Studies on Curing Behavior and Molecular Motion of Polyacrylate/Epoxy-Amine Adduct Complex System with Additional Crosslinker

WEIMING PENG, DEBEN CHEN, ZONGHUA ZHOU, ANYONG ZHONG, ZONGYIN DU

Department of Chemistry, Sichuan University, Chengdu, 610064, People's Republic of China

ABSTRACT: The curing behavior of a three-component system—polyacrylate I, epoxy-amine adduct II, and polyglycol-2-ethylhexanol–blocked 2,4-toluene diisocyanate III (the crosslinker)—was studied by torsional braid analysis and *in situ* Fourier transform infrared (FTIR). Results show that the curing process consists of two close steps. The first step is a deblocking and curing period (the main period), in which the deblocked isocyanate group reacted with the hydroxyl in polyacrylate and epoxy-amine adduct to obtain a crosslinked network structure. The second step is a deep-curing period. The further deblocked isocyanate group reacted with NH group in urethane and the crosslinking density increased. The curing temperature of the first step could be lowered efficiently when the organotin catalyst was added into the system, and the curing time was shortened. Furthermore, the effect on the curing crosslinking extent of each system was studied when the types or content of the crosslinkers changed. The results show that, when the crosslinking density increased, the mutual molecular motion became more difficult and the glass temperatures (T_g) were heightened. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 247–254, 1998

Key words: *in situ* Fourier transform infrared; torsional braid analysis; curing; molecular motion; glass temperatures

INTRODUCTION

Recently, cathodic electrodeposition coating has been applied widely in automotive and light industry all over the world, and was playing a more and more important role because of its excellent anticorrosion, high throwing power, high levels of coating utilization, and low levels of pollution, etc. But, in previous reports, most of them focused on the study of the composition of cathodic electrodeposition coatings by Fourier transform infrared (FTIR).[1–4] There are few reports on the curing behavior. The work had also been done about the curing behavior of the acrylate urethane system in our laboratory.[5] It is well known that polyacrylate is suitable to all kinds of surface coatings for its high weather resistance and glossiness. However, epoxy resin with excellent anticorrosion, is usually applied as base coatings of many products, such as automotive bodies, because of its bad weather resistance and easy yellowing. So, there is great actual significance about the studies on the polyacrylate/epoxy resin complex system.[6]

In this article, a kind of crosslinking agent—polyglycol-2-ethylhexanol blocked 2,4-toluene diisocyanate—was added into the polyacrylate I/

Table I   TBA Soaker Solution

Sample No.	I (g)	II (g)	III (g)	Organotin Catalyst (mL)	Acetone (mL)
1	4	2	1	—	20
2	4	2	1	0.1	20

epoxy-amine adduct II complex system, and the curing process of the system was studied by torsional braid analysis (TBA) and *in situ* FTIR. The results show that the curing process consists of two close steps. The two tested results of TBA and FTIR coincide with each other. Moreover, the effects of different types or content of the crosslinkers on the curing crosslinking extent were studied. Results can be reflected directly by the change of T_g in Figures 9 and 10.

EXPERIMENTAL

Materials

Reagents used in the preparation of polyacrylate (I) included styrene, N,N-dimethyl aminoethyl methacrylate (MNA), butyl acrylate (BA), and 2-hydroxy propyl methacrylate (HPA). All of these reagents are chemical pure grade. Epox 601 (diglycidyl ether of bisphenol A, Mn = 900) and diethylamine (chemical pure grade) were used in the preparation of epoxy-amine adduct (II). Reagents used in the preparation of PG-TDI-2EH resin (III) included poly(ethylene glycol)s [PEGs (#400)](extra pure grade), 2-ethylhexanol (2EH;

extra pure grade), and toluene 2,4-diisocyanate (TDI).

Dibutyltin dilaurate (analytical grade; Beijing Chemical Plant, Beijing, China) was used as a catalyst in this article.

Instruments

A GDP-2 polymer Material Dynamic Mechanic Test Instrument, a Nicolet-170sx FTIR Instrument, and a Ycc-1612-AP/IP computer temperature programmer-controller were used.

Synthesis

Polyacrylate (I)

n-Butyl alcohol (100 mL) was charged into a three-necked flask and then heated to 80°C. A mixture of styrene (0.2 mol), MNA (0.2 mol), BA (0.5 mol), and HPA (0.2 mol) was added, using 2,2′-azobis(isobutyronitrile) as the initiator. The whole mixture was kept at that temperature for 5 h to give the polyacrylate (I).

Epoxy-Amine Adduct (II)

An epoxy resin (Epox 601, 90 g) and ethylene glycol monoethylether (50 mL) were charged into

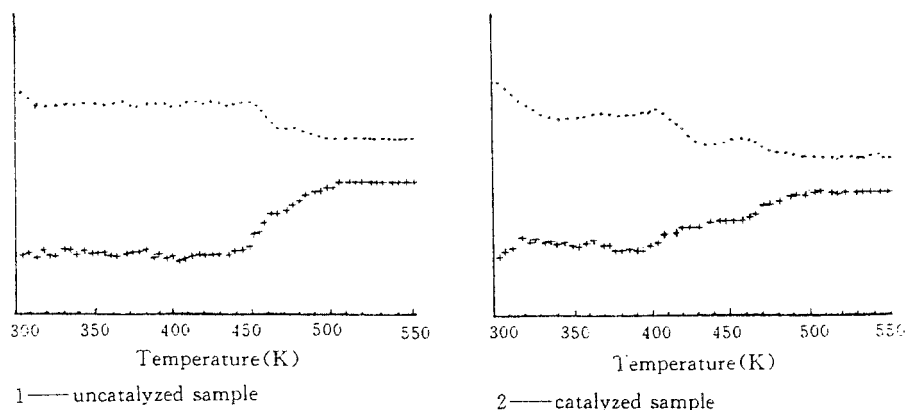
1——uncatalyzed sample

2——catalyzed sample

Figure 1   Relative rigidity and logarithmic decrement curves *vs.* temperature for the reaction of polyacrylate, epoxy-amine adduct, and crosslinker. (1) system 1; (2) system 2; (+) relative rigidity; (●) logarithmic decrement.

Table II   Curing Temperatures (K) of Two Samples

Sample No.	First Curing Step (K)	Second Curing Step (K)
1	445−460	465−501
2	399−432	467−503

a three-necked flask, then heated to 80°C to dissolve the epoxy resin. Diethanolamine (10.5 g, 0.1 mol) was then slowly added, and the whole mixture was kept at that temperature for about 3 h until no free epoxy groups were evident to give the epoxy-amine adduct (II).

PG-TDI-2EH Resin (III)

In a three-necked reaction vessel, a half-blocked TDI was prepared by slowly adding PG [PEG (#400), 40 g, 0.1 mol] to TDI (34.8 g, 0.2 mol). The mixture was kept at room temperature for 30 min and gradually heated to 70°C for 2 h. Upon completion, a calculated quantity of 2EH (26, 0.2 mol) was added dropwise into the vessel in an ice bath. The whole mixture was kept at room temperature for 1 h and was gradually heated to 50°C for an additional 2 h to give PG-TDI-2EH resin (III). The product was characterized by FTIR.

The other kinds of crosslinkers in this dissertation—PPG (#1000)-TDI-2EH (IV), BC-TDI-TMP (V) and BC-TDI-DEA (VI)—could be synthesized by the method previously described.

Study of the Curing Process and Molecular Motion TBA

Glass fiber braids that had been impregnated with the solution shown in Table I and dried in a
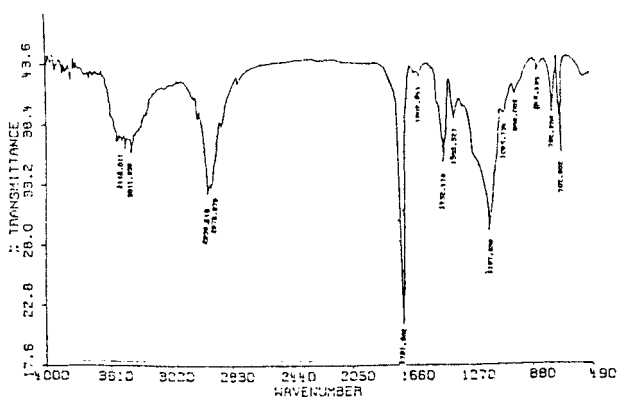
Figure 2   FTIR spectrum of polyacrylate (I).
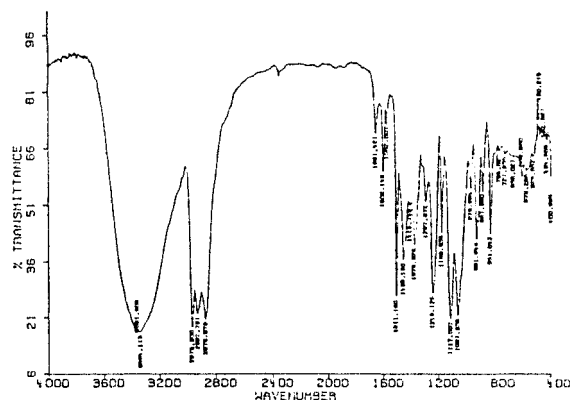
Figure 3   FTIR spectrum of the epoxy-amine adduct (II).

vacuum at 50°C for 5 h were mounted in the TBA apparatus under different test conditions. The heating temperature rate is 2°C min^{-1}.

In Situ FTIR Spectroscopy

The Nicolet-170sx-FTIR and temperature controller were used. Samples were analyzed in the absorbance mode at a resolution of 4 cm^{-1} by signal-averaging 15 scans in the temperature range of 140–250°C. The heating rate was 2°C min^{-1}. The analytical wavelength range was between 400 and 4000 cm^{-1}. Accuracy of the measurement of the temperature controller was 0.1°C.

RESULTS AND DISCUSSION

Heating TBA Test

The change in relative rigidity and logarithmic decrement on TBA spectra, as shown in Figure 1,
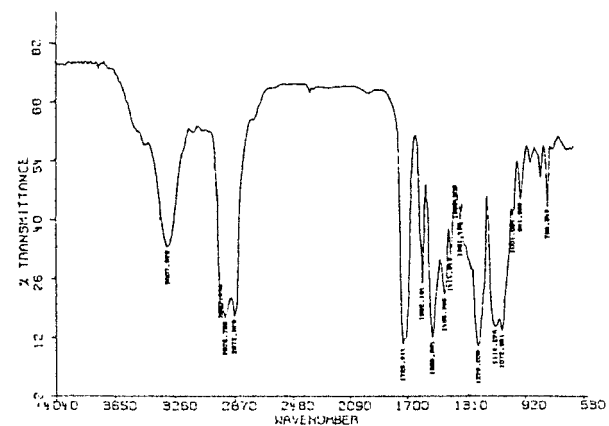
Figure 4   FTIR spectrum of the crosslinker (III).

Figure 5 FTIR spectrum of the mixture of three components.

indicates that the curing process consists of two close steps. When the organotin catalyst was added into the system, the curing temperature of the first step could be lowered efficiently and the curing time was shortened, but there was no effect on the cure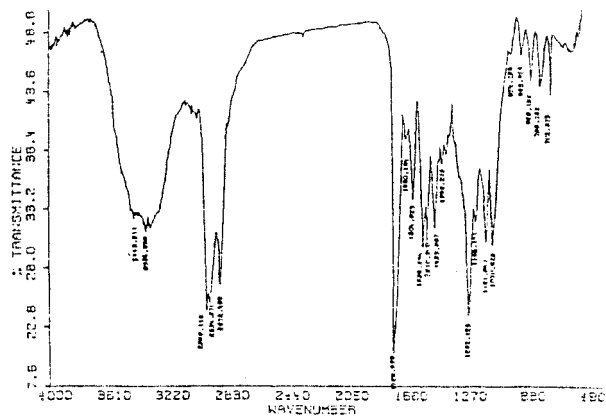 of the second step. That is, the range of the curing temperature of the second step is similar to that without a catalyst. Moreover, the appearance, hardness, and toughness of the cured film after the first step are better than those of the second step. Curing temperatures obtained are shown in Table II.

Based on the experimental phenomena and previously described results, we can draw the con-

clusion that the curing process consists of two steps. This phenomenon is connected with the structure of the blocking agents. Usually, the deblocking reaction of the blocked isocyanate depends on the transfer of the hydrogen from urethane to the blocking agent. The easier the transfer, the easier the deblocking reaction and the lower the curing temperature. The central atoms are nitrogen and oxygen, respectively, for the isocyanate group blocked by the amine or amide group and hydroxyl. In the deblocking process, it is much easier for oxygen to take the hydrogen from urethane, and for a deblocking reaction to happen, because the electronegativity of oxygen is larger than that of nitrogen. Compared with NH, there is less linkage length and larger linkage heat for OH. Its combination is more firm. Therefore, we can infer that the first curing step is the deblocking and crosslinking period. In this period, the deblocked isocyanate dissociates gradually and the blocking agents are released. Then, the free isocyanate group reacts with the hydroxy group of the resins and form stabler urethane. A crosslinking network is obtained. The second step is a deep-curing period. In this period, the free isocyanate reacts further with the NH group in urethane. The crosslinking extent increased, and the network structure became more tight.

In the reaction of the isocyanate and hydroxy groups during the first curing step, quadrivalent tin ion can form quadribasic cyclic-activated com-

Table III   Attribution of the IR Vibration Peaks

Polyacrylate I (cm⁻¹)	Epoxy-amine Adduct (cm⁻¹)	Crosslinker III (cm⁻¹)	Mixture (cm⁻¹)	Vibration Mode
3448	3362	3459	3448	ν(O—H)
	3334	3308	3354	ν(N—H)
2951, 2879	2974, 2876	2958, 2872	2959, 2872	ν(C—H)
1731	1723	1730	1729	ν(C=O)
1603	1609	1602	1605	δ(N—H) (amide I band)
			1536	δ(N—H) (amide II band)
1452	1459	1456	1454	δ(C—H) (methyl)
		1228	1232	δ(N—H) (amide III band)
1167			1168	ν(C—O) (fatty ester)
		1116, 1072	1122, 1071	ν(C—O) (ether)
	831		829	δ(C—H) (p-substituted benzene)
		816, 768	768	δ(C—H) (1,2,4-substituted benzene)
702			702	δ(C—H) (monosubstituted benzene)

Figure 6 FTIR spectra of the three-component system at various temperatures during the heat curing process.

in Figures 2–4. Figure 5 is the spectrum of the mixture of the three components. Attribution of the IR characteristic vibration peaks are shown in Table III, in which $1512-1557$ cm^{-1} is the characteristic peak of NH in urethane, $3147-3661$ cm^{-1} is the covibrational peak of NH and OH, and 702 cm^{-1} is the mono-substituted benzene peak of CH. It was used as the reference group because it had no change in the curing process. Herein, we chose the range from $723-679$ cm^{-1} in the calculation of the absorbance area of the CH group. FTIR spectra of the system under different conditions during the heating curing process is shown in Figure 6. Figure 7 shows the enlargement of the change about $1512-1557$ cm^{-1} peak in Figure 6.

The change of NH in urethane against the temperature can be obtained through the [NH]/[CH] absorbance area ratio plotted against the temperature. The changing curve of the total amount of NH and OH can be obtained, too. The change of the two main characteristic peaks of the system against the temperature during the heating curing process is shown in Figure 8.

From the figures and tables herein, we can

plex with the hydroxy group after organotin catalyst was added. The dipole moment of the hydroxy group in complex increased, and the linkage length increased too. Electrons of nitrogen in the isocyanate group transfer to the alcoholic protons, at the same time, electrons in alcoholic oxygen transfer to carbon in isocyanate. Thus, urethane was formed. The course of the catalytic reaction is described herein

In Situ FTIR

Constant Heating FTIR

The infrared (IR) spectra of polyacrylate I, epoxy-amine adduct II, and crosslinker III are shown

Figure 7 Enlarged FTIR spectra of the change about $1512-1557$ cm^{-1} peak during the heat curing process.
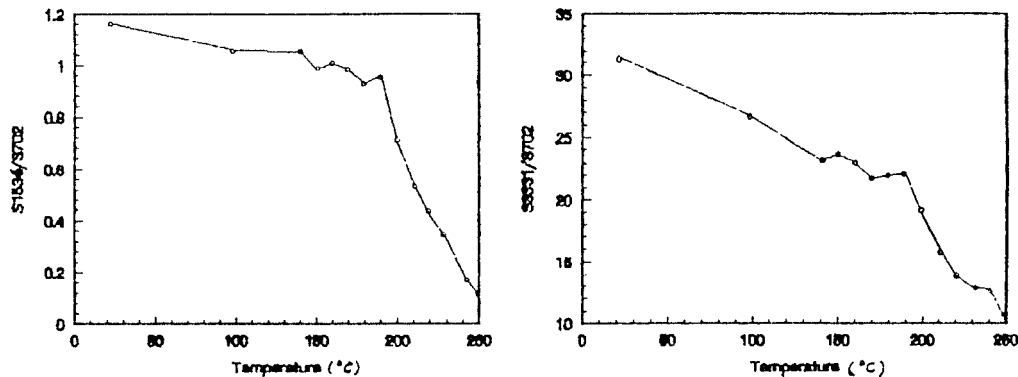
Figure 8 Change of the two characteristic peaks of the system during the heat curing process.

ascertain that 1536 cm^{-1}, which is the NH characteristic peak of urethane, changed little before 200°C. After that, it decreased suddenly. This shows fully that there was no change about the amount of NH before 200°C, or in the first curing step. On the other hand, it verified that active hydrogen in the second curing step came from NH in urethane, thus verifying further the correctness of the mechanism about TBA.

In the figures, 3147−3661 cm^{-1} is the covibrative peak of NH and OH, including a little OH peak of n-butyl alcohol and ethylene glycol ethyl ether solvents. The intensity of the peak decreased somehow before 140°C because of the volatility of the solvents. After that, its change was similar to NH in 1536 cm^{-1}. In the second curing step, blocking agents molecule reached the boiling point and volatilized greatly after 200°C. The deblocked isocyanate group reacted with NH in urethane at that temperature, and the amount of OH and NH decreased greatly, which is shown in IR spectra where 3147−3661 cm^{-1} peak decreased suddenly.

Isothermal FTIR

The two isothermal curing processes of the system at 170°C and 205°C were studied by isothermal FTIR. The results show that there was little change about the two characteristic peaks at 170°C; and, even if there was any decrease, it was because of the volatility of the solvents. Thus, the curing reaction stayed only at the first period. However, the regular patterns of the change on the isothermal curing process is similar to that in the heat curing process at 205°C. These phenomena show that the two curing steps were all existent. Meanwhile, the curing extent was directedly affected by the temperatures. The higher the temperatures, the deeper the curing extent.

Molecular Motion

The system was studied again by heating TBA after it had been cured. It changed from the glass state to the rubber state, and from the relationship between the molecular crosslinking extent

Table IV   Ratio of the Materials of TBA Solution

Sample No.	I (g)	II (g)	III (g)	IV (g)	V (g)	VI (g)	Acetone (mL)
1	2	1	1.0				15
2	2	1		1.0			15
3	2	1			0.5		15
4	2	1				0.5	15
5	2	1				1.0	15
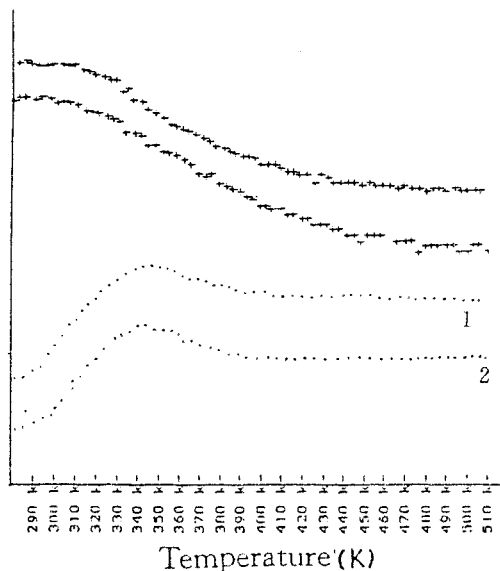
Figure 9 TBA spectra of cured sample 1 and sample 2.

Table V Effects on T_g with Different Types or Content of Crosslinkers

Sample No.	1	2	3	4	5
T_g (K)	345	340	370	400	420

CONCLUSIONS

1. The curing behavior of the system was studied by TBA. It can be ascertained that the curing process consists of two close steps: the first deblocking curing period (the main period) and the second deep-curing period. When the organotin catalyst was added into the system, the curing temperature of the first step could be lowered efficiently, and the curing time was shortened.
2. From the view of the molecular structure, the curing process of the system was studied by *in situ* FTIR. The result agrees with that of TBA.
3. From the view of the molecular motion, the curing crosslinking extent of the systems and T_g was studied. It was found that, when the crosslinking density increased, the molecular network was tight after cure and mutual mo-
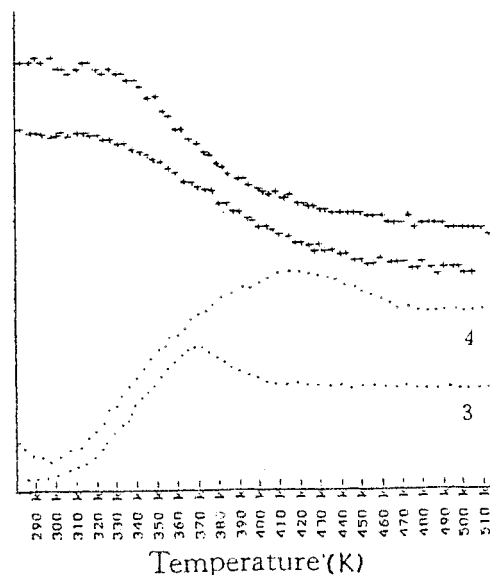
and T_g, the crosslinking property of several kinds of crosslinkers can be verified. The ratio of the materials in several systems are shown in Table IV.

As shown in Figures 9 and 10, it is a physical changing process. The systems remained in a glassy state after cure. When the temperatures were heightened, the systems could change from the glass state to the rubber state. There were glass temperature peaks at 345 K and 340 K for sample 1 and sample 2, respectively. It can be explained that the crosslinking points were not more, the external molecular chains were still fairly long; thus, the molecular mobility was strong, and the molecular chains were fairly flexible. However, there were glass temperature peaks at 370 K and 400 K for sample 3 and sample 4, respectively. It shows that the two kinds of crosslinkers—including diethanolamine and trimethylol propane blocking agents—had a great crosslinking extent, so that the molecular network was more tight and the motion between molecules became difficult. Thus, T_g's were heightened. Furthermore, comparing the effects on T_g for sample 4 and sample 5, when a different content of the crosslinker was added, we can ascertain that the crosslinking density of the systems increased, whereas the content of the crosslinker increased. The relevant T_g was heightened. Results are shown in Table V.

Figure 10 TBA spectra of cured sample 3 and sample 4.

lecular motion was more difficult. Thus, T_g's were heightened.

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