

Effect of Amino-Polycarbonate on the Curing Kinetics and Morphology of Epoxy Resin

DONGMEI HAO, XIAOZHEN TANG, XINLING WANG, YINPEI LUO

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China

Received 27 June 2000; accepted 29 November 2000

ABSTRACT: The curing kinetics and the glass transition behavior of amino-polycarbonate with diglycidyl ether of bisphenol-A epoxy resin systems were studied by differential scanning calorimetry (DSC). The ASTM E-698 method was chosen to determine the kinetics parameters of the curing reaction, including the activation energy, preexponential factor, rate constant, and 60-min half-life temperature. The amino-polycarbonate was able to accelerate the curing reaction, reduce the apparent active energy, and decrease T_g of the systems. A homogeneous amino-polycarbonate/epoxy resin network was observed in scanning electron microscopy (SEM) pictures. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 833–838, 2001

Key words: epoxy resin; polycarbonate; curing kinetics; morphology

INTRODUCTION

Epoxy resin is a versatile material widely used in fields such as electronics, adhesives, and advanced composites because of its good properties. However, its widespread use is limited in many high-performance applications because of its inherent brittleness. Hence, improved toughness of the brittle epoxy resin is greatly desired.

Fracture toughness of epoxy resin has often been successfully increased by incorporation of a second component, such as a rubber or a thermoplastic polymer. Rubber toughening of epoxy resin, predominantly using amino-, carboxylic-terminated butadiene-acrylonitrile rubber (CTBN),^{1–3} increased the fracture toughness. However, toughness improvements in rubber-modified epoxy resin usually resulted in a

significant decrease in the modulus. For this reason, an alternative was needed and studies demonstrated that the polymer thermoplastics, such as poly(ether sulfone) (PES)^{4–5} and poly(ether imide) (PEI),⁶ could enhance toughness without sacrificing strength or other desirable properties of epoxy resin.

In recent years, polycarbonate (PC)^{7–14} was used to toughen epoxy resin. In this article, the amino-PC was synthesized on the basis of the reaction between the amino and the PC. The effect of the amino-PC on the kinetics parameters was investigated by dynamic curing scan and morphology of the epoxy resin/amino-PC systems.

EXPERIMENTAL

Materials

The epoxy resin used was diglycidyl ether of bisphenol-A (DGEBA; Shanghai Shuzhi Fac-

Correspondence to: D. Hao.

Journal of Applied Polymer Science, Vol. 82, 833–838 (2001)
© 2001 John Wiley & Sons, Inc.

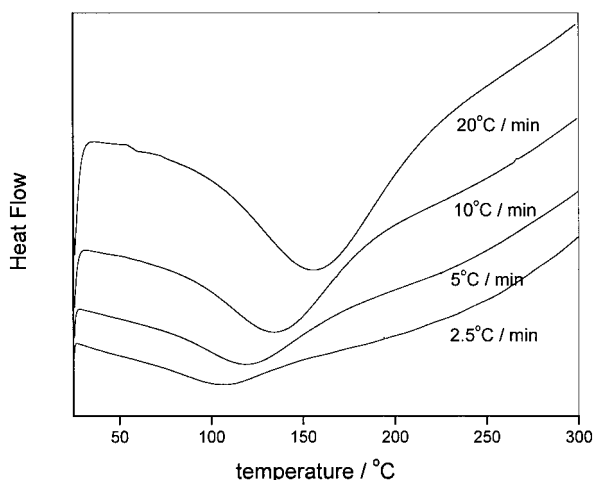


Figure 1 DSC curves of epoxy resin/amino-PC (25 phr) systems at various heating rates.

tory, Shanghai, China). The biphenol-A PC was supplied by Dow Chemical Co. The \bar{M}_n and \bar{M}_w measured by gel permeation chromatograph (GPC) were 28,300 and 59,700, respectively. Diaminodiphenyl methane (DDM) was obtained from Shanghai Shiji Factory (Shanghai, China). Methylene chloride (CH_2Cl_2) and methanol (CH_3OH) were obtained from Thengya Chemical Factory (Beijing, China), and tetraethylenepentamine (TTEPA) was obtained from Shanghai Ranliao Chemical Factory (Shanghai, China).

Sample Preparation

PC was dissolved into CH_2Cl_2 and then mixed with 0.5 mL TTEPA at room temperature for 30 min. After reaction, the solution was washed with $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution six times and dried at 70°C for 24 h under vacuum. Amino-PC¹⁵ was obtained.

The amino-PC was dissolved into the epoxy resin at 160°C for 20 min to form a homogeneous epoxy resin/amino-PC mixture. When the mixture was cooled down to 90°C , 27 phr of melted DDM was added and mixed by using a high-torque stirrer for about 5 min. After degassing for 15 min, the mixture was poured into the stainless mold, cured for 1 h at 90°C , then 4 h at 160°C , postcured for 2 h at 200°C , and cooled to ambient temperature.

Characteristics

Differential Scanning Calorimetry (DSC)

A power-compensated DSC (Perkin-Elmer Pyris-1) was used for dynamic cure experiments and data analysis. Uncured samples (5–7 mg) were placed in DSC aluminum pans and then placed inside the DSC cell/oven. The thermograms of the samples were recorded at four different heating rates, 2.5, 5, 10, and $20^\circ\text{C}/\text{min}$, in the temperature range of $25\text{--}300^\circ\text{C}$. The thermograms were car-

Table I Curing Characteristic of Epoxy Resin/Amino-PC Systems

Epoxy Resin/ Amino-PC Systems	Φ ($^\circ\text{C}/\text{min}$)	T_i ($^\circ\text{C}$)	T_{onset} ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	ΔH (J/g)	A_p
100 : 0	2.5	81.1	106.0	125.4	167.1	170.7	49.9
	5	94.6	116.5	142.8	197.7	217.2	51.4
	10	101.0	130.3	160.5	216.1	226.0	52.1
	20	111.2	147.4	180.2	240.4	178.1	53.0
100 : 10	2.5	66.3	88.5	112.0	161.0	91.3	52.1
	5	73.8	92.0	126.8	182.0	106.3	48.0
	10	81.1	104.8	143.8	207.8	99.0	51.5
	20	91.8	119.8	163.0	233.2	109.2	50.5
100 : 15	2.5	56.4	80.7	110.0	174.2	82.0	50.7
	5	65.5	88.0	122.8	189.7	73.3	47.7
	10	80.5	99.9	140.5	201.0	60.4	51.6
	20	91.9	118.3	160.6	222.4	88.9	51.7
100 : 25	2.5	55.1	76.9	105.1	169.5	42.2	37.7
	5	67.8	86.3	122.5	184.9	43.0	51.0
	10	64.5	94.5	136.0	197.6	60.3	47.7
	20	85.2	110.1	156.5	224.4	48.4	48.7

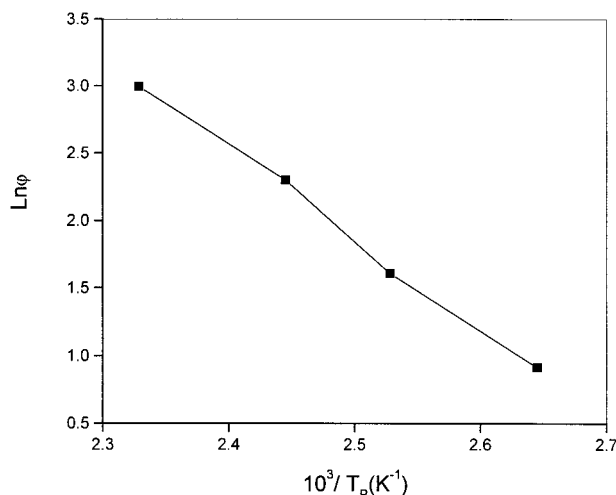


Figure 2 Plot of $\ln \theta$ versus $10^3/T_p$ of the epoxy resin/amino-PC (25 phr) systems.

ried out in the inset gas (N_2) at 20 mL/min. The exothermic transition associated with curing reaction could be characterized by defining the following temperatures: T_i , the onset temperature of curing; T_f , the temperature for completion of reaction, and T_p , the exothermic peak temperature.

Morphology

A scanning electron microscopy (SEM) was used to examine the fresh fracture surface of the samples. All samples were sputter-coated with gold by vapor deposition by using a vacuum sputterer before SEM examination.

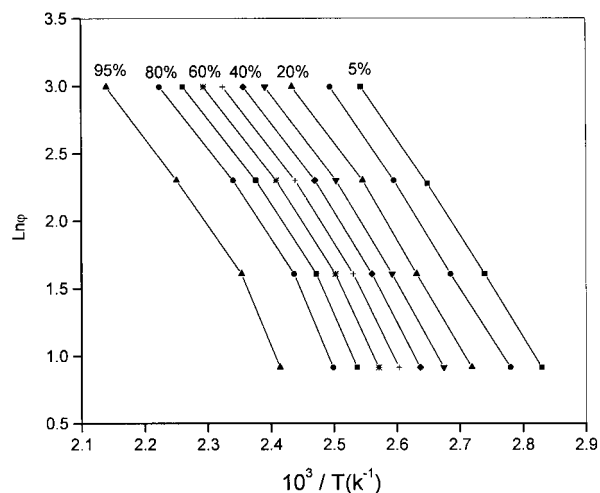


Figure 3 Plot of $\ln \theta$ versus $10^3/T_p$ for the epoxy resin/amino-PC (25 phr) systems at different conversions.

RESULTS AND DISCUSSION

Curing Kinetics

DSC was one of the most well-known and effective methods used to obtain the information of the cure reaction of epoxy resin.

Figure 1 shows the general thermograms by dynamic DSC analysis for the epoxy resin/amino-PC systems. The reaction rate, proportional to the rate of heat generation, passed through a maximum and then decreased. The exothermic peak temperature (T_p) increased with an increase in the heating rate. Table I indicates the T_p and the decrease of heat of curing reaction (ΔH) with an increase in the concentration of amino-PC. These results indicate that amino-PC reacted

Table II Kinetics Parameters Analyzed by the Exothermic Profiles of Epoxy Resin/Amino-PC Systems^a

Epoxy Resin/ Amino-PC Systems	T_p (°C)	E (KJ/mol)	A	K (min ⁻¹)	$t_{1/2}$ (min)
100 : 0	160.5	54.3	1.21×10^6	0.00952	73
100 : 10	143.8	54	2.18×10^6	0.01902	36
100 : 15	140.5	53.3	2.03×10^6	0.02252	31
100 : 25	136.0	52.8	2.10×10^6	0.02767	25

^a $k = A \exp(-E/RT)$, where $T = 350K$.

Table III Kinetics Parameters (E , $\ln A$, and 60 min Half-Life Temperature) of Epoxy Resin/Amino-PC Systems at Different Conversion Levels from DSC Dynamic Cure Analysis

% Conversion	a-PC			
	0	10	15	25
	$(E/\text{KJ/mol})$			
5	58.9	59.6	58.3	57.4
10	57.8	58.9	56.8	57.8
20	56.5	56.9	56.2	57.9
30	55.7	55.9	55.4	58.0
40	55.0	54.6	55.0	58.3
50	54.6	53.8	54.4	58.2
60	54.1	53.0	54.1	58.2
70	53.7	52.2	53.6	58.3
80	53.1	51.5	53.5	58.3
95	51.8	50.7	54.9	58.1

% Conversion	a-PC			
	0	10	15	25
	$(\ln A)$			
5	16.6	18.0	17.7	14.0
10	16.0	17.3	16.9	14.0
20	15.2	16.3	16.2	14.1
30	14.8	15.7	15.7	14.1
40	14.4	15.0	15.3	14.1
50	14.1	14.5	14.9	14.1
60	13.8	14.1	14.6	14.2
70	13.6	13.7	14.2	14.2
80	13.2	13.2	13.9	14.2
95	12.4	12.4	13.7	14.3

% Conversion	a-PC			
	0	10	15	25
	$(60 \text{ min Half-Life Temperature}/^\circ\text{C})$			
5	62.7	46.5	43.5	101.1
10	66.9	51.6	47.6	103.2
20	71.8	56.8	53.7	103.1
30	75.1	61.0	57.9	102.7
40	77.6	64.0	61.8	104.3
50	80.2	67.1	65.0	103.1
60	82.7	70.2	68.5	102.7
70	85.5	73.5	72.2	102.6
80	88.6	77.5	76.8	102.5
95	96.7	88.7	89.4	99.5

with epoxy resin and resulted in a decrease in the parts of the functional epoxy groups that reacted with the amine curing agent. Consequently, the crosslinking density decreased and the cure rate increased with an increase of amino-PC.

Kinetics parameters were obtained on the basis of the variation of the T_p with respect to the heating rate (φ). From the set of dynamic profiles at different heating rates (2.5, 5, 10, and 20°C/min), Figure 2 showed that the active energy (E) was obtained from the slope of the linear fit of $\ln \varphi$ versus $10^3/T_p$. The nearly symmetrical curves in DSC thermograms suggested that the reaction followed the autocatalytic kinetics reaction, which was further supported by the Ozawa plot (Fig. 2). The curing kinetics were analyzed by the ASTM E-698 method. Table II showed the curing kinetics parameters of the epoxy resin/amino-PC (10–25 wt %) systems. The active energy (E) at the exothermic peak temperature in epoxy resin/amino-PC systems was lower than that (54.3 KJ/mol) of the pure epoxy resin systems. In addition, the 60-min half-life temperature decreased but the cure rate constant (k) and preexponential factor (A) of the systems increased with an increase in the concentration of amino-PC (10–25 wt %). This means that epoxy resin reacted with amino-PC in addition to the reaction of epoxy resin/amine occurring mainly in the high temperature.

Figure 3 showed the plot of $\ln \theta$ versus $10^3/T_p$ at different conversion levels for the epoxy resin/amino-PC (10–25 wt %) systems. The curves in Figure 3 complied with the Ozawa plot. It indi-

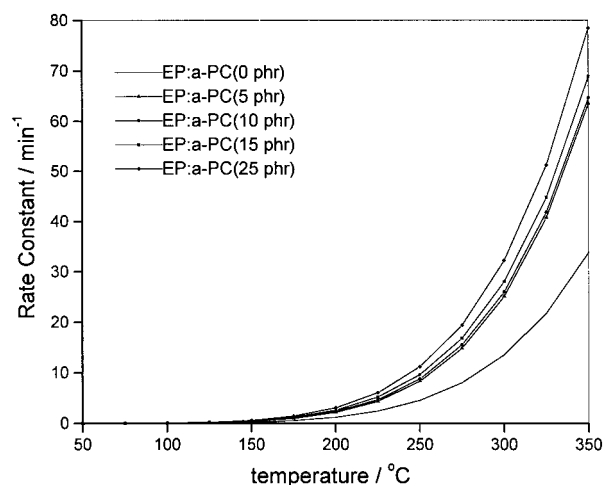


Figure 4 Comparative DSC heating profiles of rate constant of the systems.

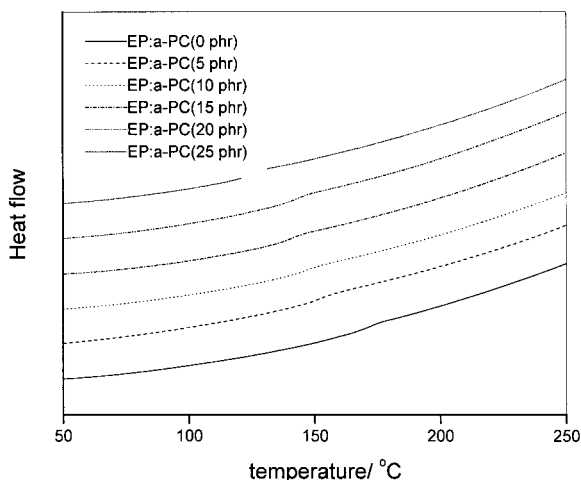


Figure 5 DSC runs of the epoxy resin/amino-PC systems.

cated that the reaction of epoxy resin/amino-PC systems followed the autocatalytic kinetics reaction. Table III presented a variation in the kinetics parameters at different conversion levels for epoxy resin/amino-PC systems. Figure 4 plots the cure rate constant versus temperature of the systems. The rate constant increased with an increase in the concentration of amino-PC.

Thermal Properties of Epoxy Resin/Amino-PC Systems

The effect of amino-PC on glass transition temperature (T_g) of the systems was shown in Figure 5. The DSC results (Fig. 5) showed that the epoxy resin/amino-PC systems had only one T_g . This indicated that the amino-PC was compatible with the epoxy resin. It was clear that an increase in amino-PC resulted in the decrease of T_g of cured

resin. The T_g variations of the systems depend on several factors, including degree of crosslinking, plasticization, chain end, and flexibility. Lin et al.¹⁶ attributed the variations to the lower crosslinking density because of the different chemical reactions involved with different amounts of amino-PC.

Morphology

Figure 6 shows the SEM micrographs of the cured epoxy resin/amino-PC samples. Micrograph (a) shows the fracture surfaces of the pure epoxy resin, which displays the typical brittle fracture features and a homogeneous phase morphology. Micrographs (b) and (c) show the micrographs of epoxy resin/amino-PC systems. It is clear that the micrographs of Figure 6(b-c) were just as homogeneous as the pure epoxy resin [Fig. 6(a)], which agreed with the DSC results. The fractured surfaces of these samples displayed some visible river marking. Moreover, the micrographs of the samples exhibited more extensive river marking with the increase of amino-PC to the epoxy resin. It was suggested that the systems resulted in a more ductile deformation behavior.

CONCLUSION

With an increase in amino-PC, it accelerated the curing reaction and reduced the apparent active energy, and 60-min half-life temperature, but increased the cure rate constant (k) and preexponential factor (A) of the epoxy resin/amino-PC systems. The systems followed the autocatalytic kinetics reaction. All cured systems were found to exhibit a truly homogeneous phase with a single

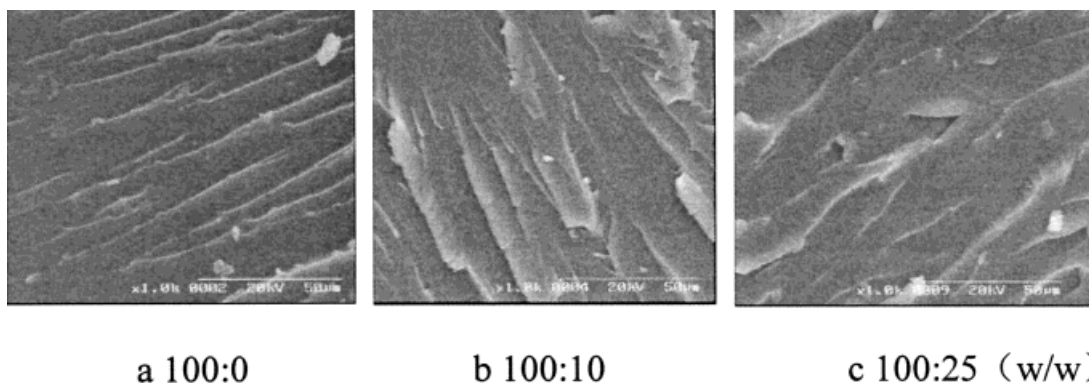


Figure 6 SEM photographs of fracture surface of epoxy resin/amino-PC systems.

T_g from DSC. SEM also demonstrated the compatibility of the epoxy resin and amino-PC systems.

REFERENCES

1. Nae, H. N. *J Appl Polym Sci* 1986, 31, 1.
2. Kirshenbaum, S. L.; Bell, J. P. *J Appl Polym Sci* 1985, 30, 5.
3. Manzione, L. T.; Gillham, J. K.; McPherson, C. A. *J Appl Polym Sci* 1981, 26, 3.
4. Raghava, R. S. *J Polym Sci, Part B: Polym Phys* 1987, 25, 5.
5. Bucknall, C. B.; Partridge, I. K. *Polymer* 1983, 24, 5.
6. Bucknall, C. B.; Gilbert, A. H. *Polymer* 1989, 30, 2.
7. Mera, H.; Umetani, H. *Jpn. Pat.* 02,170,882, 1990.
8. Chen, M. C.; Hourston, D. J.; Sun, W. B. *Eur Polym J* 1992, 28, 12.
9. Martuscelli, E.; Musto, P.; Ragosta, G.; Scarinzi, G. *Angew Makromol Chem* 1994, 217, 63.
10. Bucknall, C. B.; Partridge, I. K.; Jayle, L.; Nozue, I.; Fernyhough, A.; Hay, J. N. *Polym Prepr* 1992, 33, 1.
11. Martuscelli, E.; Musto, P.; Ragosta, G.; Scarinzi, G. *Angew Makromol Chem* 1993, 204, 121.
12. Rong, M. Z.; Zeng, H. M. *Chin Phys Lett* 1996, 13, 2.
13. Woo, E. M. *Polym J* 1997, 29, 6.
14. Li, M. S.; Ma, C. C. M.; Lin, M. L.; Chang, F. C. *Polymer* 1997, 38, 19.
15. Foldi, V. S.; Campdell, T. W. *J Polym Sci* 1962, 56, 163.
16. Lin, L. M.; Chang, K. H.; Chang, F. C. *J Polym Sci, Part B: Polym Phys* 1997, 35, 13.