

**The properties on the copolymer of 4,4'-bismaleimidodiphenylmethane(BMDPM)  
with active monomer containing triazine ring**

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**Abstract:**

In this paper, the properties on the copolymer of 4,4'-bismaleimidodiphenylmethane (BMDPM) with 2,4,6-tris(2-allylphenoxy)-1,3,5-triazine (TAPT) was studied. The data from DSC, TGA and DMA shows that the active monomer containing triazine ring can improve some properties of BMDPM resin.

**Key Words:**

4,4'-bismaleimidodiphenylmethane (BMDPM)      properties      copolymer  
2,4,6-tris(2-allylphenoxy)-1,3,5-triazine (TAPT)

## **Introduction**

Bismaleimides (BMIS) such as BMDPM, are the most important class of addition polyimides using for advanced material applications, because of their high thermal stability, nonvolatility and low cost. But, in common with other addition polyimides, unmodified BMIS suffer from brittleness due to their high crosslink densities. Several approaches have been developed to increase the impact resistance, fatigue resistance and fracture toughness of cured BMI resins. One approach includes the incorporation of a flexible extended chain into the backbone of the BMI structure to increase the freedom of thermal expansion and the tensile elongation. Another approach has involved blending BMIS with other, such as thermoplastic polymers, reactive rubber and so on, or co-reactive allylphenyl, propenylphenyl or allyl-phenoxy terminated toughening agents, while maintaining processability.

In order to obtain new kind of allyl-phenoxy triazine modified BMI resin, we prepared copolymer from BMDPM with 2,4,6-tris(2-allylphenoxy)-1,3,5-triazine (TAPT) and studied the properties of the copolymer.

## **Experimental**

### **Materials**

4,4'-bismaleimidodiphenylmethane (BMDPM) was an industrial products and was recrystallized twice from toluene before using. 2,4,6-tris(2-allylphenoxy)-1,3,5-triazine (TAPT) was prepared by our laboratory. Other materials were used as received.

### **Preparation of the copolymer and specimens**

BMDPM and TAPT in certain composition was first ground in a glass mortar and then thoroughly mixed with a vibrating mixer. The blend was sieved with a 180 mesh  $\text{cm}^{-2}$  sieve. Fine solid powder of blend (6g) was then placed in an aluminum mold with dimensions of  $5.8 \times 0.86 \times 0.62$  cm, which was placed in an oven at  $160^\circ\text{C}$ . The temperature was maintained for 30 min so that a transparent melting liquid was

obtained. After 6h, the liquid mixtures had turned completely solid. The temperature was then elevated and kept at 180°C for 8h, 200°C for 2h, 220°C for 5h, and 240°C for 2h to completely cure the material. The impact and flexural specimens of the blends were thus obtained. The shear specimens of the blend were obtained by the following procedure: the fine solid powder of the blend just mentioned was placed on a metal plate that had been heated to 160°C. After melting, the blend was applied quickly to two heated aluminum plates (the dimension of both the plates was 7.02×2.02×0.20 cm, and the applied area of the blend was 2.02×2.02 cm). The applied areas of aluminum plates were quickly overlapped and moved to an oven. The heat procedure was the same as that of the impact and flexural specimens. A slight difference was that the aluminum was heated under a pressure of 1Kg/cm<sup>2</sup>.

## Instrumentation

Curing behaviors of TAPT/BMDPM copolymers were studied using a Dupont DSC2910 differential scanning calorimeter at a heating rate 10°C min<sup>-1</sup> in nitrogen. Thermal stability of the cured copolymers was determined on a Dupont TGA2950 thermogravimetric analyzer at a heating rate 10°C min<sup>-1</sup> in air. Dynamic mechanical analysis of the cured copolymers were carried out on a Dupont DMA983 tester at a heating rate of 5°C min<sup>-1</sup> in nitrogen. The dimension of the specimens of the cured copolymers for DMA analysis was 5cm×0.2cm×0.05cm.

The impact test was carried out using a Charpy tester according to China State Standard GB25711-81. The shear test was carried out using a tension tester according to China State Standard GB1450.1-83.

## Results and Discussion

### Copolymerization of TAPT with BMDPM

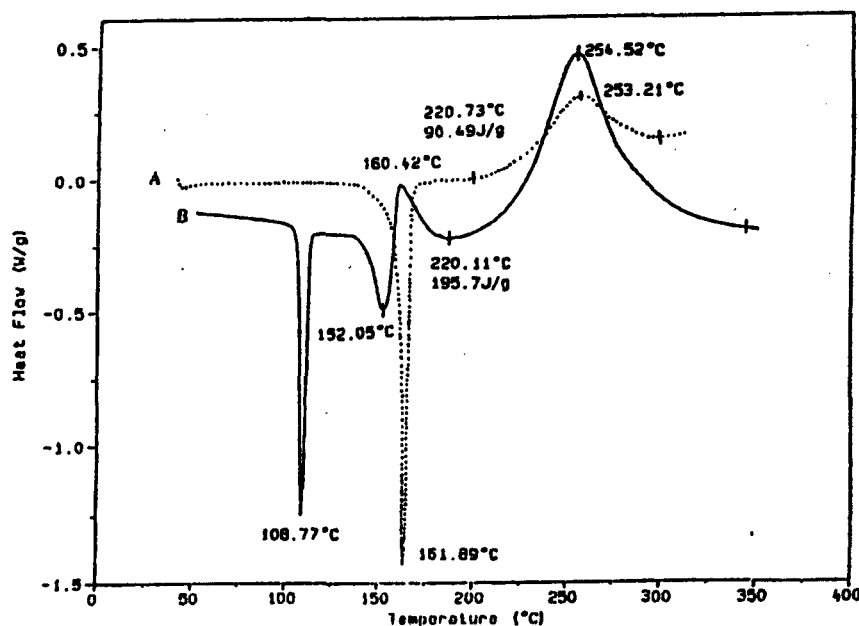


Figure 1 DSC traces of (A) BMDPM and (B) TAPT/BMDPM copolymer

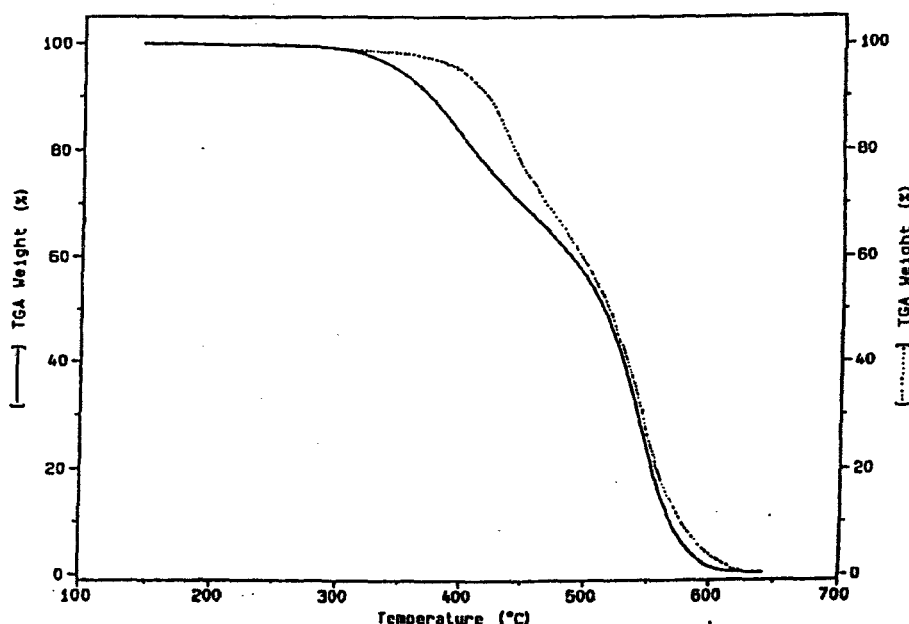
In the DSC trace of BMDPM, a sharp endotherm indicating melting is observed at 162°C (Figure 1A). Mixing of TAPT with BMDPM (30 wt %) results in a decrease in melting transition (Figure 1B) and an exothermic peak at 160°C associated with the

“ene/Diels-Alder” reaction between the BMDPM double bond and the vinylic double bond of TAPT. Exothermic transitions of curing of BMDPM or TAPT/BMDPM are also observed in Figure 1 in the temperature range 190-300°C. Heat of curing reaction ( $\Delta H$ ), fusion temperature of BMDPM (or TAPT/BMDPM), onset temperature of curing reaction, and exothermal peak position ( $T_{\text{exo}}$ ) are determined from DSC traces and listed in Table 1. An increase in  $\Delta H$  values and a decrease in  $T_m$  temperature is noted following addition of TAPT to BMDPM.

**Table 1 Comparison of Thermal Characteristics between BMDPM and BMDPM/TAPT**

Compound	$T_m$ (°C)	Onset Temperature (°C)	$T_{\text{exo}}$ (°C)	$\Delta H$ (J/g)
BMDPM	162	221	253	90.49
BMDPM/TAPT	152	220	255	195.7

### Thermal stability of the cured copolymer of TAPT with BMDPM



**Figure 2 TGA data of BMDPM (dotted line) and TAPT/BMDPM copolymer (30 wt% TAPT; solid line)**

Relative thermal stability for the cured copolymer of TAPT/BMDPM was evaluated by thermogravimetry. The results are given in Figure 2 and Table 2, respectively. A higher heat resistant temperature index ( $T_i$ ) 206°C (Table 2), indicated that TAPT modified BMDPM resin has a high level of thermo-oxidative stability.

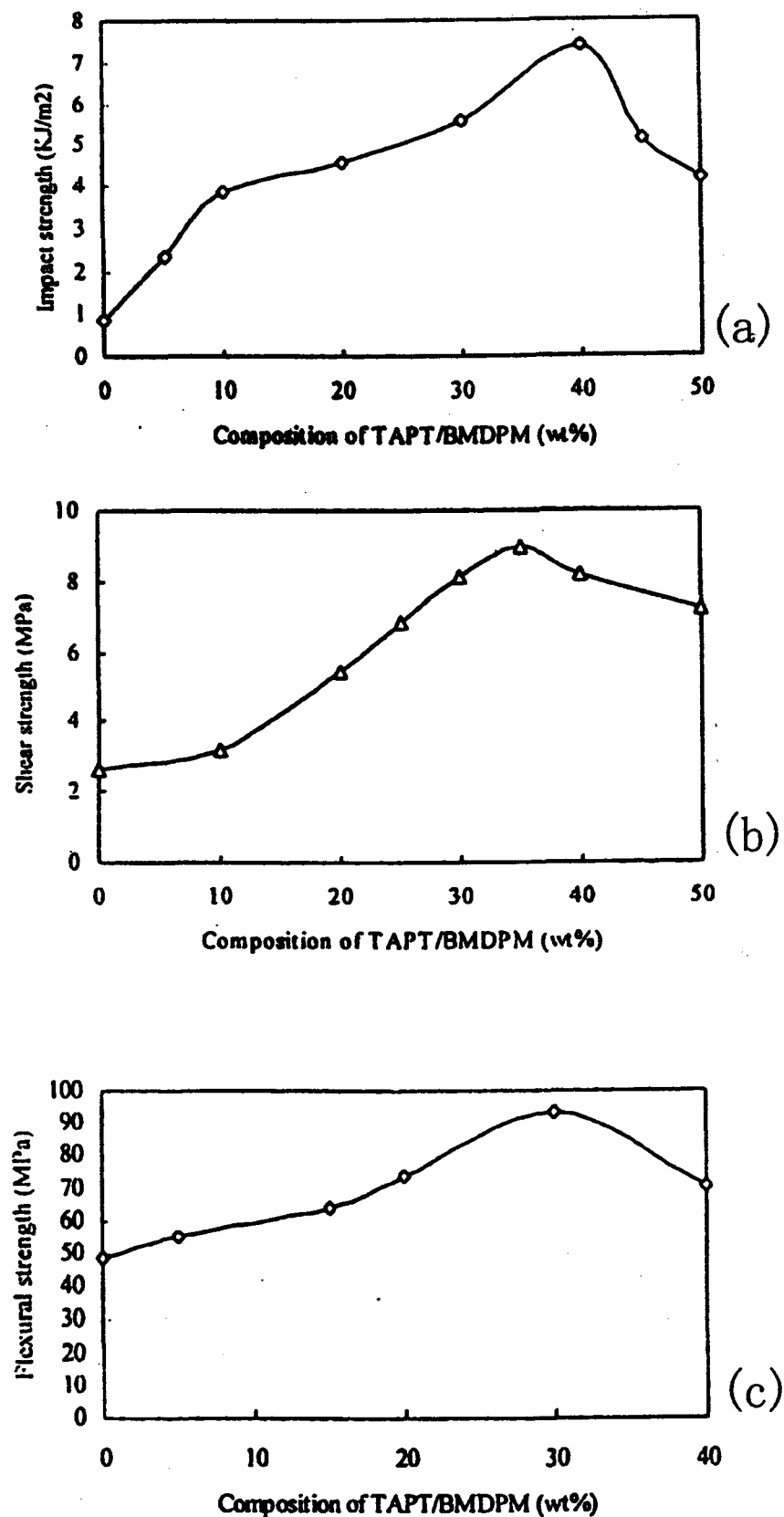
**Table 2 TGA Data of TAPT/BMDPM Copolymer<sup>a</sup>**

Compound	The Weight Loss Temperature (°C)							
	$T_5$	$T_{10}$	$T_{15}$	$T_{30}$	$T_{50}$	$T_{\text{max1}}$	$T_{\text{max2}}$	$T_i$
BMDPM	395	415	428	465	516	432	542	214
TAPT/BMDPM	347	372	392	447	513	401	543	199

<sup>a</sup>  $T_5$ ,  $T_{10}$ ,  $T_{15}$ ,  $T_{30}$  and  $T_{50}$  were the temperatures when weight loss was 5,10,15,30 and 50%, respectively;  $T_{\text{max1}}$  and  $T_{\text{max2}}$  were the decomposition peak temperature;  $T_i$  was the heat-resistant

temperature index;  $T_i = 0.49[T_5 + 0.60(T_{30} - T_5)]$ .

### Mechanical properties of TAPT/BMDPM copolymer



**Figure 3 Mechanical properties versus composition (wt%) of TAPT/BMDPM blend; impact strength versus composition (a); shear strength versus composition (b); and flexural strength versus composition (c)**

**Table 3 DMA Results of TAPT/BMDPM Copolymer**

Composition of BMDPM/TAPT Copolymer in Weight	Glass Transition Temperature (°C)
80/20	314,383
70/30	322,359
60/40	210

TAPT was expected to improve mechanical properties of BMDPM. The impact strength, flexural strength, and shear strength depending on the composition of TAPT/BMDPM copolymers by weight are shown in Figure 3. The three curves show the maximum in impact strength, shear strength, and flexural strength when the compositions of TAPT in the copolymer are 40, 35, and 30wt%, respectively. Compared with the neat BMDPM resin, the copolymer resin can attain 8.6 times the impact strength, 3.4 times the shear strength, and 1.9 times the flexural strength.

Meanwhile, all copolymers show higher impact strength, shear strength, and flexural strength. It is worthy of noting that the impact strength, shear strength, and flexural strength decrease dramatically when the compositions of TAPT exceed 40, 35, and 30 wt%, respectively. Thus, introducing TAPT to BMDPM can give the matrix good mechanical properties, and such mechanical behavior is related to the network structure of the cured resins.

The DMA results in the range 50-400°C for TAPT/BMDPM copolymers at various weight compositions are shown in Table 3. All copolymers of TAPT/BMDPM show glass transition temperatures in the range 210-390°C, and these glass transition temperatures decrease with increasing of the TAPT compositions. It is interesting that the TAPT/BMDPM cured resin has only one glass transition temperature when TAPT loading is 40%, and has two glass transition temperatures when TAPT composition is 30 and 20%. The results indicate a variety of morphology of the phases in the TAPT/BMDPM cured resin from homogenous to phase separation. This variety should be caused by forming two components in the matrix. One component is the copolymer formed by “ene-Diels-Alder” reaction of TAPT with BMDPM and another is the homopolymer of BMDPM. Because of different chemical components between the copolymers and the homopolymer, two phases with different structure and size are formed in the matrix. With variety of the composition of TAPT, the difference of the size of the phases increases or decreases. Consequently, compatibility between the two phases aggravates or improves. When the composition of TAPT is in the 30-40% range, a more compatible network is formed, which contains more “ene-Diels-Alder” reaction products. Hence, the degree of the phase separation decreases. With the increasing of tough “ene-Diels-Alder” reaction products, the mechanical properties of TAPT/BMDPM cured resin are strongly improved.

## Conclusion

The following conclusions can be drawn on the basis of this work.

- (1) TAPT/BMDPM copolymer (30wt%) has lower curing activation energy, and the cured resin has higher thermooxidative stability.
- (2) TAPT can effectively improve mechanical properties of 4,4'-(bismaleimidophenyl) methane (BMDPM). The better results were obtained when the TAPT composition was in the range 30-40 wt%.