# Investigation of Readily Processable Thermoplastic-Toughened Thermosets. I. BMIs Toughened via a Reactive Solvent Approach

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**ABSTRACT:** Moderate increases ($\sim 50-75\%$) in the toughness of bismaleimides (BMIs) were achieved with very low-molecular-weight ($\sim 1000$ g/mol) imide thermoplastics at low levels of thermoplastic loading ($\sim 10-20\%$). The thermoplastic was introduced into the BMI using a simple, one-pot, reactive solvent approach. In this approach, the reactive diluent of a two-part BMI was used as the reaction solvent for the thermoplastic synthesis. The BMI monomer was then dissolved in the thermoplastic reaction solution to yield a low-viscosity homogenous prepolymer. The viscosity of the thermoplastic solution was $\sim 6$ Pa S at 55°C. The effect of thermoplastic loading and molecular weight on viscosity was determined by rheology, and the fracture toughness of neat resin plaques was determined by compact tension. Increasing the thermoplastic loading increased prepolymer viscosity without improving toughness, while increasing the thermoplastic molecular weight increased the toughness by only 25% more than the lowest-molecular-weight thermoplastic, yet increased viscosity fivefold. Fracture surfaces showed no obvious phase separation by scanning electron microscopy. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 469–477, 1998

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

## INTRODUCTION

High-performance thermosets are of interest as matrix resins for composites for structural applications. However, the inherent brittleness of thermosets requires that they be toughened to improve damage tolerance. A considerable body of research exists in the literature on high-performance thermoplastic toughening of thermosets starting with the ground-breaking work of Bucknall and Partridge,[1] Raghava,[2] and Bucknall and Gilbert[3] and continuing uninterrupted work

through today.[4–17] Various approaches to toughening have been investigated,[15–19] and many studies on the mechanisms of toughening have been undertaken and have been thoroughly reviewed (for example, Huang et al.[20]). Most thermoset toughening methods result in decreasing other desired properties, such as $T_g$ and modulus,[21,22] while incorporation of high $T_g$, high-performance thermoplastics successfully increases the fracture toughness with only minor decreases in other desired properties (for example, Kim and Robertson,[15] Lin et al.,[17] and Rakutt et al.[23]). Consequently, this method is currently of great interest for high-performance thermosets. However, incorporation of even small amounts of thermoplastic polymer results in substantial in-

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creases in prepolymer viscosity. Even oligomeric thermoplastics cause significant increases in prepolymer viscosity, which can make processing difficult, and autoclave processing, often a preferred method of composite fabrication, may not even be possible. Autoclave processing is often limited to application pressures of 100–200 psi, so prepolymer viscosity is preferably below ∼ 5 Pa S at the initial processing temperature so that the resin possesses sufficient flow during autoclave processing.[24] Therefore, while toughening with high-performance thermoplastic offers the best balance of properties, it comes at the expense of the key advantage thermosets offer over thermoplastics, which is processability.

A second difficulty often encountered with thermoplastic toughening of thermosets is that many high-performance thermoplastics cannot be incorporated into thermoset prepolymers. This is due to the fact that these thermoplastics often possess little or no solubility in either thermoset monomers, or in solvents that are sufficiently low boiling so that they may be removed without premature curing of the prepolymer. The type and degree of thermoplastic phase separation is dependent on the relative rates of thermoplastic phase separation and thermoset cure, so even minor changes in thermoplastic backbone structure could affect the rate of phase separation and, thus, the final morphology. This, in turn, will influence the toughness of the thermoset. For example, some researchers have found a co-continuous morphology is optimal for toughness (generally ∼ 20–26% w/w),[25] while Rakutt and coworkers[23] found that a polyetherimide-toughened BMI at a similar thermoplastic loading level gave optimal toughness with a thermoplastic continuous phase and a dispersed thermoset phase. Thus, the morphology for optimal toughness appears to depend on the specific system under investigation. Because of the significant effect of thermoplastic content and phase separation rate on morphology and toughness, the limited number of thermoplastics able to be introduced into thermoset prepolymers may limit opportunities to optimize toughness in processable thermosets.

A variety of high-performance thermoplastics, including aromatic polyimides, polyphenylquinoxalines, and polyesters, among others, were able to be prepared directly in a phenolic reactive diluent "B" (Fig. 1),[26] which is one of the components of a two-part BMI formulation. Many of these thermoplastics could be prepared in solutions of up to 1 : 1 (w/w) thermoplastic to B.

Higher solids concentrations appeared possible with the more soluble resins but were not attempted. The imide thermoplastics were prepared in monomer ratios which varied from 2 : 1 to 1 : 1, diamine to dianhydride, and many of the amorphous resins remained in solution as high-molecular weight polymers. In a few instances, the thermoset monomer ("A", Fig. 1) was no longer soluble in the thermoplastic-containing solution of B, but homogenous prepolymers were obtained in many cases. On curing, the B component reacted into the BMI matrix, as it was designed to do. Therefore, this is a versatile, one-pot method for the preparation of homogenous thermoset prepolymers containing high-performance thermoplastic. The fact that homogenous prepolymer blends were obtained with a wide variety of thermoplastics, even at high solids concentrations, makes this "reactive solvent" approach a simple and effective method for studying high-performance thermoplastic toughening of thermosets. The reactive solvent method was used here as a convenient method to study the affect of thermoplastic loading and oligomer backbone structure on both prepolymer viscosity and thermoset toughness with the intent of obtaining a very processable but tough system. Once such a system is identified, toughness can be further increased by optimizing processing parameters.

## OBJECTIVE

The objective of this work was to prepare an autoclave processable prepolymer solution that could be cured to give a tough thermoset BMI. The reactive solvent approach is employed to prepare thermoplastic-containing solutions of B, and, in this preliminary study, autoclave processability is assessed by measuring the increase in viscosity of this solution. After curing, the thermoset toughness is evaluated by measuring the $K_{Ic}$ of neat resin plaques using a compact tension test.

## 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 and an ultraviolet–visible (UV–vis) detector, which was calibrated with polysty-
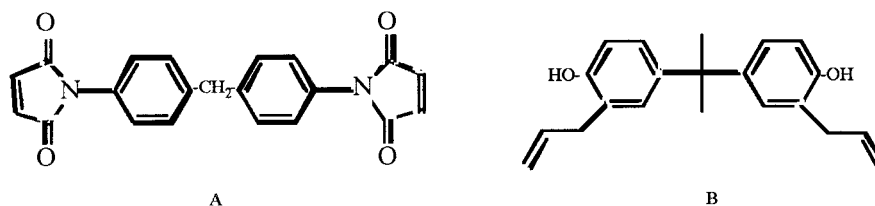
**Figure 1** Two-part thermoset system consisting of (A) BMI monomer and (B) bis-allylphenol reactive diluent.

rene standards. 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. $^1H$ nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) were done on a Varian 200 MHz instrument and a Mattson Galaxy Series 3000 instrument, respectively.

## MATERIALS

The matrix resin was a two-part BMI (Matrimid® 5292) purchased from Ciba Geigy (Hawthorne, N.Y.). The BMI, A, is a solid at room temperature, while the reactive diluent, B, is a viscous liquid at room temperature. B was employed as the solvent for the synthesis of the thermoplastic toughener. The thermoplastics studied are very low-molecular-weight aromatic imides, which are prepared directly in B from commercially available aromatic diamines (1a–c) and aromatic dianhydrides (1d–g), shown in Figure 2. The procedures employed are described in the experimental sec-



**Figure 2** Monomers employed in the preparation of thermoplastic imide tougheners.

tion. All dianhydrides used to prepare the thermoplastic were purchased from Chriskev Company (Leeward, KS). All other reagents were purchased from Aldrich, except diamine 1c, obtained from Chriskev, and diamine 1b, obtained from Frank Harris National Starch (via National Starch in Woodruff, S. Carolina).

## EXPERIMENTAL

### Procedure for the Preparation of Untoughened BMI Prepolymer

Prepolymer solutions without thermoplastic were prepared by adding B (35 g) to a reaction kettle equipped with a mechanical stir assembly and a nitrogen inlet/outlet. A (41 g) was added, and the mixture was heated and stirred to ~ 145°C until a clear solution was obtained (~ 0.4 h). Heat was immediately discontinued, and the solution was degassed under reduced pressure.

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

B (35 g) was weighed into a reaction kettle equipped with a mechanical stir assembly and with a nitrogen inlet/outlet. The required mass of each of the monomers for the thermoplastic toughener (TP) was added to B in stoichiometric ratios of diamine-to-dianhydride of 2 : 1, 3 : 2, 5 : 4, and 10 : 9, to yield amine-terminated oligomers. The total mass of monomer employed was sufficient to yield solutions of 20, 30, and 50% (w/w with respect to B) or 12, 17, and 28% overall. The solutions were stirred and heated to 185°C ± 5°C for ~ 0.8–1 h under a nitrogen purge. The temperature of the solution was then lowered to ~ 145°C and A (41 g) was added. The mixture was stirred until a clear solution was obtained (~ 0.4–1.0 h). Heat was immediately discon-

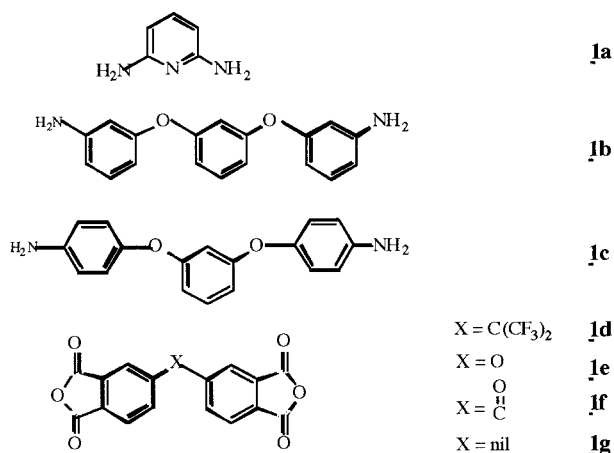tinued, and the solution was degassed under reduced pressure.

## Thermoplastic Characterization

Thermoplastic was isolated directly from B prior to the addition of A by precipitation in ethanol. The thermoplastic was collected by filtration and dried under reduced pressure. Estimates of the average thermoplastic molecular weight were made by SEC. The percentage of amine end groups was estimated by $^1$H NMR.

## Rheology

The viscosity of the thermoplastic solutions (in B) was measured at 55°C on a cone and plate set up with a 25-mm cone diameter at a 5.4° angle to determine zero shear viscosity.

## Molding Procedure

The clear prepolymer solution was degassed a second time in a preheated oven (150°C) for 0.75 h under reduced pressure and then poured into a preheated vertical mold treated with a thermally stable release agent. The prepolymer was cured at 150°C for 5.5 h followed by 3.5 h at 200°C. Samples were postcured for 6.5 h at 250°C after demolding.

## Sample Preparation for Mechanical Testing

Molded samples were cut into compact tension test pieces of $1 \times 1$ in. The edges and flat surfaces were buffed with grit paper (200, followed by 40, followed by 20), changing the direction of abrasion by 90 degrees after each buffing. The samples were then notched at the center to a depth of 5 mm, then vertically clamped, and a crack was initiated with a sharp razor blade (dipped into liquid nitrogen) by placing firmly against the notch and striking with a hammer. Two holes were then drilled perpendicular to the plane surfaces using a template. Approximately 75% of the samples prepared in this manner were suitable for testing.

## Compact Tension Testing

The procedure described in ASTM E399-86 was followed. Samples were clamped into a universal testing machine and loaded at a rate of 0.002 in./min. The stress intensity factor ($K_{Ic}$) was calculated according to the formula following[27]:

$$K_{Ic} = P_c Y a^{1/2}/BW$$

where $Y$ is $29.6 - 185.5 \, (a/w) + 655.7 \, (a/w)^2 - 1017 \, (a/w)^3 + 638.9 \, (a/w)^4$, $P_c$ is the load at crack initiation, $B$ is the specimen thickness, $W$ is the specimen width, and $a$ is the crack length. For each specimen tested, the largest and smallest values for $K_{Ic}$ were discarded. The other $K_{Ic}$ values found for the specimen were used to calculate an average $K_{Ic}$ for that specimen, and the reported $K_{Ic}$ values are the averages from multiple test specimens.

## Dynamic Mechanical Analysis

The storage modulus ($E'$) and $T_g$ of the thermosets were found by DMA using a 3-point bending mode. Thermoset $T_g$s were determined as the onset of the loss in $E'$.

## RESULTS AND DISCUSSION

As previously stated, a considerable amount of prior research has been carried out in which high-performance thermoplastics were used to toughen epoxy and BMI thermosets. However, that prior research focused on high-molecular-weight polymers and higher-molecular-weight oligomers, probably most often in the range of $\sim$ 8000–35,000 g/mol. In a review of the literature, one study was found in which a series of polysulfones was studied in which one oligomer had a molecular weight as low as 4100 g/mol.[4] The 4100-g/mol polysulfone oligomer resulted in no improvement in the toughness relative to an untoughened epoxy control, and an oligomer of 5300 g/mol gave only a 33% increase in toughness (15% w/w). No doubt, use of higher-molecular-weight thermoplastic is favored because that study and many others show that toughness increases as the molecular weight of the thermoplastic increases (for example, Cecere and McGrath,[4] Hedrick et al.,[5] and Jensen and Hergenrother[28]). However, processability significantly decreases as the molecular weight of the toughener increases. In this research, the overall objective was to prepare a readily processable prepolymer system, which can be cured to a tough thermoset. Therefore, this work focused on extremely low-molecular-weight thermoplastic tougheners to prepare low-viscosity, highly processable, prepolymer blends.
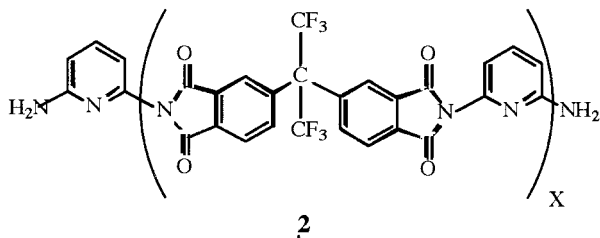
**Figure 3** Amine-terminated thermoplastic employed to study the affect of molecular weight on viscosity: 2a = ~ 700 g/mol; 2b = ~ 1200 g/mol; 2c = ~ 1770 g/mol; 2d = ~ 2200 g/mol.

## Effect of Molecular Weight on Viscosity and Toughness

It is well known that viscosity increases exponentially with molecular weight, yet relatively few studies of thermoplastic toughening report the viscosity of the thermoplastic-containing prepolymer solutions, and no studies were found for the molecular weight range focused on here. Therefore, the first study determined the effect of molecular weight on the viscosity of solutions of thermoplastic in B to establish the upper molecular weight range, which gives a suitable viscosity. One series of oligomers (2a–d, Fig. 3) was prepared, in which the loading was held constant at 20% (w/w B) and the molecular weight was systematically varied from a theoretical molecular weight of ~ 700 g/mol up to a maximum of ~ 2200 g/mol, and the viscosity of these solutions was measured. SEC gave measured molecular weights, which were close to, but slightly higher than, theoretical values, except in the case of 2d, in which the measured value was approximately 5800 g/mol. The molecular weight was controlled by altering the ratio of diamine (1a) to dianhydride (1d) added to B. Amine end groups were confirmed by $^1$H-NMR and ranged from 87% (2a) to 100% end-capped (5), with most thermoplastics being about 95% amine end-capped. The viscosity of the thermoplastic solutions, measured by rheometry, was found to increase by several orders of magnitude over pure B, even when the oligomer was ~ 700 g/mol (Fig. 4).

The thermoset toughened with 2d (20% thermoplastic in B; 10% overall), which had a molecular weight of only ~ 2200–5800 g/mol, doubled the fracture toughness relative to the untoughened control (1), going to ~ 0.8 MPa m$^{1/2}$ from ~ 0.4 MPa m$^{1/2}$. However, while the fracture toughness increased only ~ 100%, the viscosity increased by ~ 5000%, going from 0.6 to 31 Pa

S. When the thermoplastic molecular weight was kept below ~ 2000 g/mol (2a and 2b), the fracture toughness was ~ 0.6–0.7 MPa m$^{1/2}$, a 50–75% increase in toughness, yet the viscosity increase was only on the order of 1000%, from 0.6 to 6–7 Pa S. Therefore, these extremely low-molecular-weight oligomers gave a toughness increase, which was not substantially less than that obtained with 2d. From these results (Table I), it is evident that the viscosity increase in going from oligomers of ~ 1000 g/mol to more than 2000 g/mol makes the prepolymer more difficult to process with little benefit. Therefore, based on this work and the work of many others,[4,5,18,28] it appears that increasing the thermoplastic molecular weight is not rewarded by a significant increase in toughness relative to very low-molecular-weight species until thermoplastics with molecular weights of ~ 8000 or even 10,000 g/mol are used.

## Effect of Thermoplastic Loading

Toughness increases were obtained using very low-molecular-weight tougheners (2a and 2b), but were not of the desired degree. Somewhat higher values were obtained with 2c and 2d, but the associated viscosity increase was greater than desired. Therefore, the second study employed the lowest-molecular-weight oligomer, 2a, to measured the effect of increased thermoplastic loading on the viscosity and fracture toughness. The results (Table II) show that as the thermoplastic loading increased from 20 to 30% (w/w B, corresponding to ~ 10 and ~ 15% overall in thermoplastic), within experimental error, there was no change in toughness. However, the viscosity did
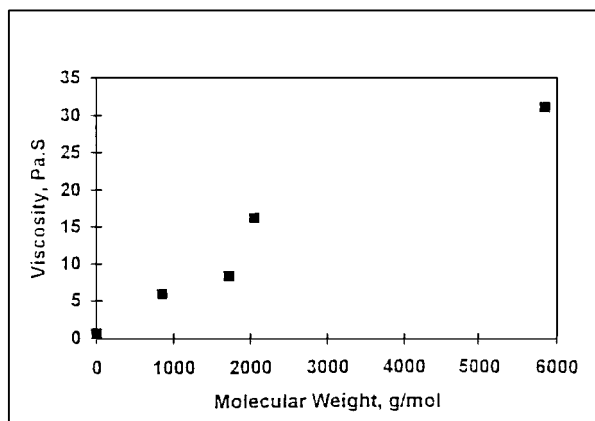


**Figure 4** Viscosity versus molecular weight of 2 at a thermoplastic loading of 20% w/w B.

**Table I Effect of Thermoplastic Molecular Weight on Viscosity and Fracture Toughness**

| Thermoplastic | Thermoplastic % (in B) | $M_n$ (g/mol; theoretical) | $M_n$ (g/mol; measured) | $K_{Ic}$[a] (MPa m$^{1/2}$) | $\Delta K_{Ic}$ (%) | Viscosity (Pa S)[b] | $\Delta$Viscosity (%) |
|---|---|---|---|---|---|---|---|
| 1 | 0 | — | — | 0.4 ± 0.1 | — | 0.6 | — |
| 2a | 20 | 700 | 858 | 0.6 ± 0.1 | 50 | 6 | 1000 |
| 2b | 20 | 1200 | 1720 | 0.7 ± 0.1 | 75 | 7 | 1100 |
| 2c | 20 | 1700 | 2053 | 0.6 ± 0.1 | 75 | 16 | 2700 |
| 2d | 20 | 2200 | 5849 | 0.8 ± 0.1 | 100 | 31 | 5200 |

[a] Errors ranged from 0.01 to 0.08 MPa m$^{1/2}$.
[b] Measured at 55°C.

increase rapidly with loading. The results showed that the desired degree of processability would not be maintained by increasing the thermoplastic loading, and, at least with 2a, increased loading would not increase the toughness. Because oligomer 2 is a relatively soluble species (cured samples were slightly opaque, but no obvious phase separation was visible, even by SEM), further research focused on less-soluble imide thermoplastic. Many researchers claim that phase separation is essential for increasing fracture toughness and that the final thermoset morphology is critical to toughness. Therefore, better fracture toughness values are expected with less soluble thermoplastic to enhance phase separation during the cure.

Prepolymer blends were prepared with different amine-terminated high-performance imide thermoplastics (3–9, Fig. 5) and cured. Thermoplastic molecular weight was limited by using a diamine to dianhydride ratio of 2 : 1 to yield thermoplastics that were expected to be less compatible than 2 with the cured BMI matrix. The measured molecular weights were $\sim$ 1200–2000 g/mol. The measured values for molecular weight and $K_{Ic}$ are tabulated (Table III). In this molecular weight range, toughness is not enhanced by going to thermoplastic loadings above 20% (w/w B), and, in some instances, higher loading decreased toughness. The differences in toughness

between different thermoplastics are small, but the results are the averages from numerous measurements from multiple specimens, and the results were reproducible. It was concluded that the toughness increases, though small to moderate, were real. Therefore, it appears that the toughest thermosets were from thermoplastics 5, 7, and 8, which are among the least soluble thermoplastics. However, based on the ability to increase the thermoplastic loading and retain a homogenous prepolymer, the least soluble thermoplastic was 9. This modified thermoset was also the only specimen that showed phase separation by SEM.

## Morphology of BMIs Toughened with Low-Molecular-Weight Imide Oligomers

As discussed above, the morphology of thermoplastic-toughened thermosets clearly influences the toughness and toughening mechanisms of the thermoset. With high-molecular-weight tougheners, phase separation occurs at low levels of thermoplastic addition. In fact, Rakutt and coworkers[23] found that phase inversion frequently occurred at thermoplastic loading levels of about 20% (w/w thermoset). The morphology of thermosets toughened with polymer and higher-molecular-weight oligomer is not usually difficult to observe with SEM. However, in this work, no mor-

**Table II Effect of Thermoplastic (2a) Content on Viscosity**

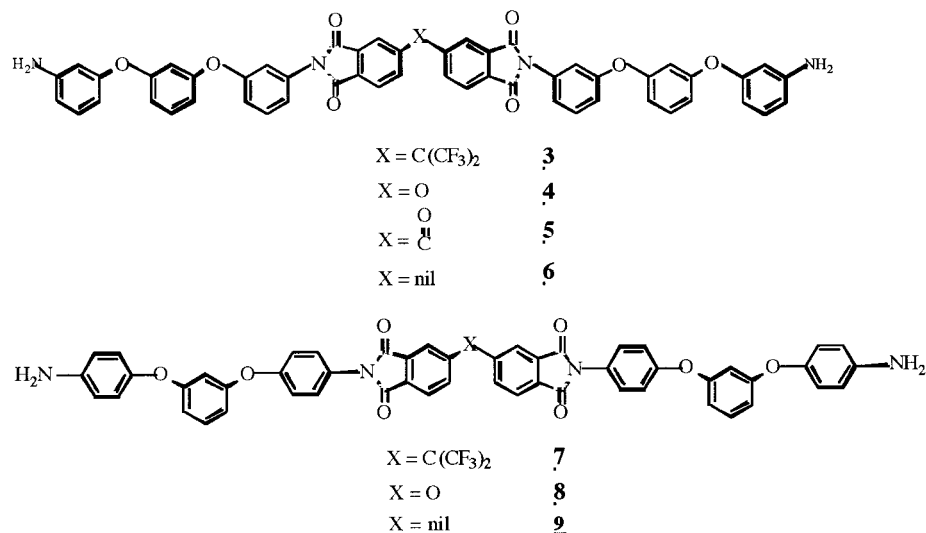| % Thermoplastic (w/w B) | Molecular Weight (g/mol; theoretical) | Molecular Weight (g/mol; measured) | $K_{Ic}$ (MPa m$^{1/2}$) | Viscosity[a] (Pa S) | $\Delta$Viscosity (%) |
|---|---|---|---|---|---|
| 0 | — | — | 0.4 ± 0.1 | 0.6 | — |
| 20 | 700 | 858 | 0.6 ± 0.1 | 6 | 1000 |
| 30 | 700 | 850 | 0.5 ± 0.1 | 70 | 12,000 |

[a] Measured at 55°C.

**Figure 5**  Imide thermoplastics employed to toughen BMI.

phological features were found in any of the thermoplastic-toughened thermosets, except in the case of 9, which appeared to possess a co-continuous-like morphology. However, some phase separation was suggested for all the materials based on the fact that the cured resin plaques were no longer transparent. DMA evidence is inconclusive. Little decrease in $T_g$ was found, even at higher levels of thermoplastic loading, and at 200°C, the $E'$ did not differ from that of the untoughened control; however, only a single tan $\delta$ peak is seen. The tan $\delta$ peak of the DMA spectra for thermosets toughened with 8 and 9 may possess a shoulder in a broad band starting around 200°C, which rises to a maximum at $\sim$ 300°C. The DMA for 2 suggests a largely homogenous material with a single broad peak from $\sim$ 225 to about 300°C but also with a shoulder. Therefore,

**Table III   Effect of Thermoplastic Structure and Loading on Fracture Toughness**

| Thermoplastic | Molecular Weight (g/mol; measured) | % Thermoplastic (w/w B) | $K_{Ic}$ (MPa m$^{1/2}$) | $\Delta K_{Ic}$ (%) |
|---|---|---|---|---|
| None | — | 0 | $0.4 \pm 0.1$ | |
| 3 | 1800 | 20 | $0.5 \pm 0.1$ | 25 |
| | | 30 | $0.5 \pm 0.1$ | 25 |
| | | 50 | $0.4 \pm 0.1$ | 0 |
| 4 | 1700 | 20 | $0.5 \pm 0.1$ | 25 |
| | | 30 | $0.4 \pm 0.1$ | 0 |
| 5 | 1200 | 20 | $0.7 \pm 0.1$ | 75 |
| | | 30 | $0.4 \pm 0.1$ | 0 |
| 6 | 1300 | 20 | $0.5 \pm 0.1$ | 25 |
| | | 30 | $0.5 \pm 0.1$ | 25 |
| | | 50 | $0.4 \pm 0.1$ | 0 |
| 7 | 2000 | 20 | $0.5 \pm 0.1$ | 25 |
| | | 30 | $0.7 \pm 0.1$ | 75 |
| | | 50 | $0.5 \pm 0.1$ | 25 |
| 8[a] | — | 20 | $0.6 \pm 0.1$ | 50 |
| | | 30 | $0.7 \pm 0.5$ | 75 |
| 9 | 1300 | 20 | $0.6 \pm 0.1$ | 50 |
| | | 30 | $0.5 \pm 0.1$ | 25 |

[a] Molecular weight could not be measured due to insolubility.

**Table IV Effect of Thermoplastic Structure and Loading on Thermoset $t_g$ and $E'$**

| Thermoplastic | $M_n$ (by SEC) | % (w/w B) | $T_g$ (°C) | $E'$ ($1 \times 10^9$ Pa; 30°C) | $E'$ ($1 \times 10^9$ Pa; 200°C) |
|---|---|---|---|---|---|
| 1 | — | — | 260 | 3.1 | 2.2 |
| 2a | 858 | 20 | 223 | 0.7 | 0.6 |
| | | 30 | 210 | 0.8 | 0.6 |
| 3 | 1800 | 20 | 250 | 3.1 | 2.0 |
| | | 30 | 280 | 3.1 | 2.1 |
| | | 50 | 239 | 3.2 | 2.5 |
| 4 | 1700 | 20 | 280 | 3.1 | 2.0 |
| | | 30 | 250 | 3.1 | 2.2 |
| 5 | 1200 | 20 | 240 | 3.3 | 2.2 |
| | | 30 | 233 | 3.3 | 2.1 |
| | | 50 | 227 | 3.2 | 2.1 |
| 6 | 1300 | 20 | 280 | 3.1 | 2.2 |
| | | 30 | 265 | 3.2 | 2.1 |
| | | 50 | 212 | 3.2 | 1.8 |
| 7 | 2000 | 20 | 293 | 3.2 | 2.1 |
| | | 30 | 270 | 3.1 | 2.1 |
| | | 50 | 254 | 3.3 | 2.1 |
| 8[a] | — | 20 | 242 | 3.5 | 2.3 |
| | | 30 | 257 | 2.9 | 2.0 |
| 9 | 1300 | 20 | 262 | 3.2 | 2.2 |
| | | 30 | 280 | 3.1 | 2.1 |

[a] Molecular weight could not be measured due to insolubility.

no definitive evidence for phase separation was found, and no morphological features are found by SEM in any of the materials, except 9. Consequently, toughness data could not be correlated with any morphological results. It was hypothesized that phases did exist in all the species but that the domain size was below the detection level of SEM. The morphology of these thermosets will be discussed in greater detail in a future publication.

## CONCLUSIONS

Very low-molecular-weight ($\sim$ 700–2200 g/mol) imide thermoplastic modifiers were investigated as tougheners for BMIs. The molecular weight of the thermoplastic was kept extremely low, generally below $\sim$ 1000 g/mol. This was done in order to minimize the increase in the prepolymer viscosity with the objective of producing a tough but autoclave processable BMI. Increases in fracture toughness of up to $\sim$ 100% greater than that of untoughened BMI controls (from 0.4 to 0.8 MPa $m^{1/2}$) were obtained with oligomer 2d ($\sim$ 2200–5800 g/mol), but the viscosity of the solution increased from 0.6 to 31 Pa S, or a $\sim$ 5000% in-

crease, at 55°C. If the thermoplastic was in the range of $\sim$ 1000 g/mol, increases in fracture toughness of up to 75% were measured, while the viscosity increase was on the order of 1000% ($\sim$ 6 Pa S). Therefore, in the molecular weight range investigated, the very modest additional increase in toughness gained by going to slightly higher molecular weight did not merit the additional increase in prepolymer viscosity.

The cured resin plaques for all thermoplastics investigated were opaque, suggesting phase separation of the thermoplastic from the thermoset; however, observation of the fracture surfaces by SEM found a featureless surface, except in the case of 9. It was hypothesized that phase-separated domains existed below the detection limits of the SEM.

Precedents for thermoplastic toughening by such low-molecular-weight thermoplastics were not found, presumably because it was assumed that they would not improve fracture toughness. This work has shown that very low-molecular-weight imide thermoplastic can give modest increases in fracture toughness without compromising either $T_g$ or high-temperature $E'$. Imide thermoplastic prepared from less-soluble amines (for example, 7 and 8) had slightly higher measured

fracture toughness values. The fact that toughness did not increase with increased thermoplastic loading and that different thermoplastics gave different fracture toughness values at similar molecular weight and loading, indicate that the effect on toughness is not due to dilution of crosslinks alone.

The increases in fracture toughness from low-molecular-weight imides are not large, but the advantage of these modifiers is that they give substantially smaller increases in prepolymer viscosity when compared with higher-molecular-weight oligomers and polymers, which have been investigated in detail. Therefore, these systems should be easily processed under very low pressures, including autoclave pressures.

The measured fracture toughness values were modest, but none of the systems was optimized, so higher increases in fracture toughness might be obtained by improving processing variables and from a different choice of oligomers, especially oligomers with less compatibility with the matrix. This hypothesis is supported by the results from the second article in this series,[29] in which these same oligomers gave improvements in fracture toughness of more than 200% when introduced into an epoxy matrix with which they are less compatible.

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