Studies of modified bismaleimide resins

Part I *The influence of resin composition on thermal and impact properties*

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The influence of the components of a modified bismaleimide (BMI) resin on the thermal properties and impact properties of these resins are investigated in this paper. Toughened BMI resin castings incorporating 0%, 5%, 10%, 15%, 20%, 30%, and 40% (by weight) thermoplastic-modified polyetherketone (PEK-C) were prepared. The modified resins were characterized and analysed using dynamic mechanical thermal analysis (DMTA), thermogravimetric (TG) analysis, free beam impact tests, and scanning electron microscope (SEM) techniques. The results indicate that a typical 4,4′-bismaleimidodiphenyl methane (MBMI)/0,0′-diallybisphenol A (DABPA) two-component system modified with 4,4′-bismaleimide diphenyl ether of biphenyl A (MEBMI), Allyl phenol epoxy (AE), and PEK-C has a high glass transition temperature (Tg), excellent thermal stability, and outstanding impact strength. This novel toughened BMI resin is expected to find use in advanced composites. © *1998 Kluwer Academic Publishers*

1. Introduction

BMI resins have undergone rapid development during the past two decades. The main aim of the development was to offer resins with high toughness, excellent heat resistance, and low cost while maintaining epoxy-like processing. Much research has focused on improving the toughness of BMI resins for use as aircraft structural materials.

Recent reviews [1–3] have highlighted the past, present, and future directions for toughening BMI. In summary, BMI has been modified by several different methods: (1) synthesis of BMI monomers with flexible or long segments in the backbone [4, 5]; (2) linear chain extension using aromatic diamines and aminobenzoic hydrazide to reduce cross-link density [6, 7]; (3) blending of BMI with epoxies [8, 9]; (4) copolymerization of allyl-type compounds [10, 11]; (5) incorporation of thermoplastic resins with excellent heat resistance and ductility [12, 13]; and (6) use of aromatic dicyanate esters to blend with BMI [14, 15]. The first three methods have the disadvantage of lowering the Tg and the rigidity of cured resins, however; the sixth method has less adverse effect on the high temperature and processability, but it is usually difficult to treat the residues of preparing cyanate ester monomers (usually excessive cyanogen halide were used) safely locally.

Most modified BMI resins are based on a two-component system—MBMI and DABPA. Use of flexible and long-segment backbone BMI monomers will improve toughness and processability. An important consideration when incorporating thermoplastic resin into BMI is to access the compromise between the increase in fracture toughness and the reduction in hot/wet properties. It was difficult to prepare modified BMI resin castings, however, because the viscosity of uncured resin was too high to be degassed when thermoplastic resin was incorporated.

Lan [16] suggested that the incorporation of AE should be expected to yield a novel, modified BMI resin with excellent toughness and high heat resistance.

Castings of BMI resins modified with different content PEK-C were prepared successfully in our laboratory. The main aim of this paper is to study the influence of several modifiers—MEBMI, PEK-C (Fig. 1) and AE—or mixtures of them, on the thermal and impact properties of the two-component system comprising MBMI and DABPA.

2. Experimental
2.1. Materials
MBMI (Hubei Research Institute of Chemistry, China), MEBMI (Tianjin Synthetic Materials Industrial Institute, China), DABPA (Hubei Research Institute of Chemistry, China), and PEK-C (Suzhou Institute of Engineering Plastics, China) were all used as received; AE was prepared based on bisphenol A, epoxy (diglycidyl ether of bisphenol A) and DABPA in the presence of catalyst in our laboratory according to Lan [16] (Fig. 2); carbon fiber T800HB-12000-40B was from Toray Corporation.
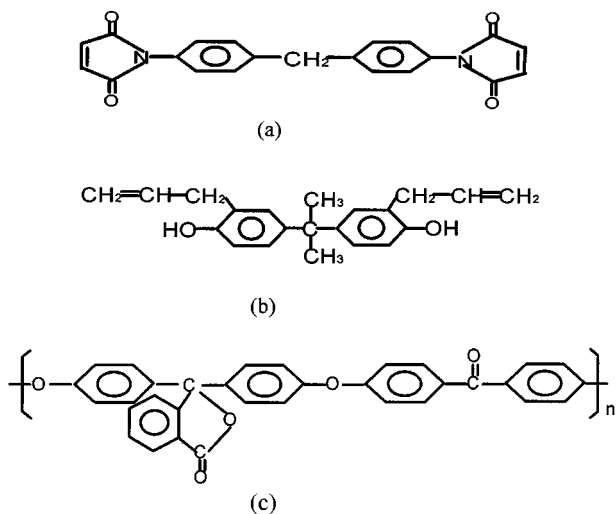
(a)

(b)

(c)

Figure 1 (a) MBMI, (b) MEBMI, (c) PEK-C ($n = 15 \sim 25$).

2.2. Experiment

2.2.1. Preparation of BMI resin castings and BMI/T800 laminates

The blends of modified BMI components were heated and degassed immediately in a vacuum oven at 130 °C for 30–60 min, then cured at 150 °C for 2 h and 200 °C for 2 h. The sample was post cured at 230 °C for 4 h.

Autoclave cure cycle for BMI/T800 composites is 150 °C/2 h + 180 °C/2 h + 200 °C/4–5 h; the pressure applied is 0.6–0.7 mPa.

2.2.2. Impact test

Free beam impact tests were carried out on a XCJ-40 impact test machine (Changchun Materials test equipment factory) according to GB1043-79 at room temperature. The dimension for impact test specimens (not notched) is 55 mm × 6 mm × 4 mm, and the number of the test specimens is 10 for one group.

2.2.3. Thermal analysis

The Tg of the modified BMI resins was evaluated by DMTA; the heating rate was 2 K/min and the frequency chosen is 1 Hz. The thermal stability of the various BMI resins were measured by TG in nitrogen atmosphere at a rate of 2 K/min.

2.2.4. Fracture surface inspection

The fracture surfaces of the impact specimens used to determine impact strength were examined by an AMRAY-1000B type SEM. Samples were coated with a thin layer of gold-palladium to reduce any charge built up on the fracture surface.

3. Results and discussion

3.1. Impact properties

In order to obtain information on the influence of various components on the properties of the modified BMI resins, a two-component system of MBMI/DABPA (molar ratio = 1:1) was selected as the fundamental formulation, and MEBMI, AE, PEK-C, or their blends were incorporated. Several modified formulations were formed, see Table I. The properties of the modified BMI resins are summarized in Table II.

Impact strength is one of the important parameters for illustrating the fracture toughness of a resin. According to GB1043-79 (Chinese Standard),

Free beam impact strength = A/S

A work consumed; unit: kJ, J

S Cross-section area; unit: m^2

So the unit of the impact strength is kJ/m^2.

The real mean of the impact strength is the work consumed per unit cross-section area. As shown in Tables I and II, the incorporation of MEBMI monomer with a relatively flexible and long-segment backbone will enhance the impact strength slightly when comparing resins I and II. One reason is that the content of MEBMI was relatively low. Incorporating MEBMI would decrease the viscosity of the uncured resin, however,

TABLE I Formulations of modified BMI resins

Resin system	MBMI/MEBMI (molar ratio)	AE (wt %)	PEK-C (wt %)
I	1/0	0	0
II	4/1	0	0
III	4/1	0	20
IV	4/1	20	0
V	4/1	20	20

TABLE II Properties of modified BMI pure resins

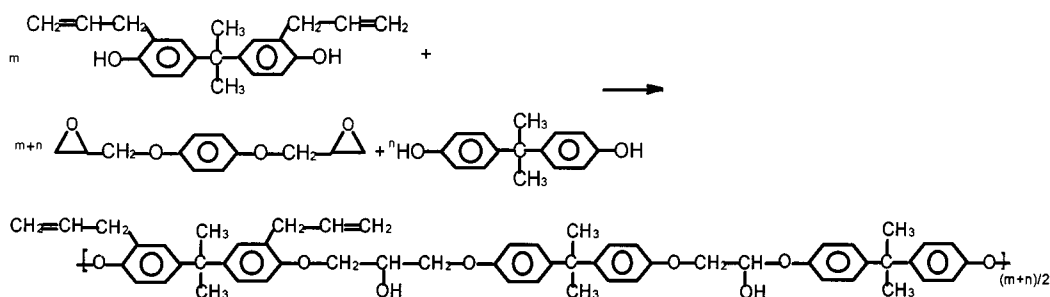| Resin system	Tg (°C)	Thermal decomposition temperature (°C)			Impact strength (kJ/m^2)
		T_d^i	T_d^{max}	T_d^f	
I	315	378	386	485	6.0
II	310	375	440	480	6.3
III	245	374	432	485	17.0
IV	292	374	430	478	7.1
V	238	371	425	500	18.9

Figure 2 $m = 2 \sim 5$; $n = 2 \sim 5$.

which would contribute to improving the processability. Comparing resin IV to II and resin III to II, respectively, it is apparent that incorporation of 20% AE increases the resin's impact strength from 6.3 kJ/m^2 to 7.1 kJ/m^2 whereas 20% PEK-C increases it to 17.0 kJ/m^2. When MEBMI, AE, and PEK-C were incorporated simultaneously, the impact strength of the modified BMI resin was promoted as high as 18.9 kJ/m^2, three times greater than that of the unmodified resin I.

The fracture surfaces of impact specimens were characterized and analysed by the SEM technique. It is common practice in the polymer field to use micrographs of this type to deduce the toughening results. As shown in Fig. 3, the unmodified cured resin I exhibited only one phase, no plasticity, but many white stripes on the frac-ture surface, which indicates a brittle fracture (Fig. 3a). SEM photographs still showed a brittle fracture with some slight improvement of toughness as MEBMI or modifier AE was incorporated (Fig. 3b and d). When 20% PEK-C was added, great changes in the morphology of the fracture surface were observed, as shown in Fig. 3c and e. Particles of PEK-C led to a two-phase morphology, and the white stripes disappeared completely, a significant tougher fracture surface was obtained. Hence, the SEM results reflect the corresponding impact strength of BMI resins.
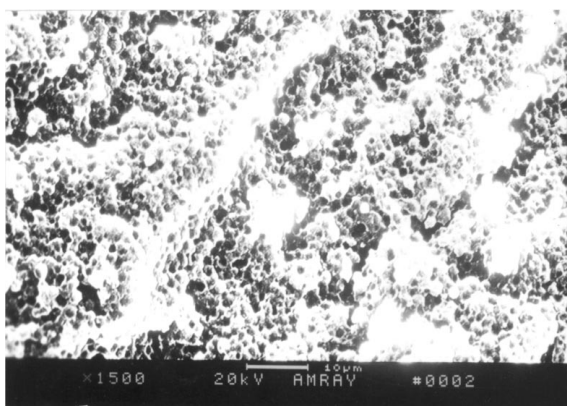
The influence of different PEK-C contents on the impact strength and thermal properties of the modified BMI resins was also studied; the results are summarized in Table III.
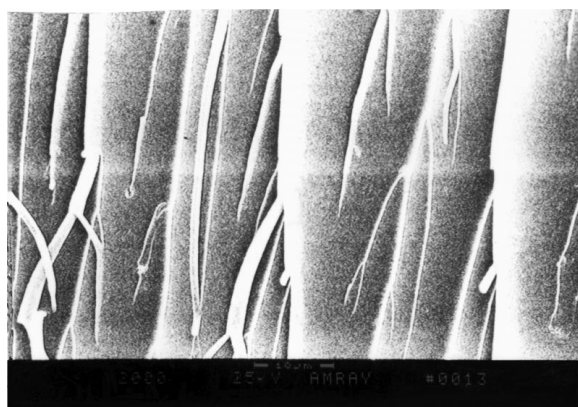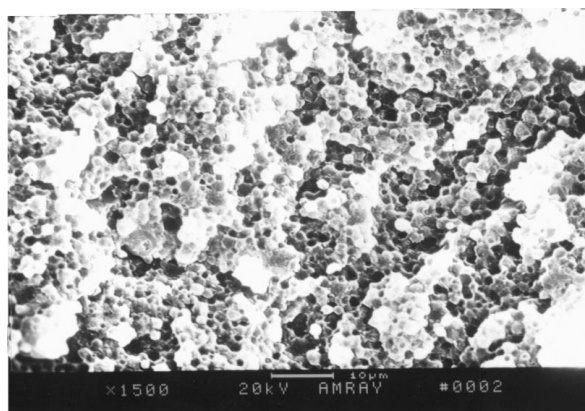

(a)
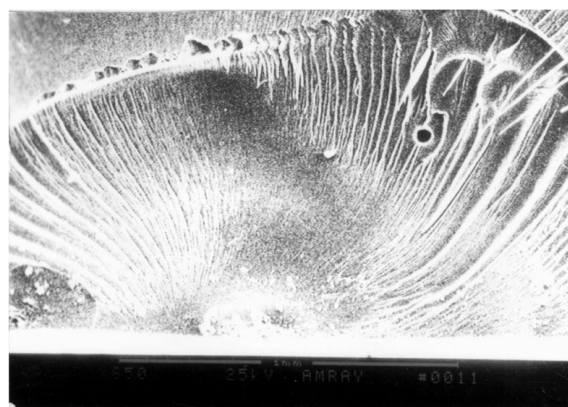
(b)

(c)

(d)

(e)

Figure 3 SEM photographs of fracture surfaces of modified BMI resins. (a) resin I ×2000, (b) resin II ×1000, (c) resin III ×1500, (d) resin IV ×1000, (e) resin V ×1500.

TABLE III Properties of modified BMI resins with different PEK-C contents

Resin system	IV	VI	VII	V	VIII	IX
PEK-C (wt %)	0	5	10	20	30	40
Impact strength (kJ/m^2)	7.1	8.2	8.9	18.9	13.0	13.0
Tg (°C)	310	231	231	238	225	228

As shown in Table III, the impact strength of BMI resins modified with PEK-C is strongly dependent on the PEK-C concentration; an increase of PEK-C concentration led to a high-impact strength value that reached a peak when 20% PEK-C was incorporated. The number of PEK-C particles increases with the increasing PEK-C concentration, so the opportunities
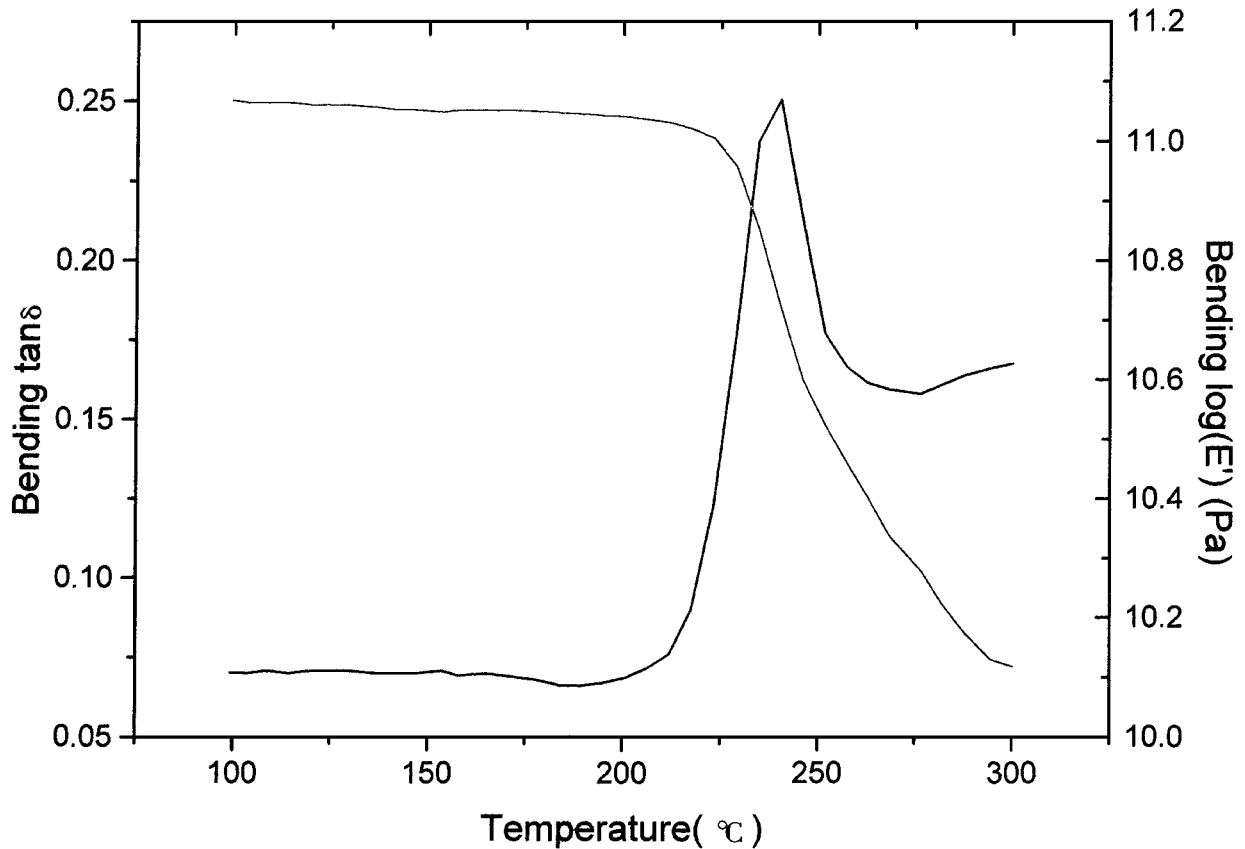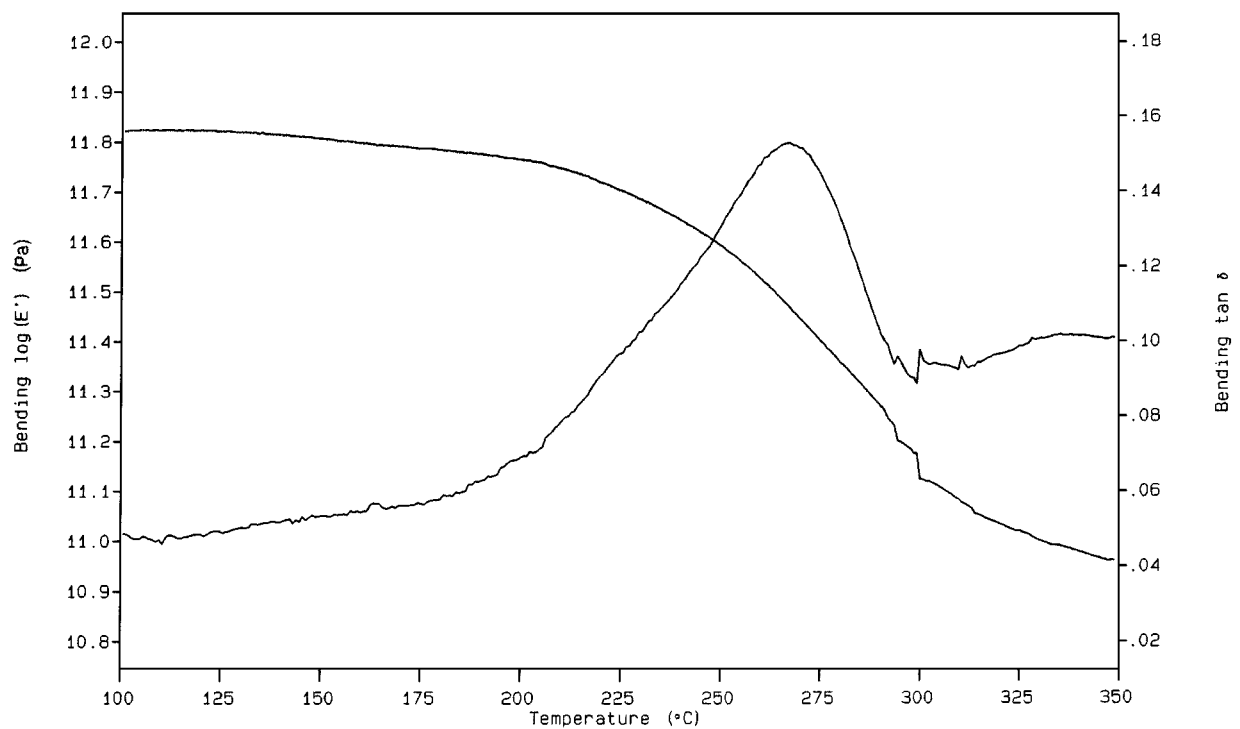

Figure 4 DMTA curve of resin V.

Figure 5 DMTA curve of resin V/T800 composite.

for cracks touching PEK-C particles increases and the crack termination is improved. This is believed to be the main reason for the impact strength of BMI resin increasing with the concentration of PEK-C.

When PEK-C content exceed, 20%, however, the increasing PEK-C concentration leads to a decrease of the impact strength of the BMI resin. When too much PEK-C is incorporated, it becomes difficult to disperse PEK-C particles homogeneously, leading to aggregate and producing a stress concentration. On the other hand, when the number of PEK-C particles is too large, the distance between two particles become too short and the number of cracks produced exceeds a critical value [17], so the fracture toughness is reduced.

3.2. Thermal properties
The maximum of loss peak on the DMTA curve corresponds to the Tg of the tested resin. As shown in Tables II and III, Tg decreases with the addition of MEBMI, AE, and PEK-C. The Tg corresponding to the BMI resin modified with MEBMI, AE, and PEK-C is 238 °C (Fig. 4). BMI resins incorporating 5, 10, 20, 30, and 40 wt % PEK-C do not show any significant difference in Tg (Table III). The Tg of resin V/T800 composite is 266 °C, 28 greater than that of the corresponding resin V. The DMTA curve of above composite is shown in Fig. 5.

The thermal stability of these modified resins was determined by TG analysis. The initial decomposition temperature (T_d^i), final decomposition temperature (T_d^f), and temperature of maximum rate of weight loss (T_d^{max}) in a nitrogen atmosphere are shown in Table II. The T_d^i, T_d^f, and T_d^{max} of modified BMI resins decrease with incorporation of MEBMI, AE, and PEK-C, but the reduction of these values is not significant.

All the above thermal analysis results indicated that the modified BMI resins still have excellent heat resistance and good thermal stability.

In a future paper [18], a composite based on T800 and Resin V modified with MEBMI, AE, and PEK-C will be reported as having good processability, excellent mechanical properties, and high toughness simultaneously.

4. Conclusion
The impact strength of the BMI resin depends strongly on the concentration of PEK-C incorporated; the typical MBMI/DABPA two-component system modified with MEBMI, AE, and PEK-C simultaneously has outstanding impact toughness, excellent thermal stability, relatively high Tg, and good processability. It is expected to be an important novel candidate for a high toughness BMI resin with good comprehensive properties.

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