

Thermal Behavior and Cured Products of Mixtures of Two Different Bismaleimides

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Synopsis

The thermal behavior of a new bismaleimide, 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane (BBMI) and its mixtures with a conventional monomer, bis(4-maleimidophenyl)methane (BMI) were investigated by differential scanning calorimetry. The melting point of BBMI was 142°C, lower than that of BMI, although its molecular weight is about twice that of BMI. Each of these bismaleimides and their mixtures showed a melting point when heating, but did not have a distinct freezing point when cooling because of vitrification. The unobserved freezing curve was estimated by calculation based on Schröder's equation using melting point and molar heats of fusion in both bismaleimides. The cured product of BBMI has thermal stability as good as that of BMI. Moreover, the cured product of BBMI has a high flexural strength and a high flexural elongation owing to the introduction of flexible ether bonds and long phenoxy groups within the monomer structure.

INTRODUCTION

Bismaleimide resins are good heat-resistant polymers. They are suitable for use in a wide range of composite materials since they contain unsaturated end groups that can thermally polymerize without the formation of volatile by-products which cause voids; at this point they differ from other conventional condensation-type polyimides. In particular, they have been utilized to make multilayer printed wiring boards for large-scale computers and FRP for aerospace industries.¹⁻³

Bis(4-maleimidophenyl)methane (BMI) is generally used as a component of bismaleimide resin compounds, but BMI monomer has a high melting point and does not flow easily in the uncured state. Moreover, the cured product is highly brittle. Therefore, BMI is often used after improving it with additives or tougheners such as diamines, dithiols, and reactive elastomers. But introducing such additives causes a lowering of the glass transition temperature (T_g) and/or the thermal decomposition temperature (T_d) of the cured products. Their electrical properties also become inferior owing to their high dielectric constant and high moisture sensitivity compared with additive-free compounds.

So, a new bismaleimide was synthesized to introduce flexible ether groups and a long phenoxy chain within a monomer structure.⁴⁻⁶ This bismaleimide monomer has a high molecular weight, which makes it possible to reduce the crosslinking density of the cured product. Consequently, the bismaleimide monomer by itself is expected to be suitable for making thermally stable composite materials because the cured product has good mechanical properties. Physical properties, such as the melting point of new bismaleimide with a flexible

ether groups, are not yet confirmed clearly. Melting points reported by several authors do not agree with each other. It is presumed that this is due to variations in purity or the crystal structure.

This paper reports on the identification of a new bismaleimide and the thermal behavior of mixtures of it and the conventional bismaleimide, BMI, as elucidated by differential scanning calorimetry (DSC). In addition, the properties of the cured products using the characterized bismaleimides were investigated.

EXPERIMENTAL

Materials

The bismaleimides used were commercially available (Mitsui Toatsu Chemicals, Inc.). 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane (BBMI) was recrystallized from acetone after dissolving it at 50°C and cooling the solution to -5°C. A light yellow powder was obtained.

ELEMENTAL ANAL: Calcd for (C₃₅H₂₆N₂O₈): C, 73.7%; H, 4.56%; N, 4.91%; O, 16.8%. Found: C, 73.6%; H, 4.75%; N, 4.76%; O, 16.9%.

Bis(4-maleimidophenyl)methane (BMI) was similarly recrystallized from the chloroform-methanol mixture (volume ratio 1 : 1). A yellow powder was obtained. The mixtures of two bismaleimides were prepared by mixing both powders with a 16Z type agitator (Ishikawa Factory) for 30 min.

Apparatus

Differential scanning calorimetry (DSC) was performed on a Rigaku Denki Model 8240 differential scanning calorimeter at a heating rate of 10 K min⁻¹ (10 K/60 s) in the air. The sample weight was about 10 mg and the onset temperature of fusion was regarded as the melting point. This judgment is confirmed by the heating curves of each bismaleimides using the above-mentioned DSC apparatus as an isochronal furnace. The temperature in the flat region of the heating curves is consistent with the onset temperature of fusion.

The IR spectra were obtained on a Hitachi Model 260-50 spectrometer by the KBr method. The ¹H-NMR spectra were obtained on a Hitachi Model R42 FT-NMR spectrometer by use of acetone-d₆ as a solvent at 35°C. Flexural testing was carried out on a Shimadzu Model DDS-5000. The flexural velocity was 2 mm min⁻¹.

Thermal gravimetric analysis was carried out a Shinku-Riko TGD-7000RH model at a heating rate of 5°C min⁻¹ in helium atmosphere. The decomposition temperatures were defined as the temperatures corresponding to a 5% weightloss.

RESULTS AND DISCUSSION

Identification of BBMI

The IR spectra and structural formulae of 2,2-[4-(4-maleimidophenoxy)phenyl]propane (BBMI) and the conventional bismaleimide monomer,

bis(4-maleimidophenyl)methane (BMI), are shown in Figure 1. Both bismaleimide monomers have several absorbance peaks in common owing to the maleimide ring⁷; 1150, 1395 cm^{-1} (C-N-C), 1705 cm^{-1} (carbonyl), 3110 cm^{-1} (C=C-H): phenyl ring; 710, 820, 1500, 1600 cm^{-1} . In addition, BBMI has some characteristic peaks at 1450 and 2950 cm^{-1} due to the methyl group in the propane backbone and at 1010 and 1240 cm^{-1} representing an ether bond.⁸

The ¹H-NMR spectrum of BBMI is shown in Figure 2. The peak at 1.7 ppm is assigned to the methyl group in the propane backbone. At high magnetic field, the peak corresponding to the protons of the phenylene group adjacent to the ether bond (i.e., H_c and H_b) appears at 6.9–7.0 ppm. Next, the proton of the maleimide ring exhibits a peak at around 7.1 ppm. Finally, peaks due to the phenylene ring protons far from the ether bond (H_a and H_a) occur at the low magnetic field, 7.25–7.4 ppm. The integrated intensities of proton peaks agree closely with the calculated value.

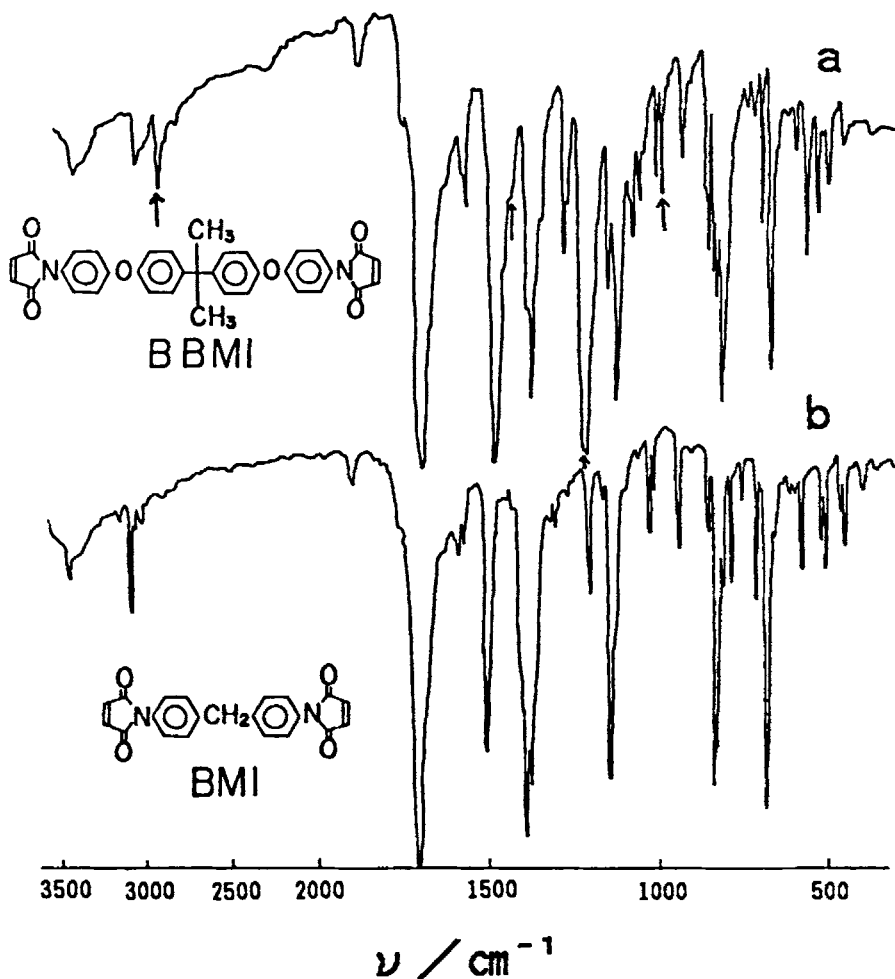


Fig. 1. IR spectra of the two bismaleimides: (a) BBMI; (b) BMI.

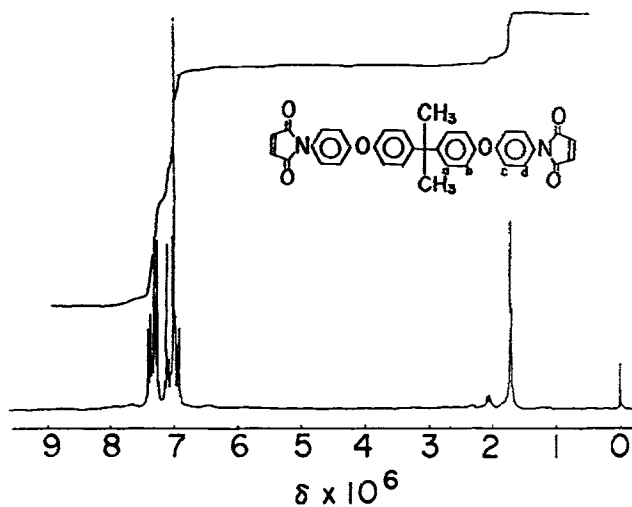


Fig. 2. $^1\text{H-NMR}$ spectrum of BBMI.

ANAL: Calcd: methyl, 23%; phenylene, 62%; maleimide, 15%. Found: methyl, 19%; phenylene, 66%; maleimide, 14%.

Judging from the IR and NMR spectra mentioned above and the elementary analysis in the Experimental section, the purity of BBMI used in this work is found to be quite high. The purity measured by liquid chromatography is about 99%.

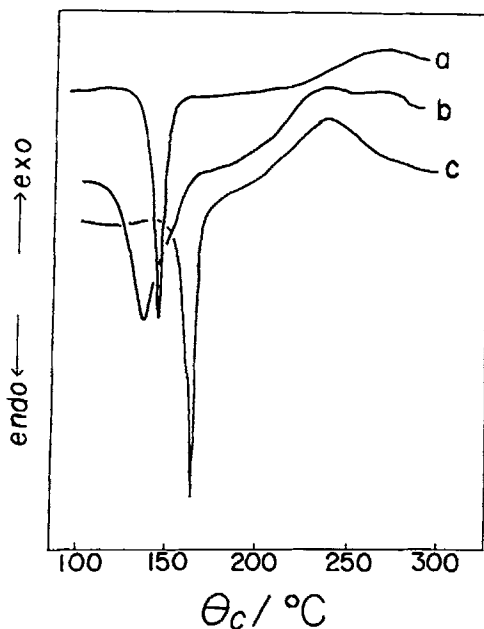


Fig. 3. DSC curves of two bismaleimides and their mixture. Molar fraction of BBMI: (a) $x = 1$; (b) 0.39; (c) 0.

DSC Measurement of the Bismaleimides and Their Mixtures

The DSC curves of two bismaleimides and their mixture (BBMI molar fraction $x = 0.39$) are shown in Figure 3. Each bismaleimide exhibits a high, sharp endothermic peak on fusion. The melting point of BBMI is relatively low, 142°C, which is 16 K lower than that of BMI, although the molecular weight of BBMI is around twice that of BMI. It is presumed that the crystal structure of BBMI is not rigid and the interactions among molecules in the solid state are relatively low.

As shown in Figure 3, there is a broad endothermic peak for the mixture. The half-value width of the fusion (endothermic) peak is about 20 K (120 s), four times the values of each monomer. The melting point of the mixture is about 20 K lower than that of BBMI. So, the mixture has good workability as a composite material suitable for low temperature molding.

In the case of BMI, the exothermic peak, resulting from thermal polymerization of the double bond in the maleimide ring, appears at 240°C and the onset of exothermic behavior occurs at 180°C. The onset temperature shows almost no change by further addition of BBMI to the mixture. But BBMI alone has a high onset temperature, about 230°C. Moreover, its peak temperature is 270°C. So the double bond of BBMI is less reactive than that of BMI in a thermal polymerization reaction and in formation of the crosslinked cured product.

There is a large difference between the melting point and the curing temperature (exothermic peak, onset). Therefore, BBMI has better workability for the curing process than BMI. BMI has a very limited uncured region in the liquid state. Therefore, molding is limited to a narrow temperature range. In the case of applications with BBMI, the molding temperature can be chosen over a wider range from the melting point to the exothermic onset or peak temperature. Consequently, future utilization of BBMI to make composite materials is anticipated rather than BMI.

Figure 4 shows the molar heat of fusion ($\Delta_s^1 H$) as a function of the molar fraction of BBMI obtained from the endothermic peak area. The molar heat of fusion of the mixtures appears to follow closely an additive property. That is to say, the plot of molar heat of fusion vs. molar fraction of BBMI gives a straight line. The increase in content of BBMI results in an increase in $\Delta_s^1 H$. Consequently, it is presumed that BBMI and BMI do not undergo any chemical reaction in the fusion transition.

The $\Delta_s^1 H$ of BBMI is 34.3 kJ mol⁻¹, which is higher than that of BMI (26.3 kJ mol⁻¹) by about 10 kJ mol⁻¹. This seems to be due to the fact that the molecular weight of BBMI is relatively high. The entropy change of fusion ($\Delta_s^1 S$) is estimated by the following equation:

$$\Delta_s^1 S = \Delta_s^1 H / T_m \quad (1)$$

Here, T_m is the melting point. For BBMI and BMI, $\Delta_s^1 S$ are 82.6 and 61.0 J K⁻¹ mol⁻¹, respectively. The ratio of $\Delta_s^1 S$ of the two bismaleimides ($r = 0.74$) is almost the same as the length ratio ($r' = 0.71$) of each substituent group, $-C_6H_4OC_6H_4(COCH)_2$ ($d = 120$ nm) and $-C_6H_4(COCH)_2$ ($d = 85$ nm).

The change in melting point in the binary system as a function of the molar fraction is shown in Figure 5. The melting point of the mixture is always lower

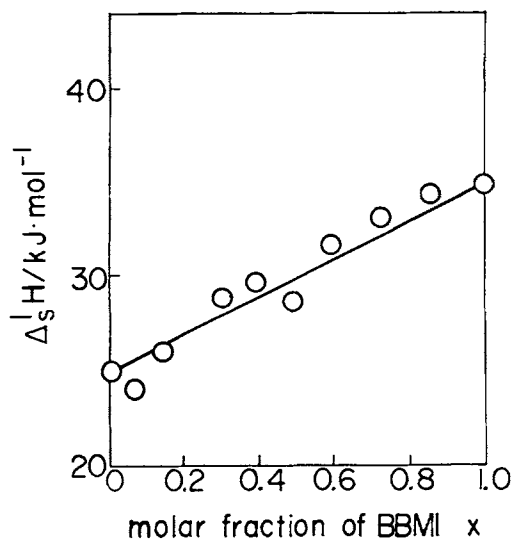


Fig. 4. Molar heats of fusion of mixtures.

than those of both bismaleimides and has a minimum value (the eutectic point). On the other hand, BBMI, BMI, and their mixture do not show any definite freezing point in a change from molten state to solid state. The DSC curves of BBMI in both the processes of heating and subsequent cooling are shown in Figure 6. The crystallized sample from solution has a distinct melting point and shows a large endothermic peak on heating (A). This molten sample does

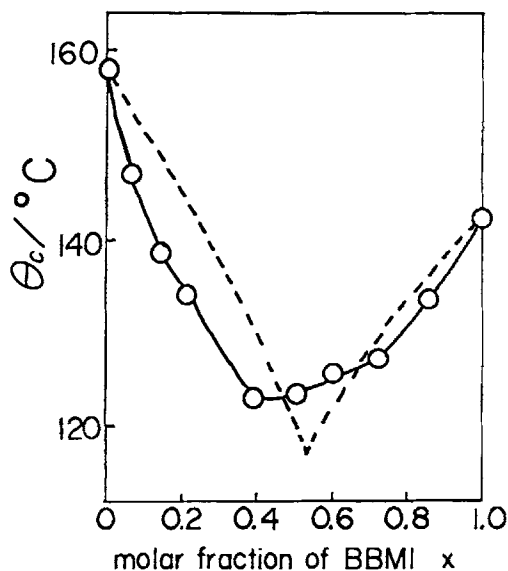


Fig. 5. Melting points of mixtures: (O) observed melting points in the heating process; (---) broken line is calculated on Schröder's equation.

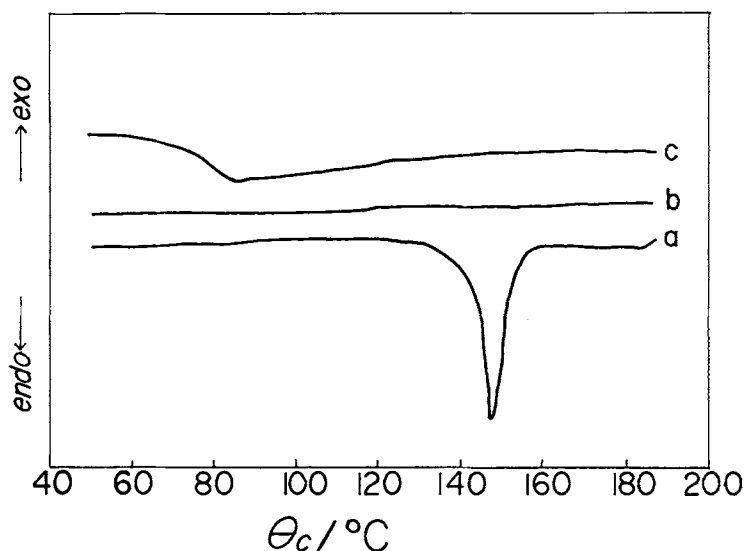


Fig. 6. DSC curves of BBMI: (a) heating at a rate of 10 K min^{-1} ; (b) cooling at a rate of 1 K min^{-1} ; (c) heating at a rate of 10 K min^{-1} .

not have a freezing point and turned to the rigid state on cooling at a rate as low as 1 K min^{-1} (B). Further, this rigid sample is subjected to the heating process again. The second order transition that is thought to be a glass transition phenomenon is observed at 80°C and fusion does not appear at the vicinity of 142°C (C). The change in heat capacity in glass transition is about $100 \text{ J K}^{-1} \text{ mol}^{-1}$. It is presumed that the molten sample does not freeze but vitrifies in the cooling process because the crystallization from the melt is very slow. It is considered that the melt can crystallize in the case of an infinitely low rate of cooling. Consequently, the observation of the freezing point by DSC is difficult. On the basis of the obtained $\Delta_s^1 H$ and melting points of both bismaleimides, the freezing point of the mixtures, which are hardly observable, are calculated based on Schröder's equation.⁹

$$\ln x = -\Delta_s^1 H^* (1/T - 1/T_m) / R \quad (2)$$

Here x is the molar fraction of solvent, T and T_m are the melting point of the mixture and pure solvent, respectively, and R is the gas constant. By using melting point and molar heat of fusion (DSC), the calculated freezing curve is obtained. The result is shown in Figure 5 with a broken line. The eutectic point is estimated to be 117°C . As shown in Figure 5, the melting curve is obtained by DSC when heating experimentally, and the freezing curve is obtained from the calculated values using Schröder's equation. The calculated freezing curve is mostly higher than the melting curve.

Properties of Cured Products

The thermal expansion behavior of the cured bismaleimides and their mixtures are shown in Figure 7. The cure was at 200°C for 2 h. In the case of BMI,

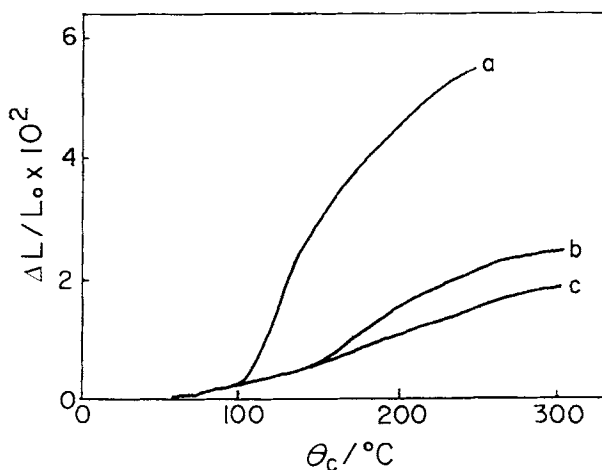


Fig. 7. Thermal expansion curves of the cured products: (a) BBMI; (b) mixture (molar ratio of BBMI : 0.39); (c) BMI, curing condition 220°C, 2 h.

the crosslinking reaction proceeded sufficiently under this curing condition since the onset of exothermic reaction owing to thermal polymerization of the double bond in the maleimide ring occurred at 180°C. Therefore, the cured products of BMI had no glass transition temperature in the range between room temperature and 300°C. On the other hand, in the case of BBMI, the crosslinking reaction hardly occurred since the onset temperature of the exothermic reaction was 230°C. The cured product had a distinct glass transition temperature (T_g) at 120°C. In the case of the mixture, the cured product had a T_g at about 200°C, higher than the T_g of BBMI. In addition, the thermal expansion of the cured product from the mixture was lower than that of BBMI alone. Therefore, the mixture compound had good curability compared with BBMI alone.

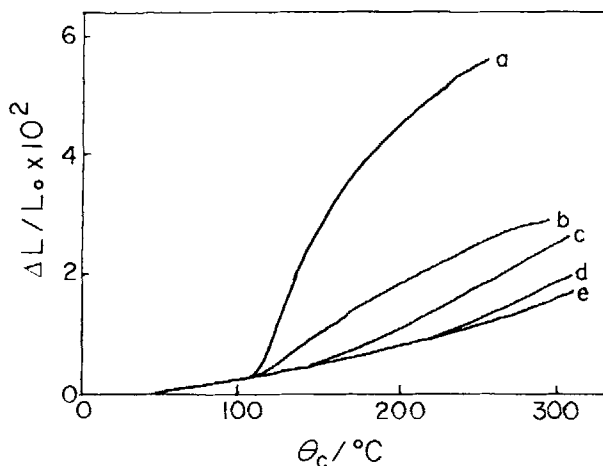


Fig. 8. Dependence of thermal expansion curves of the cured product of BBMI on post curing at 280°C. Post-curing time (h): (a) 0; (b) 1; (c) 3; (d) 8; (e) 20.

TABLE I
Thermal Properties of Cured Products

Molar ratio		E_b^a	T_d^b	E_b/T_d
BBMI	BMI			
1	0	395	733	0.54
0.39	0.61	408	743	0.55
0	1	417	763	0.55

^a E_b = bond dissociation energy (kJ mol^{-1}); cited from Ref. 10.

^b T_d = decomposition temperature (K).

Next, the cured products of BBMI alone were heated at 280°C , higher than the exothermic peak temperature of 270°C . As shown in Figure 8, the thermal expansion was reduced and the T_g changed toward high temperature as the crosslinking reaction proceeded. Consequently, a high crosslinked density cured product was obtained after 20 h and had no glass transition temperature up to 300°C .

The cured product of BBMI had a slightly lower decomposition temperature than that of BMI. Its decomposition temperature was 460°C and it has excellent thermal stability. The reason for the lower decomposition temperature than for BMI was interpreted by the Arrhenius equation:

$$k = A \exp(-E_b/RT_d) \quad (3)$$

Here k is the decomposition reaction rate, A is the frequency factor, E_b is the bond dissociation energy, R is the gas constant, and T_d is the decomposition temperature. If it was assumed that the decomposition reaction occurred rapidly when E_b/T_d had a certain critical value, the decomposition temperature is proportional to the bond dissociation energy. The bond dissociation energy between phenyl and isopropylene in BBMI was lower than between phenyl and methylene in BMI. The relationship of the bond dissociation energy and the decomposition energy is shown in Table I. It was found that the ratio of the bond dissociation energy to the decomposition temperature was almost same in the cured products obtained. In other words, the decomposition temperature was proportional to the bond dissociation energy.

TABLE II
Mechanical Properties of Cured Products^a

Molar ratio		σ	E	e
BBMI	BMI			
1	0	13.9	390	2.7
0.39	0.61	8.8	400	2.2
0	1	8.0	440	1.6

^a σ = flexural strength (MPa); E = flexural modulus (MPa); e = flexural elongation (%).

The cured product of BBMI had excellent mechanical properties as shown in Table II. The flexural strength and flexural elongation of the cured product of BBMI were about twice those for BMI. This is due to introduction of flexible ether groups and long phenoxy chain within the bismaleimide structure. The mixed compound (0.39 molar fraction BBMI) is more tractable for molding. It had both adequate curability and adequate thermal and mechanical properties of the cured product.

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