Chain-Extended Bismaleimides. II. A Study of Chain-Extended Bismaleimides as Matrix Elements in Carbon Fiber Composites

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SYNOPSIS

A series of chain-extended bismaleimide resins as matrix elements in carbon fibers were cured and characterized in terms of their thermal and thermomechanical properties. The cured resins were stable up to 430°C and EDABMI/MDA has the highest T_g value and the lowest loss modulus value. To understand the compatibility and the degree of adhesion between the resin and the fiber, their surface properties were determined in terms of the surface energy component and single-fiber pull-out tests. The surfaces of the resins were found to have a basic character. The resins containing ether groups have a higher degree of basicity than does the resin containing methylene groups. Similarly, an increasing trend in the interlaminar shear strength (ILSS) and the work of adhesion values were observed with the increasing number of the ether groups in the resin structure. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the previous article,[1] a series of bismaleimides (BMI) and chain-extended BMI resins were prepared with a BMI/diamine ratio of 3 : 2. The extent of chain extension and crosslinking reactions of BMIs might be expected to affect molecular rigidity and, thus, the thermal and the mechanical properties related to molecular motions. Donnelan and Roylance,[2,3] studied the cure of 4,4′-bismaleimidodiphenylmethane (MDABMI) and 4,4′-diaminodiphenylmethane (MDA) in different mol ratios in melt, and from the thermomechanical analysis, they concluded that the properties of the polymers were found to vary with crosslink density. Fracture toughness was found to increase as the crosslink density decreased.

Understanding the interfacial characteristics of the polymer composites is a requirement for optimizing the filler or the fiber to resin compatibility. If the resin system is characterized for its surface

acid–base character, it is possible to find a good fiber match for the resin. This is a subject of increasing importance, because more complicated thermosetting resin systems such as epoxies or BMI toughened or mixed with thermoplastics that have high glass transition temperatures for improved toughness have been prepared.[4] A good adhesion is essential for the transfer of stresses and, thus, the strength of the composite materials. Maximum adhesion requires maximum acid–base interaction, which is determined by (a) the surface population of acid–base pairs and (b) the free energy of the acid–base interactions (adduct or complex formations).[5] Mechanical or physical adhesion is also possible, which arises from a close contact of the resin and the fiber.

For continuous fiber composites, in particular, poor adhesion may be due to insufficient physical contact between the resin and the fiber as a result of incomplete wetting. Secondary-type attractions, such as van der Waals type or hydrogen bonding, also influence the impregnation process through their effect on the contact angle between the fiber and the resin.[6,7] A low contact angle between the resin in melt or in solution and fiber ensures a good degree of impregnation into the fiber bundle.

In this study, the developed chain-extended bis-maleimides are cured and their thermal, thermo-mechanical, and surface properties are determined. The calculated adhesion values between the resin and the carbon fibers are correlated to the experimentally measured interlaminar shear strength (ILSS) values obtained by the single-fiber pull-out technique.

Background to Surface Energy Calculations

In a recent publication, the surface properties of bismaleimide and polyimide structural polymer blends were investigated by contact angle measurements.[8] The total surface energy of a resin (γ_s) can be considered as composed of two parts, the Lifshitz-van der Waals (γ_s^{LW}) and the acid–base component (γ_s^{AB}). The former represents the long-range dispersion forces, and the latter represents the short range H-bonding or acid–base interactions. This is written as the sum of the two components, i.e.:

$$\gamma_s = \gamma_i^{LW} + \gamma_i^{AB} \qquad (1)$$

where the acid–base term is

$$\gamma_i^{AB} = 2(\gamma_i^+ \gamma_i^-)^{1/2} \qquad (2)$$

The subscript (i) denotes the i'th phase and the superscripts plus and minus denote the surface free energy contributions due to the Lewis acid and Lewis base, respectively.

The adhesion between a solid (s) and a liquid (L) is given as

$$(1 + \text{Cos } \Theta)\gamma_L = 2(\gamma_L^{LW}\gamma_s^{LW})^{1/2} + \gamma_{sL}^{AB} \qquad (3)$$

$$\gamma_{sL}^{AB} = 2((\gamma_s \cdot \gamma_L^-)^{1/2} + (\gamma_L \cdot \gamma_s^-)^{1/2}) \qquad (4)$$

where γ_L^{AB} represents the short-range Lewis acid-base interactions, $(\gamma_L^{LW}\gamma_s^{LW})^{1/2}$ represents the Lifshitz–van der Waals component, and Θ denotes the contact angle of the liquid on the solid surface.

EXPERIMENTAL

Characterization of Cured Resins

Netzsch-429-type TGA and DTA were used to investigate the thermal behavior of the cured resins. Samples were cured 24 h at 250°C and postcured 48 h at 200°C. Thermal analysis was performed by heating samples (10 mg) in air at a heating rate of 10°C min^{-1}.

Dynamic mechanical properties of the cured resins were determined using a General V4.1C DuPont 2000-type DMA analyzer, with rectangular bar specimens (11.93 × 11.26 × 0.85 mm size) at a heating rate of 5°C min^{-1} and over a temperature range from 150 to 370°C at constant frequency mode with amplitude 0.05 mm.

Surface Energy Determination

The contact angle data were used to determine the surface energy and its components of the cured resins. For the determination of contact angles of the resins, several glass rods coated with the resin films were prepared from a solution of the resins. A series of 4% (w/w) solutions of the resins dissolved in m-cresol were prepared. The surface of the glass rods were coated by dipping the rods vertically into the solution and then the solution container was lowered by a speed-controlled stage. The rods were then put into an oven at 100°C for 2 h to evaporate the solvent. The films were then cured for 1 h at 180°C, 24 h at 250°C, and, finally, postcured at 200°C for 48 h.

After the cure cycle was completed, the film-coated glass rods were suspended from the balance by a steel wire hook.[4] A stage velocity of 1.5 μm s^{-1} was used to bring the rods into contact with the probe liquid. From the weight digital readout of the microbalance, forces were calculated and the contact angle values were determined[5,9] from the following relationship:

$$F = p \cdot \gamma \cdot \text{Cos } \Theta \qquad (5)$$

where F is the measured force; p, the perimeter of the rod; and Θ, the contact angle of the probe liquid on the rod.

Methylene iodide was used as a probe liquid for the Lifshitz–van der Waals interactions (LW), and ethylene glycol and formamide are used to probe for the acid–base interactions. Before each experiment with a probe liquid, the film-coated glass rod was dried at oven for $\frac{1}{2}$ h and a different rod used for each experiment. Finally, the perimeter of the glass rods were determined by using n-octane, which was assumed to make a zero contact angle with the film-coated glass rod.

Surface Characterization of Carbon Fibers

Carbon fibers were refluxed in dichloromethane and washed with acetone and distilled water. Contact angle measurements and surface energy calculations
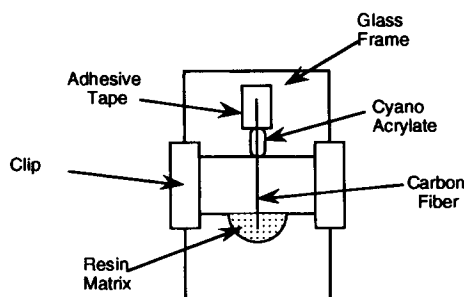
Figure 1 Diagram of a single fiber assembly used in pull-out tests.

of the carbon fibers were done by the same method described above and in previous studies.[10-14]

Single-Fiber Pull-out Tests

In the pull-out experiment, a single fiber partially embedded in a block of resin is pulled out by applying a tensile force to the free end of the fiber assuming that the interlaminar shear stresses (ILSS) are uniformly distributed along the immersion length. The mean value of the ILSS, ∂, of the fiber-matrix interphase is given by

$$\partial = F_{max}/\pi \cdot d \cdot l \tag{6}$$

where d and l are the diameter and the embedded length of the fiber, respectively, which are measured with a length calibrated optical microscope. F_{max} is the maximum force corresponding to the pull-out process.[15-17] In this test, Lloyd's tensile tester (Lloyd LR 5 K) with a specially designed grib is used. The test samples are prepared by bringing two flat glass plates within 1 cm distance to each other. The slides were then secured from the two sides with clips. A single fiber is mounted vertical to the separation between plates and one end is tightened on one of the glass plates by its total length ($\sim$ 1 cm) by a cynoacrylate adhesive. To the other end, with about 100 μm of the fiber length resting on the glass plate, a 15% w/w resin (dissolved in DMF) solution is dropped and it is dried 1 h at 100°C and then the whole system is cured 2 h at 250°C and postcured 1 h at 150°C (Fig. 1).

RESULTS AND DISCUSSION

Thermal Analysis of Maleimide-terminated Cured Resins

The thermogravimetry curves of the cured resins were characterized in terms of initial decompo-

sition temperature (T_d), temperature of 10% weight loss $(T_{10\%})$, and temperature of maximum rate of decomposition (T_{max}). The results of TGA and DTA are given in Table I. The values for methylene and ether linkage-containing resin are close to each other with about 15°C higher T_d and T_{max} values for MDA. These values are within acceptable ranges for advanced composite applications.

Dynamic Mechanical Analysis of Maleimide-terminated Cured Resins

The DMA results of the three cured resins (MDABMI/MDA, EDABMI/MDA, EDABMI/EDA) are given in Figures 2 and 3. There are two effects that influence the mechanical response of these materials. The first is the cohesive energy density and the second one is the crosslink density of the cured resins. Comparison of MDABMI/MDA and EDABMI/EDA shows (Fig. 2) that EDABMI/EDA has about 25°C higher T_g value probably due to higher intermolecular attractions. It is also interesting to note that MDABMI/MDA has a higher crosslink density than has EDABMI/EDA indicated by a higher E' value at low temperatures and the typical shape of the DMA response for highly crosslinked matrices [Fig. 2(a)]. This result is expected from the data in the preceding article where the MDABMI/MDA resin is found to have a lower molecular weight than that of the EDABMI/EDA resin. Among the three cured resins investigated, EDABMIMDA has the highest T_g and the lowest loss modulus values [Fig. 2(c) and Fig. 3(c)]. The rigid nature of EDABMI/MDA is the result of two effects: It probably has a larger crosslink density than that of EDABMI/EDA (due to the lower molecular weight of the resin), and its cohesive energy density is larger than that of MDABMI/MDA due to the etheric linkages. The combination of these two effects

Table I Results of TGA and DTA Analysis of Cured Maleimide-terminated Resins (Values Are in °C)

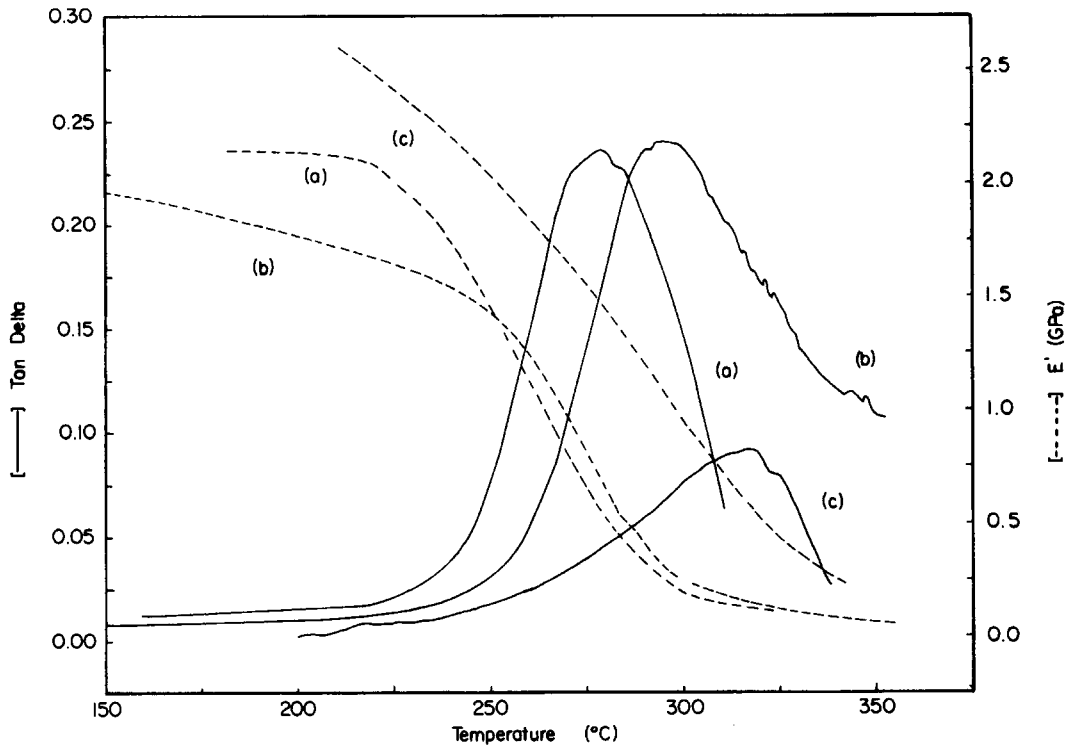| Resin	T_d	T_{max}	$T_{10\%}$
MDABMI/MDA (IV)	430	640	455
EDABMI/MDA (V)	415	625	430
EDABMI/EDA (VI)	415	620	450
PDABMI/EDA (VII)	410	630	425

Figure 2   DMA results of cured (a) MDABMI/MDA, (b) EDABMI/EDA, and (c) ED-ABMI/MDA where E' is the flexural storage modulus.
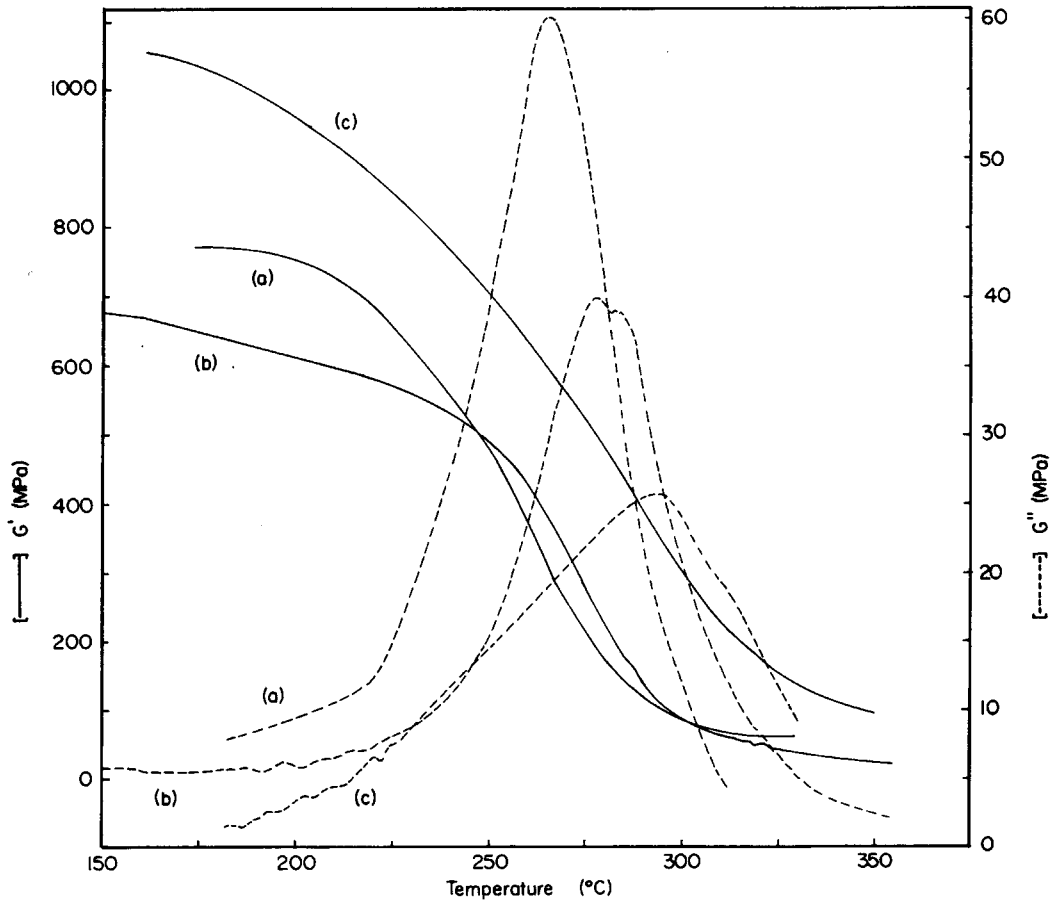

Figure 3   DMA results of cured (a) MDABMI/MDA, (b) EDABMI/EDA, and (c) ED-ABMI/MDA where G' and G'' are the shear storage modulus and the shear loss modulus respectively.

Table II Surface Energy Components of the Probe Liquids Used (mJ/m^2)[14,18]

Liquid	γ_L	γ_L^+	γ_L^-	γ_L^{LW}
Methylene iodide	50.8	—	—	50.8
Ethylene glycol	48.0	3.00	30.0	29.0
Formamide	58.8	2.28	39.6	39.0
n-Octane	21.8	—	—	21.8

gives rise to the observed mechanical behavior of EDABMI/MDA.

Determination of Surface Energy Components

Resin surfaces are characterized in terms of LW, acid, and base components. The LW component (γ_s^{LW}) of the surface free energy component is calculated by using methylene iodide as a liquid probe assuming γ_{sL}^{AB}, component in eq. (3) is negligible.

The acid–base interaction terms can then be found by employing the data of two polar liquids and rearranging eq. (3),

$$\gamma_{sL}^{AB} = (1 + \text{Cos } \Theta)\gamma_L - 2(\gamma_L^{LW}\gamma_s^{LW})^{1/2} \quad (7)$$

The individual γ_s+ and γ_s- are then calculated from the simultaneous solution of eq. (4) for the two probe liquids. The surface tensions of the probe liquids are given in Table II.

The results of the surface free energy measurements and pull-out tests are given in Table III. In general, the results shows that the resin surfaces are basic. The degree of basicity is highest in EDABMI/EDA (VI). The conclusion is that introduction of ether groups instead of methylene groups into the polymer chain increases the degree of basicity.

The interlaminar shear stress values are tabulated in Table III with the calculated work of adhesion values with unsized fibers used in the experiments. The cured resin and the carbon fiber employed have predominantly basic character. The acid–base interactions in these samples are minimal, and, therefore, LW-type interactions are responsible for the calculated work of adhesion values. On the other hand, the observed increase in the ILSS value for matrix EDA–EDA is thought to be due to the higher cohesion of this resin that results in a more rigid matrix which is supported by the DMA analysis. It is known that ILSS is not solely dependent on adhesive energies; matrix rigidity among other factors also influence its value.

CONCLUSION

For the three cured maleimide-terminated chain-extended resins chain extension via EDA decreases the crosslink density due to larger amounts of units between the maleimide groups in the resin structure. On the other hand, a large amount of EDA units increase the cohesive energy density of the resin and the polymer with increased T_g and higher T_m for the resin that result in a more rigid material. The chain extension does not appreciably change the thermal properties of the cured resins. Analysis of the surface energies of the resins indicate that ether groups contribute to the basic character of their surface, which suggests that they will be compatible with carbon fibers that have acidic surface moieties. The ILSS determinations also show that the larger cohesive energy density of EDA–EDA is responsible for the observed increase in the ILSS value with the implication that mechanisms other than adhesive nature also contribute to ILSS.

Table III Experimental Surface Energy, the ILSS, and Work of Adhesion (W_a) Values of the Cured Resins

Resin	γ^+ (mJ/m^2)	γ^- (mJ/m^2)	γ^{LW} (mJ/m^2)	ILSS* (MPa)	W_a^* (mJ/m^2)
MDABMI/MDA (IV)	0.5	2.8	30.1	4.5	74.5
EDABMI/MDA (V)	0.1	8.3	30.8	4.9	74.4
EDABMI/EDA (VI)	0	28.5	28.2	6.9	69.0

* Against unsized Celion G40-700 carbon fiber with $\gamma^{LW} = 40.7$ mJ/m^2, $\gamma^+ = 0.0$ mJ/m^2, and $\gamma^- = 16.6$ mJ/m^2.

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