

Curing Behavior of Acrylate–Urethane System

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SYNOPSIS

The curing behavior of a two-component system—acrylate copolymer **I** (the main resin) and monobutyl glycol ether and diethanolamine blocked 2,4-toluene diisocyanate **II** (the crosslinker)—was studied by torsional braid analysis (TBA), Fourier transform infrared (FTIR), and differential scanning calorimetry (DSC). The results show that the curing process consists of two steps: First, the hydroxyl-blocked isocyanate group (NCO) thermally dissociates to produce a free isocyanate group, which can react with the hydroxyl of the acrylate copolymer. Second, the amino-blocked isocyanate thermally dissociates and regenerates a free isocyanate group which can react with the hydroxyl group of the acrylate copolymer. Thus, the crosslinked network is obtained. When the organotin catalyst was added into the system, the curing temperature and the curing time was shortened efficiently. The Arrhenius apparent activation energy for curing was calculated in this study. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Acrylate–polyurethane is an excellent polymer material, especially when it is treated by electrodeposition coating as it will provide protective, decorative, and anticorrosive properties. Its application plays an important role in industry. Usually, the acrylate–polyurethane electrodeposition coating is composed of two parts: One is the acrylate copolymer containing a hydroxyl group (the main resin) and the other is blocked diisocyanate (the crosslinker). When the electrodeposited film is heated, the blocked diisocyanate regenerates a free isocyanate group which can react with the hydroxyl group of the acrylate copolymer and an acrylate–polyurethane crosslinked network is obtained. Studying the temperature at which blocked isocyanate dissociates is very important. Previous reports only focused on the deblocking of diisocyanate blocked by only one kind of blocking agent.^{1,2} There are few reported methods to estimate deblocking temperature by the chemical structure of a molecule.²

In this article, two isocyanate groups of the 2,4-toluene diisocyanate (2,4-TDI) molecule were blocked

by two different kinds of blocking agents, the monobutyl glycol ether and diethanolamine, to prepare an urethane oligomer as the crosslinker. The curing process was investigated using TBA,^{4,5} FTIR, and DSC techniques.⁶ The results show that the curing process was divided into two steps. The relationship between the chemical structure of blocking agents and the curing mechanism is also discussed.

EXPERIMENTAL

Synthesis

Synthesis of Acrylate Copolymer I

Styrene (St), 0.2 mol, methyl aminoethyl methacrylate (MNA), 0.2 mol, 2-hydroxypropyl acrylate (HPA), 0.2 mol, and butylacrylate, 0.5 mol, were radically copolymerized using AIBN as the initiator and *n*-butyl alcohol as the solvent.

Synthesis of Blocked TDI II

2,4-TDI, 1 mol, was charged into the flask and 1 mol monobutyl glycol ether (BC) was added slowly to it at 80°C. After 1 h, 0.34 mol diethanolamine was added into the flask and kept at 120°C for 2 h. The product was characterized by FTIR.

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Table I The TBA Soaker Solution

Sample No.	I (g)	II (g)	Organotin Catalyst (mL)	Acetone (mL)
1	4	1	0	15
2	4	1	0.04	15
3	4	1	0.08	15

Study of the Curing Process

Torsional Braid Analysis (TBA)

Glass fiber braids, after having been impregnated with the solution shown in Table I and dried in vacuum at 50°C for 10 h, were mounted in a TBA apparatus GDP-2 (Polymer Material Dynamic Mechanic Test Instrument) under different test conditions.

Fourier Transform Infrared Spectroscopy (FTIR)

The mixture of I and II, with a weight ratio of 4 : 1, was dissolved in acetone. A Nicolet-170sx Fourier transform infrared spectrophotometer (FTIR) and a temperature controller were employed. The 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 analytical wavelength range was between 400 and 4000 nm.

Differential Scanning Calorimetry (DSC)

The mixture of I and II with the weight ratio of 4 : 1 was dried in a vacuum at 40°C. A DuPont 1090 thermal analysis instrument was employed for the DSC analysis. The experiment were carried out in an air atmosphere flowing at 80 mL/min and at heating rate of 5°C/min.

RESULTS AND DISCUSSION

TBA Test at Constant Heating Rate

The changes in relative rigidity and logarithmic decrement on TBA spectra, as shown in Figure 1, indicate that every curing process was divided into two steps. From the spectra, the curing temperatures were obtained and are shown in Table II. From the comparison of TBA spectra of the three systems, it is clear that organotin catalyst can lower the first curing temperature, but almost had no effect on the second curing temperature.

FTIR

The FTIR spectrum of the acrylate copolymer and crosslinker are shown as Figures 2 and 3, respectively, and the FTIR spectrum of the mixture of the acrylate copolymer and crosslinker is shown in Figure 4. The characteristic C—H group belonging to the mono-substituted benzene, at about 702 cm⁻¹ on the FTIR spectrum, had no change in the curing process, so it was used as the reference group. We chose the range 720–679 cm⁻¹ in the calculation of the absorbance area of the C—H group. The changes of the OH group, the O—H stretching vibration at about 3148–3735 cm⁻¹, were observed at different temperatures in the heating-curing process. The FTIR spectra at every temperature were

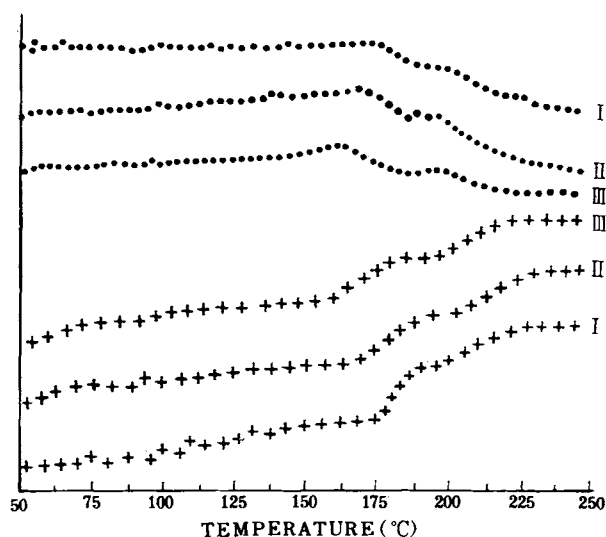


Figure 1 Relative rigidity and logarithmic decrement curves vs. temperature for the reaction of the acrylate copolymer with crosslinker: (I) system 1; (II) system 2; (III) system 3; (+) relative rigidity; (●) logarithmic decrement.

Table II The Curing Temperatures (°C) Under Different Conditions

	System 1 ^a	System 2	System 3
The first curing temperature	175	168	155
The second curing temperature	197	199	195

^a The TBA soaker solutions of systems 1, 2, and 3 correspond to sample nos. 1, 2, and 3 shown in Table I, respectively.

collected and are shown in Figure 5. Since, in fact, the curing reaction is the reaction of the OH group and the NCO group, through detecting the changes of the OH group we could know the extent of the curing reaction. The [OH]/[CH] absorbance area ratios (Abs. ratio) were plotted against the temperatures to derive Figure 6, in which the relation between the extent of the curing reaction and temperature was obvious.

When the mixture was heated to 140–150°C, the Abs. ratio of [OH]/[CH] had no significant change, but from 150 to 180°C, the Abs. ratio of [OH]/[CH] decreased sharply. This was the first step of the curing process. However, when the temperature reached 190°C, the Abs. ratio of [OH]/[CH] began increasing. This phenomenon may be due to the diethanolamine produced in the curing process, which could not vaporize in time; its residue contained the OH group which influenced the FTIR spectra. Then, at 210°C, the Abs. ratio of [OH]/[CH] decreased again; this was the second step.

DSC

The DSC spectrum of the mixture of the acrylate copolymer and crosslinker at about 154 and 200°C

is shown in Figure 7. Two endothermic peaks were generated.

Analysis of the Curing Behavior

From the results of TBA, FTIR, and DSC, we can draw the conclusion that the curing process was divided into two steps: The first curing step begins at about 160°C and the second begins at about 200°C. This opinion has not been reported in previous studies. It is considered that the curing behavior depends on the molecular structure of the crosslinker. The structure of the crosslinker is given below:

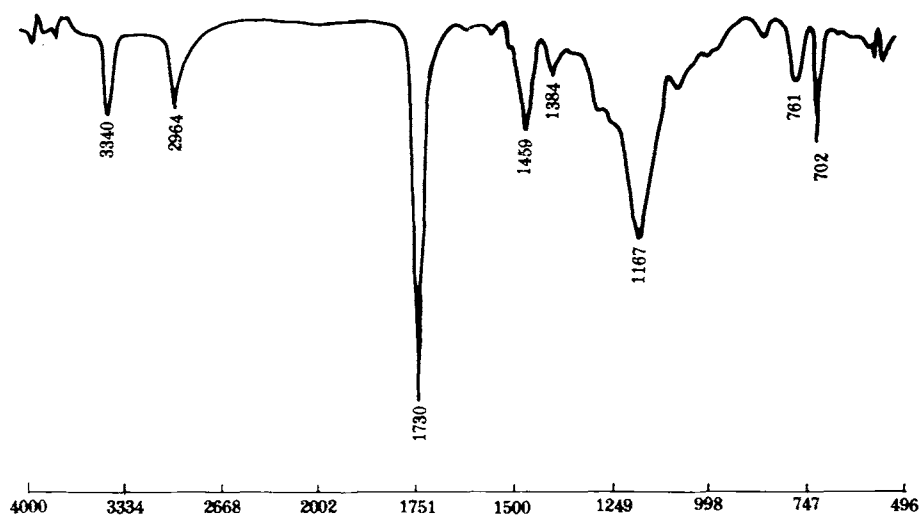
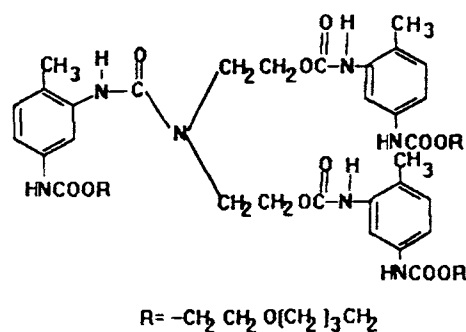


Figure 2 The FTIR spectrum of the acrylate copolymer.

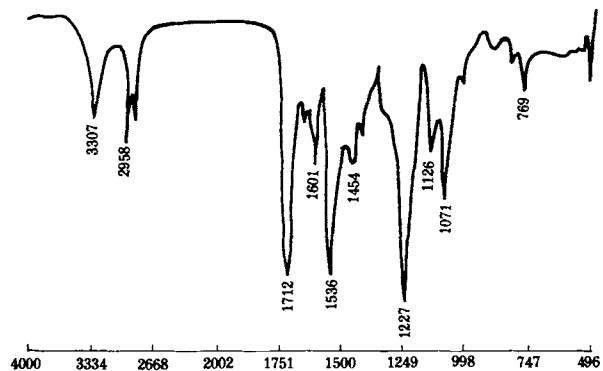


Figure 3 The FTIR spectrum of the crosslinker (II).

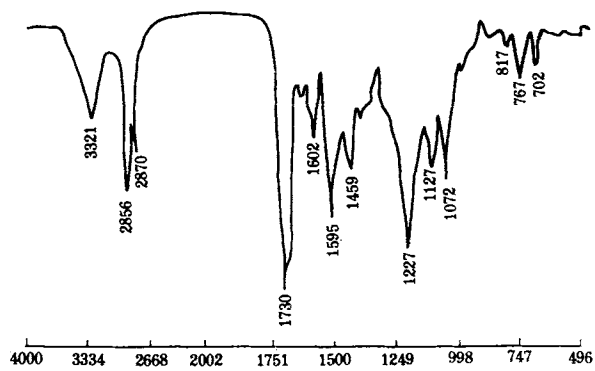


Figure 4 The FTIR spectrum of the mixture of the acrylate copolymer and crosslinker at room temperature.

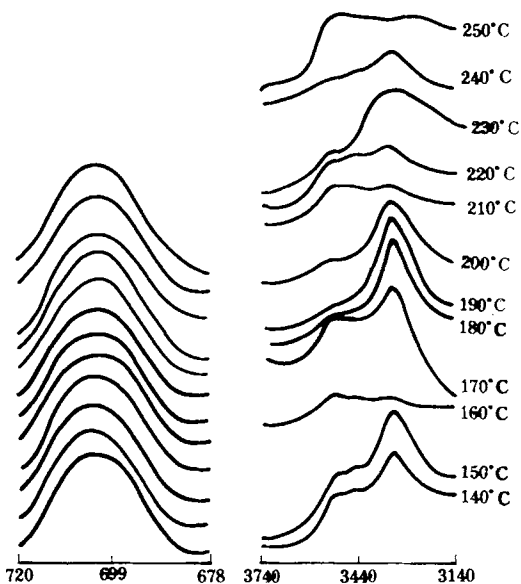


Figure 5 The series of FTIR spectra of the mixture of acrylate copolymer and crosslinker generated at various temperatures (parts).

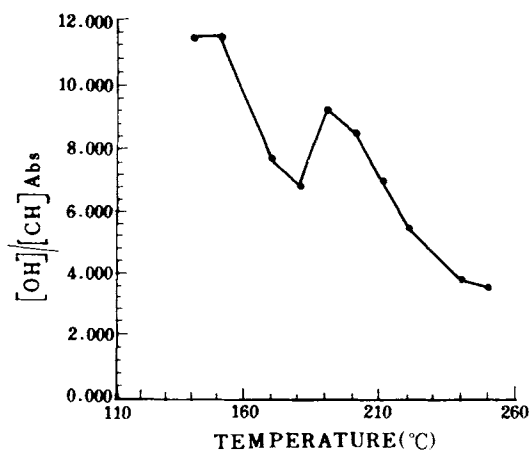


Figure 6 The absorbance area ratios of [OH]/[CH] as a function of temperatures for the mixture of acrylate copolymer and crosslinker.

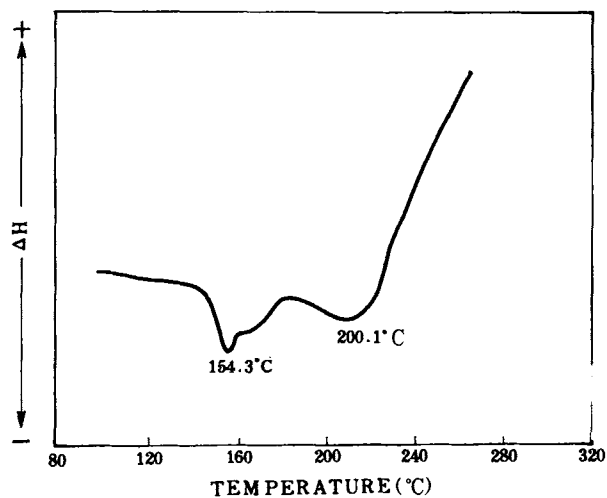


Figure 7 The DSC spectrum of the mixture of acrylate copolymer and crosslinker.

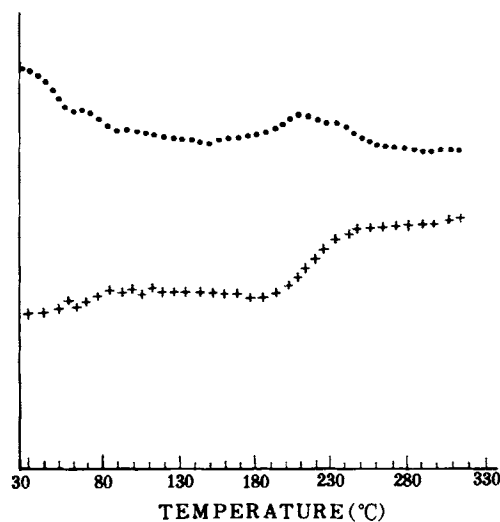


Figure 8 Relative rigidity and logarithmic decrement vs. temperature curves for the reaction of acrylate copolymer and 2-EH and TMP-blocked TDI crosslinker.

Table III Assignment of the IR Vibration Peaks

Acrylate Copolymer	Crosslinker	Vibration Mode
3321		$\nu(\text{OH})$
	3307	$\nu(\text{N}-\text{H})$
2961, 2667	2959, 2669	$\nu(\text{C}-\text{H})$
1730	1712	$\nu(\text{C}=\text{O})$
	1601	$\delta(\text{N}-\text{H})$ (amide I band)
	1536	$\delta(\text{N}-\text{H})$ (amide II band)
1484-1386	1454-1414	$\nu(\text{C}-\text{H})$ (methyl)
	1227	$\delta(\text{N}-\text{H})$ (amide III band)
1066	1071	$\nu(\text{C}-\text{N})$
	820, 769	$\delta(\text{C}-\text{H})$ (1,2,4-substituted benzene)
761, 701		$\delta(\text{C}-\text{H})$ (benzene of monosubstituted)

In the crosslinker, there are two kinds of blocking groups to block diisocyanate, i.e., the amino and hydroxyl groups. Usually, the thermal dissociation of blocked isocyanate is based on the transition of the hydrogen atom of urethane to the blocking agents. If the central atom of the blocking agent has higher electronegativity, the transition of the hydrogen atom to the blocking agent is easier.⁷ Comparing the OH group with the NH group, the central atoms are oxygen and nitrogen, respectively, and the electronegativity of oxygen is greater than that of nitrogen, so the oxygen can abstract the hydrogen much easier. Moreover, when the oxygen abstracts the hydrogen, the OH group so formed has a stronger bond between O and H than the bond between N and H. Thus, in

first curing step, the OH group-blocked isocyanate thermally dissociates to produce free isocyanate which can react with the OH group of the acrylate copolymer to form a more steady structure. In the second curing step, amino-blocked isocyanate thermally dissociates, and the free isocyanate reacts with the OH group of acrylate copolymer. Thus, the crosslinked network can be obtained.

To verify the above explanation, 2-ethyl hexanol (2-EH) and trimethylol propane (TMP)-blocked TDI crosslinker was synthesized. In this crosslinker, all the blocking groups of isocyanate are OH groups. This crosslinker was mixed with the acrylate copolymer in the weight ratio of 1 : 4, and TBA and DSC experiments were carried out. The results are shown on Figures 8 and 9.

In Figure 8, there is only one transformation in relative rigidity and logarithmic decrement curves. In Figure 9, there is only one endothermic peak. These phenomena testified to the explanation about the curing behavior.

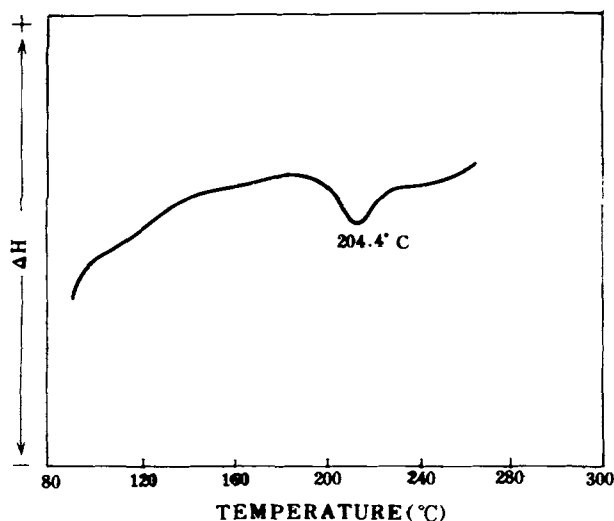


Figure 9 The DSC spectrum of the mixture of acrylate copolymer and 2-EH and TMP-blocked TDI crosslinker.

Isothermal TBA

The results of isothermal TBA test at different temperatures are shown in Figure 10. The gelation times were obtained from the relative rigidity and logarithmic decrement vs. time curves and are shown in Table IV.

For a given system, when it reaches the gel point, the extent of the reaction is constant and is independent of the temperature. The log of gelation time vs. $1/T(\text{K})$ was plotted. The data can often be fitted with a straight line over a significant temperature range (Fig. 11). From the Arrhenius equation,

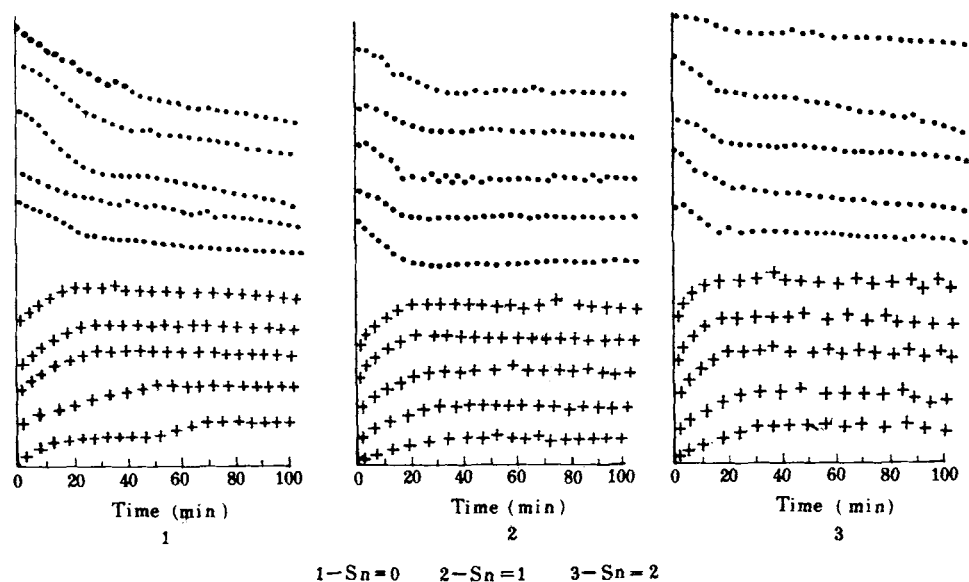


Figure 10 Relative rigidity and logarithmic decrement vs. time curves for the reaction of the acrylate copolymer with crosslinker.

$$\log t_{\text{gel}} = \frac{E_a}{2.303RT} + B$$

where B is a constant and apparent activation energy E_a can be obtained. The Arrhenius apparent activation energy E_a was obtained from the slope of $\log t_{\text{gel}} - 1/T$ curves and is shown in Table V. The organotin catalyst can lower the Arrhenius apparent activation energy efficiently.

Table IV The Curing Time (min)

Sn %	150°C	160°C	170°C	180°C	190°C
0	70	48	26	24	20
1	35	30	25	20	18
2	30	25	17	14	12

Table V The Arrhenius Apparent Activation Energy E_a (kJ/mol)

Sn %	0	1	2
E_a	54.86	39.46	29.63

CONCLUSIONS

When acrylate copolymer containing OH group reacts with TDI, blocked by two different blocking groups, the curing process was divided into two steps, which is in correspondence with the thermal dissociations of isocyanates blocked by different kinds of blocking agents. When the central atom of the blocking group has stronger electronegativity, the dissociation of blocked isocyanate is easier, and cur-

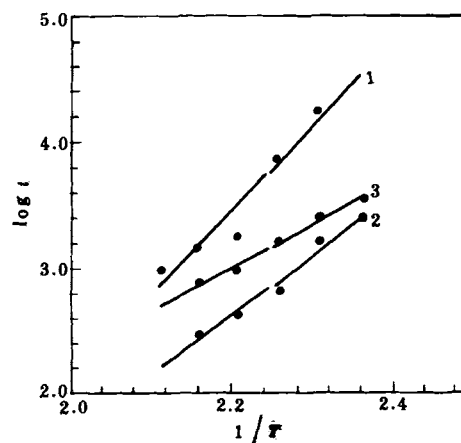


Figure 11 Arrhenius plot: gelation time vs. $1/T$.

ing is also easier. The organotin catalyst can lower the Arrhenius apparent activation energy.

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