Processing of Polyimide Casts with γ -Ray Irradiation

Zhen Wang (王薇) Qingxuan Li (李青璇) Pengyang Deng (邓鹏飏) Mengxian Ding (丁孟贤)

State Key Laboratory of Polymer Physics and Chemistry,

Polymer Chemistry Laboratory, Chinese Academy of Science and China Petro-Chemical Corporation,

Changchun Institute of Applied Chemistry, Chinese Academy of Science,

Changchun, 130022, P. R. China

INTRODUCTION

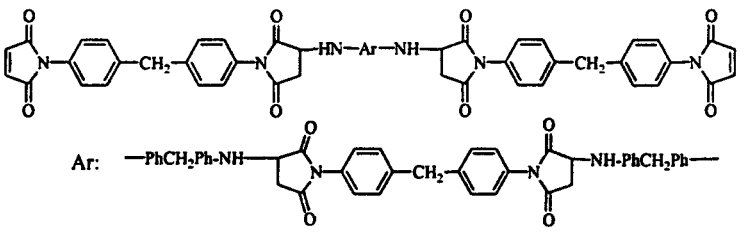
Typical routes to processing thermosetting polyimides resins require temperature above 200 °C. As a result, tooling costs for fabricating components from these composites can be quite high. Resin-transfer molding (RTM) processing can lead to as much as a 50% reduction in manufacturing costs over traditional fabrication methods. [1-3]. But it also needs curing at high temperature for a quite long time, which influences on the processing of composite greatly. Therefore how to reduce the processing temperature is one of the hotspots in the field of PI research [4].

In this paper, the polyimide casts were fabricated directly from the active solution of BMI oligomer by irradiation at room temperature. Their properties were described. And the influence of the content of BMI, addition of styrene, and radiation dose were also discussed.

EXPERIMENTAL

1. Synthesis of BMI oligomer

The BMI oligomer was synthesized followed the literature [5]. The molar ratio of BMI and MDA was 3:2 (Scheme 1). The BMI oligomer has good solubility in the active solvent N,N-Dimethylacrylamide (DMAA). IR of the BMI oligomer: 3200-3650cm^{-1}(N-H), 1720cm^{-1} (C=O), 1510cm^{-1}, 1390cm^{-1} (C-N).



Scheme 1 BMI Oligomer

2. Irradiation Polymerization of BMI in Active Solvent

The BMI was dissolved in DMAA. The solution was sealed in a thick plastic bag after replacing air with nitrogen, It was irradiated at room temperature in a ^{60}Co-radiation source. The irradiated casts were postcured at 180℃ for 4h.. Water absorption was obtained by immersed in water for 48h at room temperature. Thermal properties of casts were tested on Perkin-Elmer 7 thermal analysis; the mechanical properties were determined on INSTRON 1121.

RESULTS AND DISCUSSION

BMI casts gain easily high gelation with the γ -ray irradiation (Table 1). The 5% of weight loss of pure DMAA is over 380℃. But the H_2O absorption is quite high because of the hydrophilic DMAA. The water absorption of the resins decreases with the increase of BMI content in cast. For example, the H_2O absorption of cast containing 50% BMI is 6%. While the BMI casts' T_g rises with the increase of the BMI content and radiation dose. The remnant weight of casts at 600℃ increases

with the increase of the BMI content (Figure 1). From Table 1, we can find that the heat treatment is important to BMI casts. After postcure, both of the T_g and thermal stability increase rapidly, which may refer to the complete reaction improved by heat treatment.

Table 1. Influence of Radiation Dose and the Concentration of BMI in DMAA on the Thermal Properties of Casts

Percent of BMI (%)	Radiation Dose (KGy)	T_g (℃)		Temperature of Weight Loss (℃)		Gelation (%)	H_2O Absorption (%)
		No postcure	Heat postcure[a]	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	—[b]	160	220	358	86	55
	50	100	150	274	374	88	52
	100	108	150	290	374	87	52
	200	—	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	—	176	343	375	90	6
70	100	—	170	385	405	80	—

[a] Postcure condition: 180℃ for 4h; [b] Not determined

The mechanic properties of the BMI casts go up with the increase of the BMI content and the radiation dose (Table 2). When the concentration of BMI is 50%, the flexural strength reached 151Mpa; the compress modulus reached 129Mpa; the impact strength went up to 35KJ/m^2. Their mechanical properties are around that for common BMI and epoxy resin. Because the uncured cast is in liquid state, its processing techniques can be good to be fabricated with bag injection or RTM processing potentially.

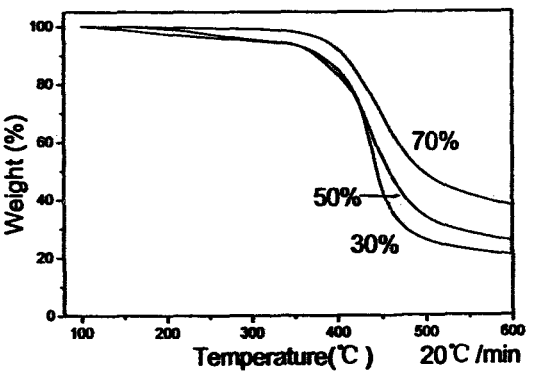


Figure 1. TGA Curve of BMI Casts with Radiation Dose of 100KGy

Owing to the hydrophilic DMAA, the water absorption of casts should be diminished by addition of hydrophobic monomer such as styrene, DMMA, or by the enhancement of BMI. From Table 3, we can see that the H_2O absorption decreases rapidly by addition of styrene. Heat treatment also can reduce the water absorption of the casts. The postcured cast containing 30% BMI in the active solvent DMAA/Styrene=1/1 (w/w) had 2% water absorption, which was better than epoxy resin; while the water absorption is 52% without styrene added. However, the gelation decreases

slightly under the same radiation dose comparing with those without addition of styrene.

Table 2. Influence of Radiation Dose and the Concentration of BMI on the Mechanical Properties of Casts

Percent of BMI (%)	Radiation Dose (KGy)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Compress Strength (MPa)	Compress 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	—	1115	26
	50	143	3036	123	1380	33
	100	139	3212	123	1450	46
50	20	110	2775	107	1205	17
	50	114	2858	116	976	24
	100	151	3050	129	1488	35

Table 3. Influence of the Addition of Styrene on BMI Cast

Percent of BMI (%)	DMAA/Styrene (w/w)	Radiation Dose (KGy)	Gelation (%)	H_2O Absorption (%)	
				No Postcure	Heat Postcure
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

The Tg of casts decreases with the addition of styrene. The radiation dose has no influence on the glass transition temperature when dose reaches up to 150KGy. When the radiation dose is below 150KGy, heat treatment can increase the thermal stability of cast (Table 4); but heat treatment has no effect when radiation dose reaches 200KGy.

Table 4. Influence of Added Styrene on the Thermal Properties of the BMI Cast [a]

MAA/Styrene (w/w)	Radiation Dose (KGy)	Tg (℃)	Temperature of Weight Loss (℃)	
			5%	10%
2/1	150	142	382	402
2/1	200	151	354	390
1/1	150	119[b]	345[b]	365[b]
1/1	150	121	360	380
1/1	200	121[b]	386[b]	405[b]
1/1	200	120	384	405

[a] BMI content is 30%; [b] No postcure

The flexural and impact strength go up with the increase of BMI content. The highest impact strength is $43JK/m^2$ for the resin with the 40% BMI (Table 5). When the addition of styrene reached 50%, the flexural and impact strength decrease; but the compress strength goes up. The mechanical

strength of the cast modified by styrene was independent on the postcure.

Table 5. Mechanic Properties of Casts with DMAA/Styrene as Solvent

Percent of BMI(%)	DMAA/Styrene (w/w)	Radiation Dose (KGy)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Compress Strength (MPa)	Compress Modulus (MPa)	Impact Strength (KJ/m^2)
30	1/1	150	102[a]	3144[a]	150[a]	1270[a]	7[a]
30	1/1	150	95	3224	130	1382	8
30	2/1	150	130	3236	144	1942	20
30	2/1	200	116	3278	141	1700	12
40	2/1	100	139	3070	120	1433	36
40	2/1	150	142	2920	—	—	43

a, No postcure

CONCLUSIONS

BMI casts were fabricated with γ-ray irradiation at room temperature from BMI oligomer dissolved in the active solution. The thermal and mechanical properties of BMI casts go up and the water absorption diminishes with the increase of BMI content and the radiation dose. Postcuring is important for the properties of BMI casts too. The addition of styrene has great effect on the properties of casts. When styrene was added with some percent, the thermal and mechanical properties except compress strength decreased slightly, but the water absorption was greatly reduced which caught our attention.

REFERENCE

1. Vannucci R. D., *NASA Report*, 1995
2. Meador M. A., *NASA Report*, 1998
3. Colton J. S., *Polym. Comp.*, 1998, Dec, 19(6), 732
4. Zhen Wang, *PhD Dissertation*, Changchun Institute of Applied Chemistry, CAS, 2002
5. Yerlikaya Z., Oktem Z., Bayramli E., *J. Appl. Polym. Sci.*, 1996, 59, 165