

Copolymers Derived from Bismaleimide Oligomer with Active Solvent

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ABSTRACT: An oligomer from 4, 4'-bis(maleimido)diphenyl methane and methylenedianiline were dissolved in active solvent *N,N*-dimethyl acrylamide in a solid content up to 50–70%; the solution was poured in a sheet-shaped module and irradiated by ^{60}Co with the dose from 20 to 350 kGy at room temperature. The polymerized sheet was postcured at 180°C to obtain a transparent red-orange sheet with tensile strength above 100 MPa. The glass transition temper-

ature before and after postcuring was around 100°C and 150–180°C, respectively. Styrene was used along with DMAA to decrease the water absorption for the copolymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2879–2882, 2004

Key words: bismaleimide; *N,N*-dimethyl acrylamide; irradiation; casting

INTRODUCTION

Polyimides (PIs) are the most thermostable polymeric material, at least among the commercialized polymers up to now, and are of great importance for many high technology applications.^{1–2} Furthermore, after nearly 50 years of development, most processing requirements have been satisfied by structure modification, that is, soluble, compression moldable, injection moldable, resin transfer molding (RTM) processing, and vapor depositable PIs have been achieved and utilized in many application fields including aerospace, electric, microelectronic, membrane, even photoelectronic industries.^{3–4} However, all PIs mentioned above have to be processed in either solution or thermoplastic state. As we know, the tooling costs for fabricating PIs composites can be quite high. Although the traditional RTM processing can lead to as much as a 50% reduction in manufacturing costs over traditional fabrication methods,^{5–6} it still needs curing at high temperature for a long time, which influences the process of composite greatly. To our best knowledge, no castable polyimide has been reported until now. The castable polyimide implies the polymer in flow state can be cured at relatively low temperature without evolution of solvent or by-product, then served at higher tem-

perature.⁷ The castable PIs have potential application in packing materials for the electric or microelectronic industry. It could be copolymerized with gamma rays irradiation by introducing some active solvent, such as *N,N*-dimethyl acrylamide, styrene, 4-vinylpyridine, or methyl methacrylate, into soluble polyimide as solvent.^{8–11} In this article, we would like to report a kind of castable polyimide composed with bismaleimide and reactive solvent. The BMI cast was polymerized under irradiation at room temperature.

EXPERIMENTAL

Materials

N,N-dimethyl acrylamide (DMAA) was purchased from Aldrich and used without further purification. BMI was purchased from HONG Hu Chemical Factory (Hong Hu, China), mp 157–160°C, and used without further purification. Styrene and THF (Beijing Chemical Factory, Beijing, China) were distilled under reduced pressure. BMI oligomer was prepared according to the literature,¹² IR spectrum, 3200–3650 cm^{-1} (*N*-H), 1720 cm^{-1} (C = O), 1510 cm^{-1} , 1390 cm^{-1} (C-N).

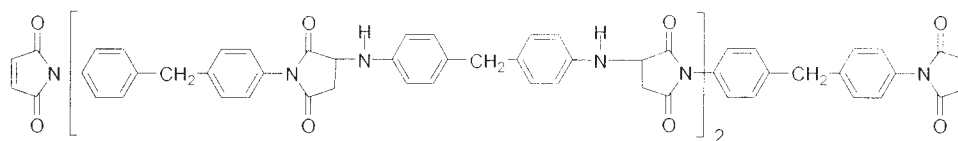
Irradiation of the oligomer solution

The degassed solution of BMI oligomer in active solvent was poured into a model under nitrogen atmosphere and irradiated at room temperature by using gamma rays generated from a ^{60}Co source with dose rate of 6 kGy h^{-1} .

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Scheme 1 The calculated molecule structure of BMI oligomer.

The ratio of H₂O adsorption of BMI cast

The increased weight ratio BMI cast after the BMI cast were immersed in water at room temperature for 48 h.

Thermal analyses of the BMI cast

The differential scanning calorimetry (DSC) experiments were carried out on a Perkin-Elmer DSC-7 system at a heating rate of 20°C/min in air. The thermogravimetric analyses were obtained at a heating rate of 10°C/min in air with a Perkin-Elmer TGA-2 thermogravimetric analyzer.

Mechanical test of the BMI cast

Mechanical tests were carried out on INSTRON 1121 with a crosshead speed of 100 mm/min at room temperature.

The gel contents test of the BMI cast

The regular samples were extracted by THF for 48 h, and dried in vacuum at 60°C overnight.

RESULTS AND DISCUSSION

The model compounds with maleic, nadic, and phenylethynyl endcaps have been tested with radiation of

⁶⁰Co source in our experiments.^{14,15} Only maleic moiety could crosslink with active solvent at room temperature. Because of the limited solubility of BMI monomer in such active solvents, the BMI oligomer (ratio of BMI : MDA = 3:2) was used in this work to increase the solubility of BMI (shown in Scheme 1). The solution of BMI oligomer in such active solvents was quoted in this work as "castable BMI."

BMI casts gain easily high gelation with the γ -ray irradiation (seen in Table I). The 5% weight loss of pure DMAA over 380°C shows it can easily crosslink with the γ -ray irradiation. But the ratio of H₂O absorption is much higher because of the hydrophilic DMAA, which restricts its use in packing materials for the electric or microelectronic industry. While the T_g of BMI cast rises with the increase of BMI content and radiation dose, the results in Table I show that a large content of gel could be obtained in small dose and increased with radiation dose. The total amount of gel was beyond the BMI oligomer used, which indicates that the active solvent has copolymerized with the BMI oligomer, because the oligomer is not able to homopolymerize without active solvent in radical condition. Postcuring could not increase the water absorption of the resin. The water absorbability of the resin decreases sharply with the increase of BMI content in cast. For example, the H₂O absorption of cast that contains 50% BMI is only 6%. The content of

TABLE I
The Effects of Concentration of BMI Oligomer in DMAA and Dose on the Properties of the Copolymer

BMI (%)	Dose (KGy)	T _g (°C)		TGA, N ₂ (°C)		Gel (%)	Water absorption(%)
		Before postcuring	After postcuring	5%	10%		
0	20	100	117	385	402	75	≥ 500
	50	100	111	405	425	89	≥ 500
	100	106	119	390	410	90	≥ 500
30	20	100	160	220	358	86	55
	50	100	150	274	374	88	52
	100	108	150	290	374	87	52
	200	109	155	334	390	90	50
50	20	103	181	250	364	80	12
	50	101	183	362	395	83	10
	100	122	175	340	370	88	7
	350	120	176	343	375	90	6
70	100	124	170	385	405	80	—

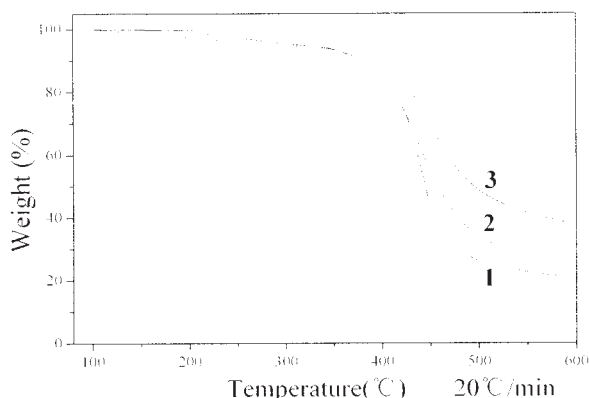


Figure 1 TGA of the resins with dose of 100 kGy. The content of BMI for 1, 2, and 3 is 30%, 50%, and 70%, respectively.

oligomer above 70% caused poor flow, and could not cast as a regular sheet. We didn't test its H₂O adsorption. The much higher T_g of the resin after postcuring than that before postcuring may result from the further thermal crosslinking of BMI oligomer.

Logically as we expected, the thermal stability of the copolymers increased with the BMI content with the same radiation dose (shown in Fig. 1).

The mechanical properties of the cured resins listed in Table II show that the flexible strength increases apparently with the increase of dose. But the flexible modulus, compression properties, and impact strength reached high levels at the dose of 30 kGy. The further increase of dose causing the decrease of impact strength may result from the further increase of the density of the crosslinking. Their mechanical properties are around the mechanical properties of common BMI and epoxy resin. Because the uncured oligomer is liquid in room temperature, it could be fabricated with bag injection or RTM processing.

The drawback of the copolymer thus obtained is the high water absorption because of the water soluble composition of DMAA. To overcome this drawback,

TABLE III
Water Absorption of the Castable Polyimides

BMI (%)	DMAA/Styrene (w/w)	Dose (KGy)	Gel (%)	Water absorption (%)	
				Before postcuring	After postcuring
30	2/1	150	80	14	9
30	2/1	200	79	12	9
30	1/1	150	75	3	2
40	2/1	100	75	15	9
40	2/1	150	79	11	6

TABLE IV
The Effect of Casting Copolymer with Styrene on Thermal Properties^a

Entry	DMAA/Styrene (w/w)	Dose (KGy)	T _g (°C)	TGA (°C)	
				5%	10%
1	2/1	150	142	382	402
2	2/1	200	151	354	390
3	1/1	150	119 ^b	345 ^b	365 ^b
4	1/1	150	121	360	380
5	1/1	200	121 ^b	386 ^b	405 ^b
6	1/1	200	120	384	405

^a The content of BMI in cast is 30%.

^b Before postcuring.

the hydrophobe styrene was introduced along with DMAA, shown in Table III. When the ratio of DMAA to styrene reached 1 : 1, the water absorption of the resulting copolymer decreased to the general level of polyimide. The water absorption of cast with the content of 30% BMI decreases to 2% after heat postcure, while the water absorption is as high as 52% without the addition of styrene. But the gel decreases a little because of the introducing of styrene.

The thermal stability enhanced with the dose could also be attributed to BMI oligomer copolymerizing with DMAA in the irradiation condition. The T_g of cast decreases with the addition of the styrene. The

TABLE II
Mechanical Properties of the Copolymers Based on DMAA

BMI (%)	Dose (kGy)	Flexible strength (MPa)	Flexible modulus (MPa)	Compression strength (MPa)	Compression modulus (MPa)	Impact strength (kJ/m ²)
0	20	79	2563	93	1150	21
	50	97	2953	119	1235	22
	100	93	2895	104	1046	30
30	20	96	2182	112	1115	26
	50	143	3036	123	1380	33
	100	139	3212	123	1450	46
50	200	131	3732	142	2682	47
	20	110	2775	107	1205	17
	50	134	2858	149	2543	24
	100	151	3050	149	2488	35

TABLE V
The Mechanical Properties of Copolymers Modified with Styrene

BMI (%)	DMAA/Styrene (w/w)	Dose (kGy)	Flexible strength (MPa)	Flexible modulus (MPa)	Compression strength (MPa)	Compression modulus (MPa)	Impact strength (kJ/m ²)
30	1/1	150	95	3224	130	1382	8
30	2/1	150	130	3236	144	1942	20
30	2/1	200	136	3278	141	1900	12
40	2/1	100	139	3070	120	1433	36
40	2/1	150	142	2920	151	2582	43

radiation dose has no influence on the glass transition temperature when dose reaches up to 150 KGy. When the radiation dose is below 150 KGy, heat treatment can increase the thermal stability of cast (seen in Table IV). But when radiation dose is below 100 kGy, we can't get a sheet because it just was a soft sheet at room temperature. Heat treatment has no influence on it when radiation dose reaches 200 KGy.

In Table V, the flexural and impact strength go up with the increase of BMI content, which show the same rule of BMI cast without styrene. When the addition of the styrene reached 50%, the flexural and impact strength decrease due to the styrene's property. The highest impact strength is 43 kJ/m² with the 40% BMI content. Generally, the mechanical properties could compare with the former BMI cast without styrene. The addition of styrene into copolymers does not decrease the thermal stability and mechanical properties but significantly lowers the water absorption of BMI cast.

CONCLUSION

Copolymer from BMI oligomer and active solvents DMAA was obtained by irradiation of ⁶⁰Co source at room temperature and postcuring at 180°C. The copolymers exhibit high mechanical properties that modulate thermal stability and T_g. The addition of styrene as cosolvent decreases the water absorption of the copolymer and did not affect the thermal stability and mechanical properties but slightly decreases T_g. Further, our work will focus on improving the casting

thermal stability, T_g, and trying to decrease the H₂O absorption of casting.

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