ~ 120°C (Table IV). The  $E'$  (Fig. 3) at 100°C was not significantly reduced ( $1.8 \times 10^9$  Pa) when compared with the unformulated epoxy control ( $1.9 \times 10^9$  Pa).

### MORPHOLOGY

The fracture surfaces of all the cured specimens were examined by SEM. The fracture surfaces



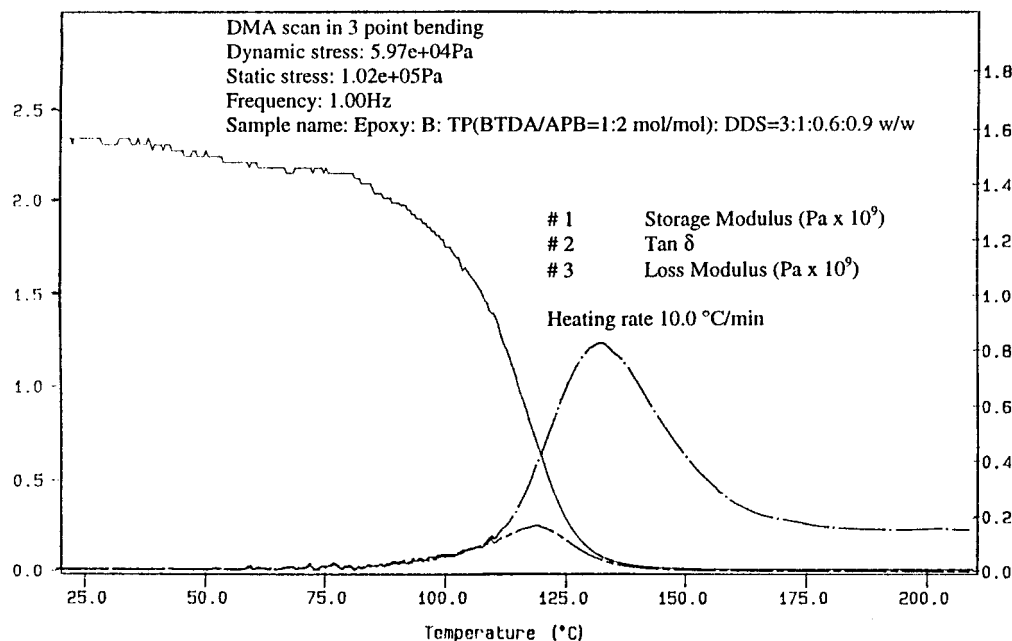
**Table IV** Effect of B and Thermoplastic on  $T_g$  and Storage Modulus ( $E'$ )

Epoxy Formulation					$T_g$ (°C)	$E'$ (Pa × 10 <sup>9</sup> ) 25°C	$E'$ (Pa × 10 <sup>9</sup> ) 100°C
Epoxy	B	DDS	% TP (wt % overall)	TP			
3	0	0.9	0	0	157	2.3	1.9
3	1	0.9	0	0	90	2.4	0.7
3	1	0.9	5	<b>2a</b>	105	1.9	1.1
3	1	0.9	10	<b>2a</b>	110	2.1	1.6
3	1	0.9	15	<b>2a</b>	106	2.4	1.3
3	1	0.9	25	<b>2a</b>	106	2.5	1.7
3	1	0.9	5	<b>3a</b>	110	2.3	1.3
3	1	0.9	15	<b>3a</b>	110	2.0	1.1
3	1	0.9	25	<b>3a</b>	110	2.6	1.5
3	1	0.9	5	<b>3b</b>	118	2.2	1.4
3	1	0.9	15	<b>3b</b>	120	2.3	1.8

showed no obvious features in all instances, except with **4a**, which showed small spherical domains with an average diameter of approximately 0.5  $\mu\text{m}$ . Thermoplastic **4a** is based on the 2 monomers that are probably the least soluble monomers used in this work, BPDA and TPER. The epoxy that was most effectively toughened was modified with thermoplastic **3b**, which was from APB and BTDA, which are somewhat more soluble monomers. It, like the thermoplastics, showed no obvious phase-separated domains by SEM, but, as with all the

thermoplastic modified epoxy thermosets, except epoxy modified with **2a**, was opaque.

It is often reported that phase separation is essential for enhancing toughness. The same thermoplastics that gave only ~ 75% improvement in toughness in BMI were able to afford up to 220% improvement in epoxy, and yet, SEM analysis showed no evidence of phase separation in either BMI or epoxy matrices in all cases but **4a**. Furthermore, it is clear that at these low molecular weights, the thermoplastics possess

**Figure 3** DMA of **3b** (5% w/w) in 3-point bending mode.

low toughness on their own, and comparison of the fracture toughness of the formulated and unformulated epoxy controls show that the toughness is not due to either plasticization or dilution of the network, which would be expected with the use of a reactive solvent. The unformulated epoxy control (epoxy and DDS; no B) had a fracture toughness of  $0.48 \text{ MPa} \cdot \text{m}^{1/2}$ . When B was employed, the fracture toughness was reduced to  $0.35 \text{ MPa} \cdot \text{m}^{1/2}$ . The fact that B reduces the fracture toughness demonstrates that the addition of the thermoplastic is responsible for the increased toughness. Furthermore, the fact that the same imide thermoplastics toughen epoxy more effectively than BMI suggest that the increase in toughness is due to less thermoplastic compatibility with an epoxy matrix. Polyethersulfones and polyetherketones of  $\sim 5000 \text{ g/mol}$  have been investigated as tougheners for epoxy and do not provide any significant improvements in toughness. Unlike the imides, polyethersulfone and polyetherketones are directly soluble in the epoxy, although, in some cases, a low boiling solvent is required, which can subsequently be removed. It may be that those thermoplastics fail to significantly toughen epoxy until molecular weights of close to  $10,000 \text{ g/mol}$  are employed because of a greater degree of compatibility with the matrix at lower molecular weights. This also explains why these resins provide lesser improvements in toughness with a BMI matrix since it would not be unreasonable to expect an imide oligomer to be more compatible with an imide thermoset than an epoxy thermoset.

If these imide thermoplastics are less compatible with an epoxy matrix, it would be expected that they phase separated at an earlier point in the cure cycle during epoxy curing than during BMI curing. Consequently, they might possess a different morphology, which many researchers have long claimed to be the most critical factor to enhance thermoset toughness.<sup>23</sup> However, what is interesting about these results is that fairly significant increases in toughness were found, and yet, as was the case with the imide toughened BMIs, no dispersed phase was observed by SEM (except with **4a**, where small spherical domains were seen) to give a morphological explanation for the increased toughness. Although no morphological reason for the toughness increase was found, the increase is not attributed to dilution of crosslink density. This conclusion was made for the 2 following reasons: some thermoplastics (for example, **3b**) gave substantially greater increases in toughness than other thermoplastics

(for example, **3a**, **4a**, **4b**) of similar molecular weight; and the formulated epoxy control specimen (epoxy–DDS–B) containing the reactive diluent B did possess a lower crosslink density, yet was less tough than the unformulated epoxy–DDS specimens.

Although higher fracture toughness increases for epoxy are reported in the literature than the maximum 220% increase found here, these increases are only achieved with much higher molecular weight thermoplastic and higher loading. Therefore, the prepolymer viscosity is much higher, and so the prepolymer is much harder to process. A careful search of the literature did not find any studies on thermoplastic modifiers as low as  $\sim 1000 \text{ g/mol}$ , but thermoplastics of  $\sim 3000\text{--}5000 \text{ g/mol}$  have been investigated and typically show increases in fracture toughness of  $\sim 0\text{--}50\%$  relative to the control values. The imide oligomers employed here gave fairly good increases in fracture toughness when used as epoxy tougheners and, based on the rheology results, were nearly as processable as the unmodified epoxy. The major drawback to this approach was that the imide oligomers employed here could not be introduced into the epoxy without the use of the reactive diluent, which did cause a drop in the final thermoset  $T_g$  and high temperature  $E'$ .

## CONCLUSIONS

A reactive solvent method was used to incorporate very low-molecular-weight ( $\sim 1000 \text{ g/mol}$ ) imide thermoplastics into epoxy with the objective of producing a tough, but easily autoclave-processable resin. The reactive solvent B was required for the formation of an homogenous prepolymer solution since the imide thermoplastic could not be solvated directly in the epoxy monomer despite the very low molecular weight employed. All the B appeared to react directly into the epoxy since the cured thermoset was hard, and there was no evidence of "blooming" or B on the mold or the oven.

Use of such low-molecular-weight thermoplastics afforded highly processable prepolymer solutions. In all cases, the prepolymer viscosity was less than  $1 \text{ Pa} \cdot \text{S}$  at  $90^\circ\text{C}$ .

Comparison of an epoxy control with a formulated control (epoxy and B, but no thermoplastic) showed the presence of the B in the thermoset network compromised both the  $T_g$  and the high temperature  $E'$ . The  $T_g$  and  $E'$  did recover some-

what on addition of the imide thermoplastic, but never recovered fully. The best values obtained for a thermoplastic-modified epoxy were obtained with the imide thermoplastic **3b**, which gave a 220% increase in toughness, a  $T_g$  of 120°C (versus 157°C for the unmodified epoxy), and an  $E'$  of  $1.8 \times 10^9$  Pa at 100°C (versus  $1 \times 10^9$  Pa for the unmodified epoxy).

SEM analysis found no obvious phase separation in most of the modified thermosets and so could not provide any morphological explanation for the increase in toughness. However, the increased toughness is not attributed to the presence of B, which would dilute the crosslink density and might plasticize the network. This conclusion is made because the fracture toughness of the formulated control specimen made from epoxy with B is less than that of the pure epoxy. The formulated epoxy control had a fracture toughness of only  $0.35 \text{ MPa} \cdot \text{m}^{1/2}$  versus  $0.48 \text{ MPa} \cdot \text{m}^{1/2}$  for the unformulated epoxy control. Therefore, the reason for the toughness increase may lie in a mechanism involving morphological features that are below the detection limits of the SEM.

This work shows that reasonable increases in toughness can be achieved with extremely low-molecular-weight thermoplastic, which has not been previously demonstrated. None of the epoxy systems employed were optimized, so higher values may be possible, although toughness increases of the level attained with high-molecular-weight thermoplastic are not expected. The results of this work suggest that for applications where good processability is essential and moderate increases in toughness are acceptable, the low-molecular-weight tougheners may have value. Nevertheless, further improvements in fracture toughness are desirable without compromising the  $T_g$  and  $E'$ , which were compromised by the methods employed here. This difficulty could potentially be minimized using a tetrafunctional epoxy; however, the best approach would be to develop a method of using imide thermoplastic without requiring B.

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