

# Modification of Bismaleimide With Allyl Compound and *N*-Phenylmaleimide

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**ABSTRACT:** Three different formulas with low-cost resins, made up of *N,N'*-bismaleimidediphenylmethane (BMI), *O,O'*-diallylbisphenol A (BA), and *N*-phenylmaleimide (NPMI) were developed. The properties of prepolymers, such as activation energies, enthalpy, and constants of reaction rate, were obtained by a kinetic programmer on DSC. Thermal and mechanical properties of neat resins were also studied. The results showed that the systems had low melting point and low viscosity. All cured resins presented excellent thermal and good mechanical properties. The mechanical properties could be affected by the quantity of NPMI and postcuring process. The water absorption is  $\leq 1.98\%$ ; heat deflection temperature (HDT) is  $\geq 250^\circ\text{C}$  after aging for 100 h in distilled water of  $90^\circ\text{C}$ . The data indicate that the BMI can be effectively improved by adding BA and NPMI, while its heat resistance and hot/wet mechanical properties can be fairly retained. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2518–2522, 2001

**Key words:** *N*-phenylmaleimide; *N,N'*-bismaleimidediphenylmethane; *O,O'*-diallylbisphenol A; modified bismaleimide

## INTRODUCTION

Earlier studies on high-performance polymers concentrated primarily on thermal stability, but little attention was paid to processability and production price.<sup>1</sup> However, for a polymer to be used as the engineering material, it must have simple processability, excellent physical properties, and relatively low price.<sup>2</sup> A polymer for engineering materials and adhesives should be adapted to conventional processing techniques at low temperature and exhibit good mechanical properties, acceptable production cost.

There are many reports on modification of bismaleimide (BMI) for improving toughness.<sup>3,4</sup>

CIBA-GEIGY introduced a bismaleimide system, XU292, with 4,4'-bismaleimidediphenylmethane (BMI) and *O,O'*-diallylbisphenol A (BA) in early 1984. It possesses outstanding toughness, good resistance to humidity, and excellent thermal/mechanical properties. To obtain a resin system of low cost and easy processability, we studied three different compositions with different weight ratio (Wt) of BMI, BA, and *N*-phenylmaleimide (NPMI). We also studied their processability, as well as their heat-resistant, mechanical, and hygrothermal properties.

## EXPERIMENTAL

### Materials

BMI was obtained from Hubei Fenggang Chemicals (China). This commercial-grade yellow pow-

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**Table I** Formula of Selected Compounds

System	Wt Ratio of BMI/BA/NPMI
1	3/1/1
2	3/1/1.5
3	3/1/2

der contains more than 85% of maleimide double bond structure. BA was obtained from Sichuan Jiangyou Material (China), an industrial-grade amber-colored viscous liquid at room temperature. NPMI is also an industrial-grade yellow powder from Lanzhou Chemical Company (China).

### Resin Preparation

Both BMI and BA were heated at 120°C for 30 min. NPMI was then added under vigorous stirring to form a clear homogeneous liquid; the liquid was maintained at the same temperature for additional 30 min (Table I).

### Differential Scanning Calorimetric Analysis

A Perkin–Elmer differential scanning calorimetric (DSC) -2C analyzer was used to study the effect on variation of ratio reactivity of each system with a heating rate 5°C/min, 10°C/min, and 20°C/min, respectively, in a nitrogen atmosphere.

### Curing Conditions

The prepolymers were poured into a preheated mold with release agent and heated to cure. A program heating process was used for all three systems, in which samples were heated at 140°C, 160°C, 180°C, and 200°C for the same time interval, about 2 h. A postcuring process was 230°C for 8 h and 200°C for 8 h, 16 h, and 20 h, in order to compare the effect of different postcuring temperatures and times on the properties.

### Properties Test

The mechanical properties of neat resin were tested by Chinese Standard methods. Flexural and impact strength was obtained according to GB/T2570-1995 and GB/T2571-1995, respectively. Heat deflection temperature (HDT) was measured by ASTM648-56 under 2°C/min heating rate, and 18.5-kg/cm<sup>2</sup> force. Thermogravimetric analysis (TGA) was conducted on Hi-Res TGA instruments equipped with a 2950 analyzer station.

**Table II** Physical Properties of Prepolymer

System	1	2	3
s.t. (°C)	100	90	80
Viscosity (110°C) PaS.	0.2	0.06	0.04

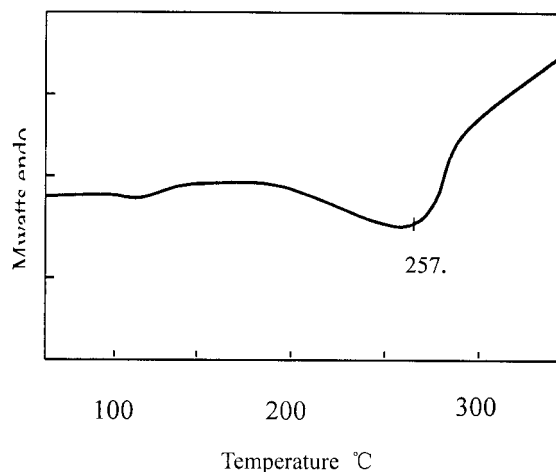
## RESULTS AND DISCUSSION

### Prepolymer Characterization

Table II shows that the physical properties of prepolymers are dependent on the quantity of NPMI when the value weight ratio of BMI/BA is constant. We can also see that if the amount of NPMI is small, the obtained prepolymer had a high softening temperature (s.t.) and a high viscosity in the molten state.

Figure 1 shows a typical DSC scan for the prepolymer of system 2 at a heating-up rate of 10°C/min. Two distinct exothermic peaks are observed, one around 120°C, and the other ~257°C. These indicate that two desirable step reactions take place. These reactions allow material to be prepolymerized at low temperature and to be B-staged like the conventional epoxy systems cured at the elevated temperature.

Table III presents the results of DSC analysis of main peak value at different heating rate for three systems of BMI/BA/NPMI.  $T_i$ ,  $T_p$ , and  $T_f$  are initial cured temperatures, peak temperatures, and final temperatures, respectively. From these data, we can obtain the initial cured temperatures at a heating rate of 0°C/min by extrapolat-



**Figure 1** Typical DSC thermogram of BMI/BA/NPMI resin at a heat rate 10°C/min.

**Table III Results of DSC Analysis on BMI/BA/NPMI Resin**

System	Heat Rate (°C/min)	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)
1	5	190.75	239.4	291.31
	10	187.08	254.1	293.22
	20	204.9	270.5	305.48
2	5	187.29	244.8	303.82
	10	187.51	257.1	299.28
	20	199.31	277.6	338.78
3	5	200.24	249.4	299.51
	10	212.63	265.1	315.31
	20	213.69	282.9	348.84

ing the plots presented in Table IV. It can be seen that the system possesses higher curing temperature than the system of XU292.<sup>5</sup> The larger the amount of NPMI used, the higher the cured temperature. The activation energies ( $E_a$ ), the enthalpy of reaction ( $\Delta H$ ), and  $\ln k$  for the prepolymers are also obtained by a kinetic programmer on (DSC) -2C analyzer.

#### Physical Properties of Neat Resins

The physical properties of neat resin systems were investigated; the results are shown in Table V. Among the three systems, system 3 has the lowest mechanical strength—even postcuring at either 200°C for 8 h or 230°C for 8 h. System 1 has the highest impact and flexural strength of the three systems. It should be noted that mechanical properties for systems 1 and 2, postcured at 230°C for 8 h, are similar.

The relationship between heat deflection temperature (HDT) and postcuring time under 200°C is shown in Figure 2. It can be seen that the longer postcuring time is used, the higher the HDT for any systems can be obtained. After postcuring for 16 h under 200°C, the HDT shows little difference between systems 1 and 2. However, at the 200°C for 20 h, the HDT value of system 1 is

**Table V Properties of the Neat Resins**

Properties	Postcuring Process	System 1	System 2	System 3
	(°C/h)			
Flexural strength (MPa)	230/8	95.5	94.5	77.2
	200/8	96.5	95.4	83.6
Impact strength (kJ/m <sup>2</sup> )	230/8	7.92	6.50	5.57
	200/8	14.6	10.0	6.50
HDT (°C)	230/8	324	300	322
	200/8	266	266	250

higher than that of system 2. The value of HDT of system 3 is the lowest among three systems; even its postcuring programmers were 8, 16, or 20 h under 200°C, respectively (Typical thermogravimetry (TG) curve of system 3 is presented in Figure 3). The maximum decomposition temperatures for three cured resins are given in Table VI. It can be seen that all maximum decomposition temperatures are  $\sim 410^\circ\text{C}$ , and the char yield at 700°C are above 39%, indicating that the three systems have good thermal stability.

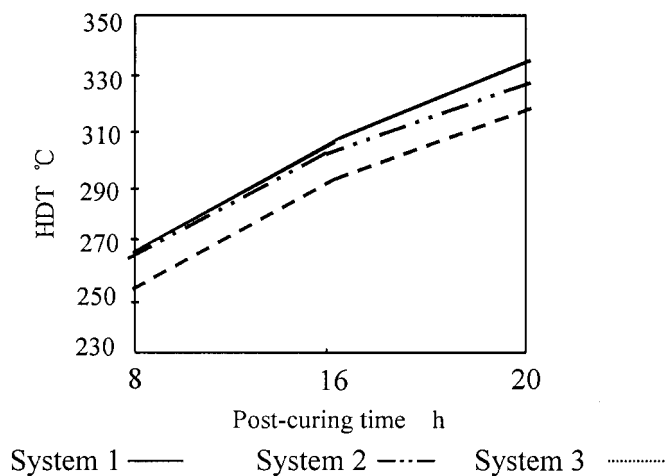
Figure 4 shows the dependence of HDT and water absorption for system 2 on aging time in distilled water of 90°C. The postcuring cycle is 16 h under 200°C. Evidently, from Figure 4, after aging for 100 h, the water absorption reached 1.98 wt %, and the HDT value is  $>256^\circ\text{C}$ . It was maintained a retention of 85% of its dried value. The results indicated that the cured BMI/BA/NPMI systems possess good hygrothermal properties.

#### CONCLUSIONS

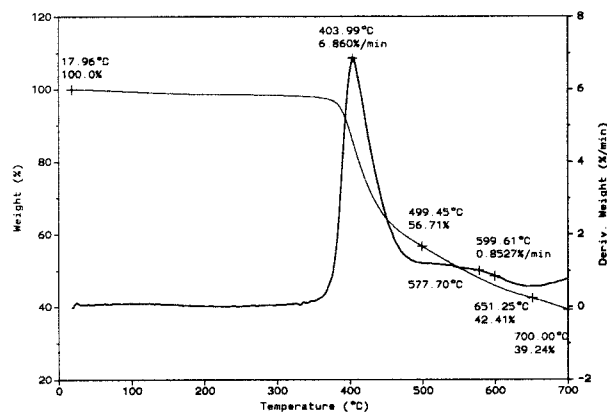
Three new systems of different BMI, BA, NPMI weight ratios were developed. Adding *N*-phenyl-

**Table IV Thermal Properties of the System Studied**

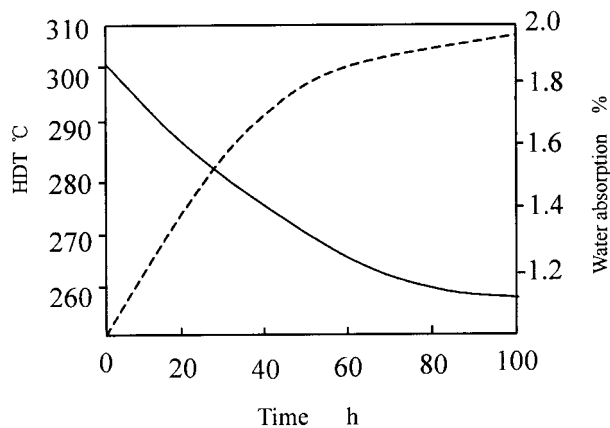
System	1	2	3
$\Delta H$ (J/g)	-215.21	-207.26	-184.71
$E_a$ (kJ/mol)	113.41 $\pm$ 2.44	112.97 $\pm$ 2.44	138.24 $\pm$ 2.981
$\ln k$ (1/s)	21.72 $\pm$ 0.46	21.37 $\pm$ 0.46	27.04 $\pm$ 0.58
Initial cured temperature (°C)	169	182	189



**Figure 2** Influence of post-curing time at 200 °C on HDT of BMI/BA/NPMI resins.



**Figure 3** Typical thermogravimetry of cured system 2.



**Figure 4** Dependence of (---) water absorption and (—) HDT on aging time in 90°C distilled water of cured resin system 2 post-curing 16 h at 200°C.

**Table VI Data of TG Curve for System of BMI/BA/NPMI**

System <sup>a</sup>	1	2	3
Max. decomp. temp. (°C)	418	413	404
Char yield at 700°C (%)	43.22	40.55	39.24

<sup>a</sup> Postcuring procedure: system 1, 200°C/8 h; system 2, 200°C/16 h; system 3, 200°C/20 h.

maleimide in BMI/BA system cannot only reduce the cost of the system, but also keep its low viscosity, excellent heat resistance, and fine mechanical properties. Although the enthalpy ( $\Delta H$ ) and the activation energies ( $E_a$ ) are slightly higher than XU292, the three systems can obtain good

mechanical, thermal, and hot/wet properties after being postcured under 200°C for a long time. The longer the postcuring time, the higher the thermal properties.

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