Characterization of Modified Bismaleimide Resin

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SYNOPSIS

A new high-temperature resin system based on methylene dianiline bismaleimide (MDA-BMI) chemistry is studied. This is a two-component resin system which is modified by 2,2'-methylene-bis[4-methyl-6-(2-propenyl)] phenol (MBMPP) and has excellent thermal mechanical properties and good toughness characteristics. This paper discusses in detail some of the characteristics of the prepolymer by reacting the two components in addition to the cured system's properties. The prepolymer has very good stability at 100–120°C with very minimal molecular weight increase. The reaction order for curing prepolymer is almost 1. The activation energy of the curing reaction is 74.12 KJ/mol. The flexural strength and modulus of the cured modified MDA-BMI and their retention at 250°C are 124 and 3774.6 MPa and 69 and 78%, respectively. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Constant development in the area of temperature resistant thermosets has been seen in recent years. In particular, thermosetting polyimides are gaining wide acceptance by both the aerospace/aircraft and electrics/electronics industries because they combine a number of unique features, such as excellent physical property retention at elevated temperature and in wet environments. Polyimides, which are well known as high-temperature-resistant polymers, may be classified into the following two different groups: condensation-type and addition-type resins. The latter resins are produced evolution of a volatile by-product. Some of the most important bisimides are the bismaleimides. The bismaleimides are cross-linked to yield polyimide resins. Their processability is almost epoxy-like.

Bismaleimides are a relatively young family of resins. In 1968, the thermal polymerization of bismaleimide was described in the patent literature.[1] The cured bismaleimides, however, are extremely brittle because of their high crosslink density. For the past two decades, extensive studies to enhance toughness of bismaleimides have been done by reducing the crosslink density in the neat resin system.

So far, the copolymerization of bismaleimides with allylphenyl/allylphenol compounds has been shown to be the most effective method for toughening bismaleimides. Zahir and Renner[2] have reported bismaleimide diallylbisphenol A compositions that offer easy processability and cured networks with excellent toughness. Allylphenol compounds coreact with bismaleimides to give linear chain extension by "ene"-type reaction, followed by a Diels-Alder reaction occuring at higher temperature. This chain extension results in tougher networks with only minimum reduction in thermal properties.

2,2'-methylene-bis[4-methyl-6-(2-propenyl)] phenol (MBMPP) is an isomer of 6,6'-diallylbisphenol A. It was synthesized for this paper and was first used to toughen methylene dianiline bismaleimide (MDA-BMI). MBMPP and MDA-BMI are represented by the following chemical structures:


methylene dianiline bismaleimide (MDA-BMI)

$$(1)$$

2,2'-methylene-bis[4-methyl-6-(2-propenyl)]phenol (MBMPP)

$$(2)$$
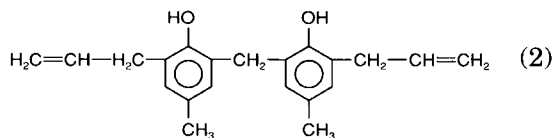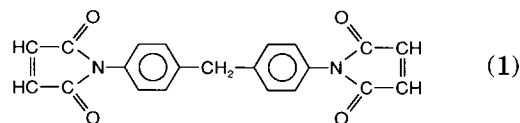
MDA-BMI modified by MBMPP was further researched in dissolving, stability of storage, differential scanning calorimetric (DSC) analysis, and flexibility.

EXPERIMENTAL

Materials

MDA-BMI was synthesized in accordance with literature.[3] MBMPP was also synthesized by the following procedure:

(3)
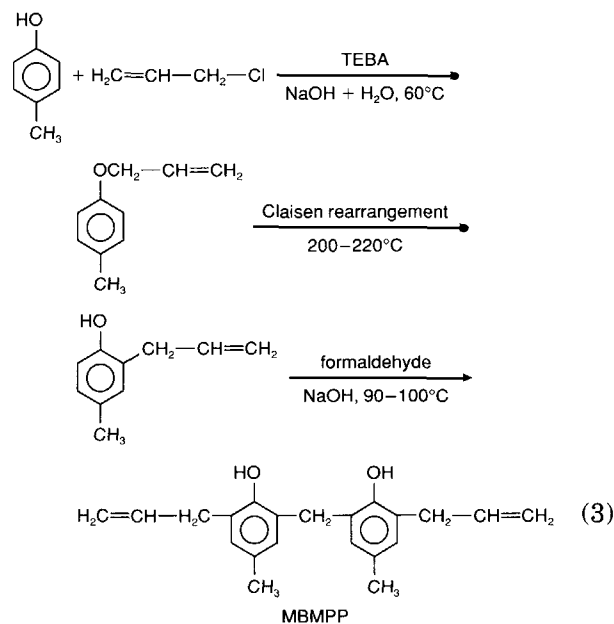
MBMPP

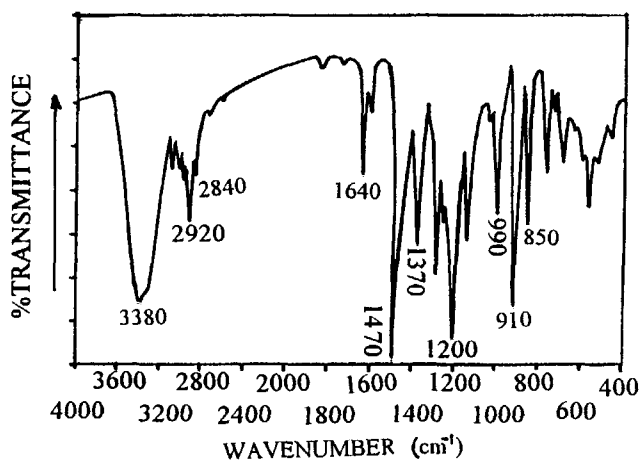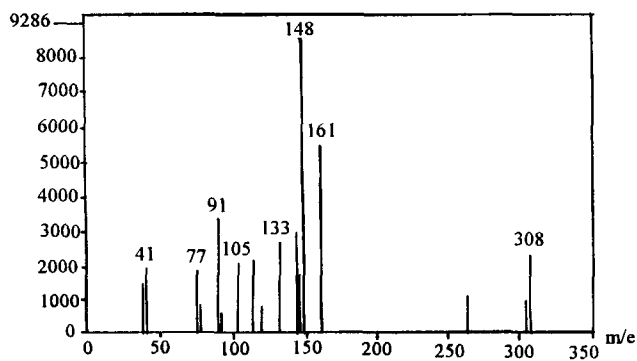The characterization of MBMPP was recorded with UV Vis spectrum (SHIMADZU UV-260 spec-

Figure 2 Mass spectrum of MBMPP.

trophotometer), IR spectrum (Nicolet FT-IR 5SXC spectrometer by KBr pellet technique), H-NMR spectrum (Spectrospin AG WP-100SY spectrometer), and mass spectrum (HITACHI M80). The UV-Vis spectra of the MBMPP in different concentrations of ethanol show the same absorption peaks in the 283 nm region. Figures 1–3 show the IR, MS, and H-NMR spectra of MBMPP. Tables I–III list typical properties of MDA-BMI, MBMPP, elemental analysis, and results of spectra analysis.

Preparation of Prepolymer/Processing

Three different formulation were evaluated to see the effect of differing stoichiometries of each on the processing and performance parameters. The MDA-BMI : MBMPP molar ratios were as follows: System 1, 1.0 : 1.0; System 2, 1.0 : 0.5; System 3, 1.0 : 0.25.

For each system, appropriate quantities of each component and dichloromethane were placed in a four-necked round bottom glass flask equipped with
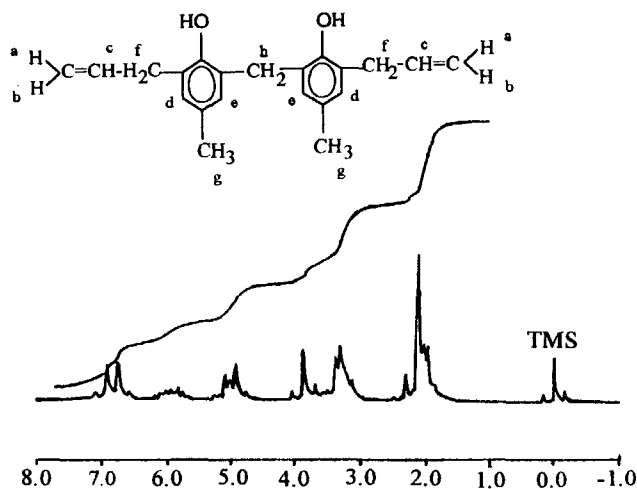
Figure 1 FT-IR spectrum of MBMPP.

Figure 3 H-NMR spectrum of MBMPP.

Table I   Physical Properties of MDA-BMI and MBMPP
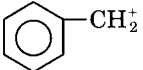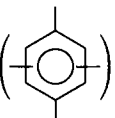
Sample	Medium of Recrystallization	Appearance	Melting Point (°C)	Yield (%)
MDA-BMI	toluene	yellow crystalline powder	156–158	80
MBMPP	heptane	yellow needle crystal	83.9–84.0	35

Table II   Elemental Analysis of MDA-BMI and MBMPP

Monomer	Formula	Found			Calculated		
		C	H	N	C	H	N
MDA-BMI	$C_{21}H_{14}N_2O_4$	69.9	7.89	4.11	70.39	7.82	3.91
MBMPP	$C_{21}H_{24}O_2$	81.33	7.81		81.8	7.79	

Note: Carried out with Carl Erba 1106 elemental analyzer (Italy).

Table III   Results of MBMPP Spectra Analysis

FT-IR Vibration Bond (cm^{-1})	H-NMR (CD$_3$COCD$_3$, δ-ppm)			MS	
	Proton	Found	Calculated	m/e	Cleavage
3380 (—OH)	a	4.96	4.93	308	Molecular ion peak
1640 (—C=C—)	b	5.11	4.96	161	M_1: CH$_2^\bullet$
1200 (C—O)	c	5.96	6.30	148	M_2: CH$_2$—CH=CH$_2$]‡
2840, 2920 (—CH$_2$—)	d	6.76	7.00	133	M_3: CH$_2$—CH=CH$_2$]$^+$
990 (=CH)	e	6.96	7.00	105	M_4: CH$_2$—CH=CH$_2$
910 (=CH$_2$)	f	3.33	3.35	91	⬡—CH$_2^+$
1370 (—CH$_3$)	g	2.15	2.27	77	⬡$^+$
850 (⬡)	h	3.87	3.85	41	$^\bullet C_3H_5$

Note: M$_1$: H$_2$C=CH—CH$_2$—(OH, CH$_3$ phenyl), M$_2$: (OH, CH$_3$ phenyl), M$_3$: (OH phenyl), M$_4$: (cyclopentadienyl cation).
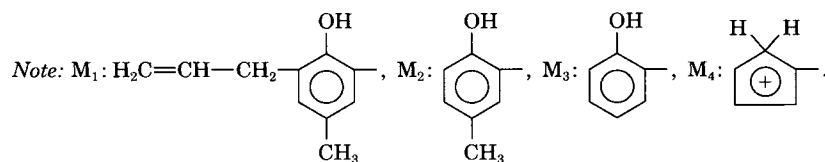
Table IV   GPC of System 3 Prepolymer

Time (100°C)	M_n	M_w	D
initial	209	227	1.1
8 h	228	454	2.0
16 h	241	558	2.3

a mechanical stirring device, thermometer, condensation receptor, and attachments for vacuum. The contents were heated while stirring. The temperature was maintained between 130–160°C until a clear homogeneous melt was obtained via solution-mixing, followed by molten-mixing occuring at elevated temperature. The melt was maintained at the previously set temperature and degassed 20–30 min, then poured into molds preheated at 180°C and cured per the following cure cycle: 180°C/1 h + 200°C/2 h + 250°C/4 h. An ordinary convention oven was used for curing purposes.

Analysis

Differential Scanning Calorimetric (DSC) Analysis

A Du Pont 1090 thermal analyzer and Perkin-Elmer DSC-4 thermal analyzer were used for DSC studies.

Gel Permeation Chromatography (GPC) Analysis

A Water's GPC 52506 was used to determine the changes in the prepolymer's molecular weight upon aging at 100°C.
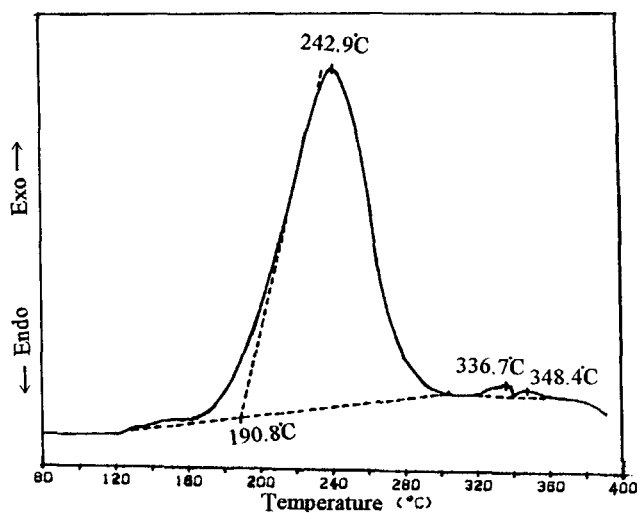

Figure 4   DSC plot of System 3 prepolymer (scanned on Du Pont 1090; heat rate, 10°C/min).

DISCUSSION AND RESULTS

Prepolymer Characterization

The term *prepolymer* used in this paper refers to a homogeneous melt obtained by prereacting the two components of MDA-BMI and MBMPP, as is explained in the experimental section. The prepolymers can be dissolved into dichloromethane, acetone, tetrahydrofuran, toluene, dimethylformamide, dimethylacetylamide, N-methylpyrrolidone, and other non-proton polar solvents. The prepolymer solution can be used in advanced compositions as an impregnant.

GPC work has proved the stability of the prepolymer. Table IV shows the GPC results. At up to 16 h aging at 100°C, the prepolymer molecular weight increased from 227 to 558, with virtually no change in molecular number values.

DSC analysis was used to observe the cure reaction of the prepolymer and cure condition for the prepolymer. Figure 4 shows a typical DSC scan for the prepolymer in System 3. Exothermic peaks are
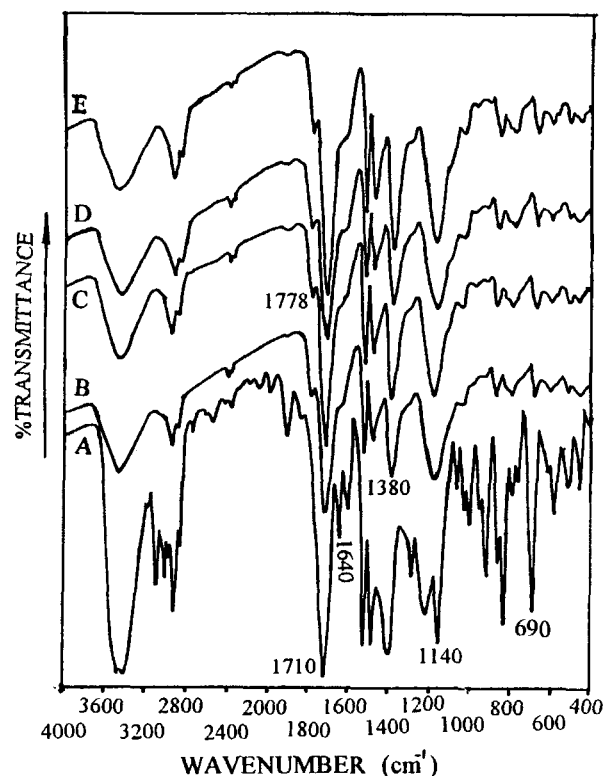

Figure 5   FT-IR spectra of prepolymer and cured polymer at different cure conditions: (A) prepolymer in System 1, (B) 180°C/1 h + 200°C/2 h + 250°C/2 h, (C) 180°C/1 h + 200°C/2 h + 250°C/4 h, (D) 180°C/1 h + 200°C/2 h + 250°C/6 h, (E) 180°C/1 h + 200°C/2 h + 250°C/8 h).
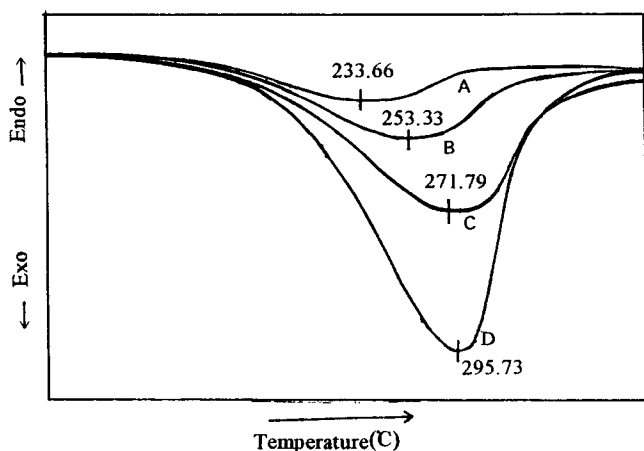
Figure 6 DSC cure of System 3 prepolymer (carried out with Perkin-Elmer DSC-4). Heat rates are as follows: (A) 5°C/min, (B) 10°C/min, (C) 20°C/min, (D) 40°C/min).

seen. The main peak around 243°C is the cure reaction and the two higher peaks, occurring around 337 and 348°C, are post-cure reactions to eliminate network defects in the form of unreacted groups. This also indicates that the prepolymer has excellent storage stability from room temperature to 100°C since no reaction occurs. Figure 5 shows the FT-IR spectra of the prepolymer in System 1 and cured MDA-BMI modified by MBMPP at various cure conditions. A strong ring-stretching vibration band appears at 1150 ± 20 cm^{-1} for bisimides, confirming the C—N—C linkage. The bands appearing at 1780 ± 10, 1720 ± 10, 1390 ± 10, and 690 ± 10 cm^{-1} are characteristic of the imide structure. The C=C stretching vibrations show the characteristic weak band at 1610 ± 30 cm^{-1}, with the band disappearing after up to 2 h curing at 250°C; therefore, the cure cycle is adequate.

Kinetics Study for Curing Prepolymer

Figure 6 shows DSC analyses for the prepolymer in System 3 cured at different heat rates. The formu-

lation was inferred by Kissinger to estimate the apparent activation energy of reaction for the curing prepolymer. Kissinger's formula is as follows.[4]

$$\frac{d \ln\left(\frac{\beta}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E}{R} \qquad (1)$$

and integrated

$$\ln(\beta/T_m^2) = -(E/R)^*(1/T_m) + C \qquad (2)$$

where β is the temperature rate, T_m is the peak temperature, E is the reaction energy, R is the gas constant, and C is the constant. In addition, the reaction order is $n = 1.26\sqrt{S}$, where S is the peak shape index.

The exothermic behavior can be treated as an autocatalytic reaction of thermal polymerization using eq. (2). The T_m, β, ΔH, and S obtained from Figure 6 are listed in Table V.

The result of linear regression for $1/T_m$ to $\ln \beta/T_m$ is $Y = -8914.75X + 6.73$. The energy of curing reaction is 74.12 KJ/mol. The regression coefficient is 0.997.

The thermal polymerization reaction is regarded as an autocatalytic reaction in which the product is in the activated biradical state. Since n is approximately 1, formation of the activated biradical product is regarded as a first-order reaction.

Neat Resin Mechanical Properties

The cured samples are brown, and their translucence is also shown with relation to the primary antioxidation of MBMPP.[5]

$$\text{Flexural strength} = \frac{3PLv}{2bd^2} \qquad (3)$$

where P is the breaking load (N), Lv is the support

Table V   Data of Curing Reaction for Prepolmer in System 3

β (°C/min)	T_m (°C)	T_m (K)	$\dfrac{10^3}{T_m}$	$\dfrac{10^5\beta}{T_m^2}$	$\ln(\beta/T_m^2)$	ΔH (J/g)	$S = a/b$	$n = 1.26\sqrt{S}$
5	233.66	506.81	1.97	1.95	−10.85	−170.08	30/51	0.97
10	253.33	526.48	1.90	3.61	−10.23	−220.83	25/40	1.00
20	271.79	544.94	1.84	6.74	−9.61	−235.12	20/42	0.87
40	295.73	568.88	1.76	12.36	−9.0	−267.33	20/41.5	0.87

Table VI   Cured Modified MDA-BMI Neat Resin Mechanical Properties

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Flexural Strength (250°C, MPa)	Flexural Modulus (250°C, MPa)
System 1	124	3774.6	—	—
System 2	104.4	3343	—	—
System 3	106.7	3610	73.5	2818.8

Note: tested by SHIMADZU AG-50KNE and in accordance with China National Standard, GB 3356-82.

span (mm), *b* is the width of the specimen, and *d* is the thickness of the specimen (mm).

Table VI shows the flexural strength and modulus for the cured modified MDA-BMI formulations. Generally, the room temperature mechanical properties for systems 2 and 3 are similar, while System 1 has higher values for toughness. System 3 also shows better toughness at elevated temperature testing.

CONCLUSION

Modified BMI system is a new two-component bis-maleimide resin system. It is a very effective candidate for advanced composite structures with good toughness characteristics. The prepolymer is also stable at 100°C up to 16 h in that the molecular weight of the prepolymer does not increase to any significant extent. DSC analysis offers evidence that the curing reaction of the prepolymer accords with a first-order reaction, and the activation energy of the curing reaction is 74.12KJ/mol.

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