# NOTES

## *High-Performance Thermoplastic Toughened BMI Matrix System. II. Interface Study*

*Bis*-maleimide (BMI) has recently attracted considerable attention as an important matrix resin for high-performance composites, due to its outstanding high-temperature performance. First-generation BMI is too brittle for primary strauture. Our toughening approach began by dissolving PEI (polyetherimide) into compatible diallyl compound (Matrimid 5292 B, Ciba Geigy) prior to coreaction with BMI resin. In this note, the toughness and interface properties were investigated for the toughened matrix system.

## EXPERIMENTAL

### Materials

The *bis*-maleimide resin (4,4'-*bis*-maleimido-diphenyl-methane) used in this study was from the BTL Special Resin Company, trade name IM-AD 94-306. Polyetherimide (Vltem 1000) was supplied from G. E. Diallyl bisphenol A (Matrimid 5292B) was from Ciba-Geigy Company.

Carbon fibers ST-3-7-6000 were from Toho Rayon Company. Some of the carbon fibers were washed with dichloromethane to remove the epoxy sizings. The PI sizing treatments for carbon fibers were prepared by mixing equal moles of benzophenone tetracarboxylic dianhydride and 4,4'-4,4'-diaminodiphenyl ether together in *N*-methyl pyrrolidone solvent. Benzophenone tetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether were from Tokyo Kasei Kogyo Company.

### Neat Resin Processing

PEI was dissolved in 5292B at 150°C, and BMI was added with mixing until a one-phase solution was obtained. The curing condition is shown below:

1. Heat from 140° to 200°C at a heating rate of 2°C/min
2. Cure at 200°C for 3 h
3. Cool from 200°C to ambient at a cooling rate of less than 2°C/min

### Test Methods

**Determination of interfacial shear strengths:** The microbond method was used to measure the interfacial shear strength.[2] The procedure involved the deposition of a small amount of resin onto the surface of a fiber as shown in Figure 1. After curing, the fiber specimen were pulled out of the microdroplet at a rate of 1 mm/min, using a Shimazu tensile tester. The experimental arrangement is shown in Figure 2. The interfacial shear strength was calculated from $\tau = F_p/\pi DL$, where $F_p$ = pullout force, $D$ = fiber diameter, $L$ = embedded length, and $\tau$ = interfacial shear strength.

**Fracture toughness $G_1c$ of neat resins:** The plane strain release rate $K_1c$ of neat resin was tested by the compact tension method according to ASTM E-399. The fracture toughness $G_1c$ was calculated from the following equation with the assumption of Poisson ratio of BMI resin = 0.35.

$$G_1c = K_1c \times \frac{1-\nu}{E^2}$$

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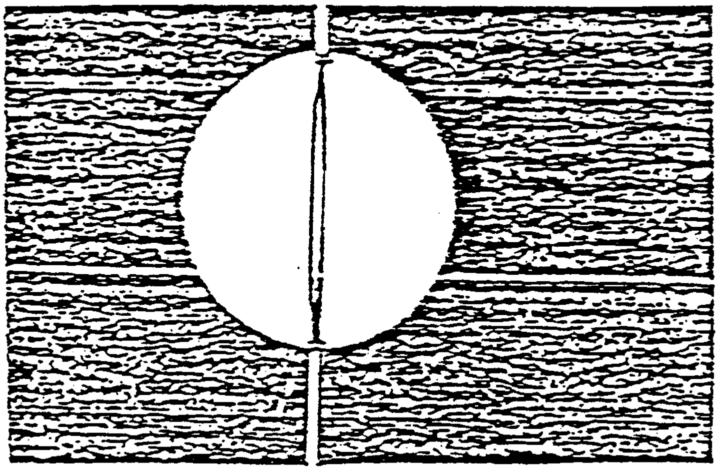

Fig. 1. Droplet shape on the carbon fiber.

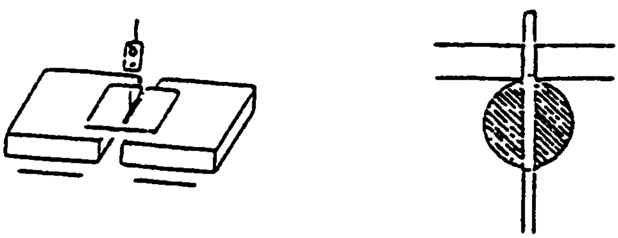

Fig. 2. Arrangement for the shear debonding of a resin droplet.

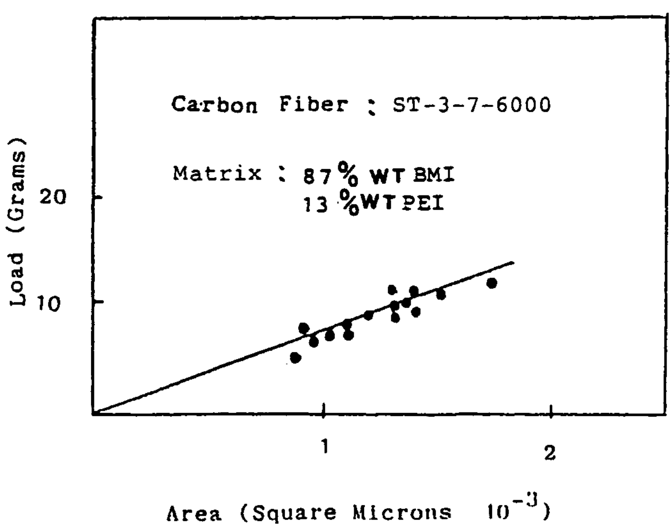


Fig. 3. Debonding load as a function of embedded area.

TABLE I
Neat Resin Formulations and Their Mechanical Properties

| | A-1 | A-2 |
|---|---|---|
| 4-4′-*Bis*-maleimido-diphenyl-methane (wt %) | 57 | 50 |
| Matrimid 5292B (wt %) | 43 | 37 |
| PEI (wt %) | — | 13 |
| RT fracture modulus [GPa] | 4.29 | 4.22 |
| $K_{IC}$ (MN/m$^{3/2}$) | 0.67 | 1.26 |
| $G_{IC}$ (kJ/m$^2$) | 0.09 | 0.33 |

TABLE II
Effect of PEI on the Interfacial Shear Strength for Toughened BMI Composites

| Property | System | RT/dry |
|---|---|---|
| Interfacial shear strength g/m$^2$ × 10$^9$ | A-1 | 7.1 ± 0.4 |
| | A-2 | 8.6 ± 0.6 |
| Edge delamination strength [KSi] [(±25)2/90]s | A-1 | 20.5 |
| | A-2 | 27.0 |

TABLE III
Effect of Postcure at 250°C on the Carbon Fiber–Matrix Bond Strength

| | Carbon fiber | Matrix (wt %) | Interfacial shear strength (g/m$^2$) × 10$^9$ |
|---|---|---|---|
| Postcure | ST-3-7-6000 | 87 BMI<br>13 PEI | 6.9 ± 0.4 |
| No postcure | ST-3-7-6000 | 87 BMI<br>13 PEI | 8.6 ± 0.5 |

TABLE IV
Contact Angle for the PEI Toughened Matrix at 140°C

| Carbon fiber | Matrix (wt %) | Contact angle ($\theta$) |
|---|---|---|
| ST-3-7-6000 | BMI | 27.5 |
| ST-3-7-6000 | 87 BMI<br>13 PEI | 28.1 |

TABLE V
Effect of Sizing on Carbon Fiber BMI-Bond Strength

| Carbon fiber | Matrix (wt %) | Interfacial shear strength (g/m$^2$) × 10$^9$ |
|---|---|---|
| No sizing | 87 BMI<br>13 PEI | 8.6 ± 0.5 |
| Epoxy sizing | 87 BMI<br>13 PEI | 8.6 ± 0.5 |
| PI sizing | 87 BMI<br>13 PEI | 8.2 ± 0.5 |

**Measurement of the wettability.** A single fiber is suspended from the arm of a recording electronic balance. A reservoir of probe liquid is brought into contact with the free end of the fiber. The wetting force value is converted to the corresponding contact angle value through the following relation[3]

$$\cos \theta = F / D\delta$$

where $\theta$ is the contact angle, $F$ is the wetting force, $\delta$ is the surface tension of the contacting liquid, and $D$ is the perimeter of the fiber.

## RESULTS AND DISCUSSION

**Effect of PEI on the neat resin properties.** Table I shows the effect of PEI on the neat resin properties.

It is obvious that PEI plays a major role in increasing the $K_{IC}$ of the neat resin.

**Effect of PEI on the interfacial shear strength.** Figure 3 shows the debonding load as a function of embedded area. A linear relationship was found between the debonding load and the embedded area. Table II illustrates the effect of PEI on the interfacial shear strength for the toughened BMI composites system. It is interesting that PEI increased both the fracture toughness and the interfacial shear strength of the toughned matrix system.

**Effect of postcure on the interfacial properties.** Table III illustrates the effect of postcure on the carbon fiber matrix bond strength. It is surprising that postcure decreased the interfacial shear strength significantly. The reason might be due to the thermal expansion mismatch between the fiber and the matrix or the degradation of the interface under high temperature.[4] The phenomenon is under investigation.

**Wettability of carbon fibers.** Good wetting of reinforcing fiber by the matrix resin is a necessary condition during the formation of composites.[5] Its importance lies in providing more intimate contact between the fiber and the resin, allowing better penetration of the resin into the fibers during processing, and reducing the entrapment of air along the fiber–matrix interface. Table IV shows the contact angle change slightly for the PEI toughened matrix.

**Effect of sizing on carbon fiber–BMI interfaces.** Carbon fibers are commonly subjected to posttreatment, including application of organic sizings, to improve their compatibility with the resin matrix and to protect the fiber tow from damage during processing.[6] Polyimide (PI) sizing is more thermally stable than epoxy sizing for high-temperature applications. Table V shows the effect of sizing on carbon fiber–BMI interfaces. The sizing treatment affects the carbon fiber–BMI bond strength slightly.

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