

Curing Behavior of Self-Crosslinkable Polyacrylate Coating: TBA and *In Situ* FTIR Studies

BIN ZHONG, DEBEN CHEN, ZONGHUA ZHOU

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

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ABSTRACT: The curing behavior of a self-crosslinkable polyacrylate coating system was studied by torsion braid analysis (TBA), thermogravimetric analysis (TGA), and *in situ* Fourier transform infrared (FTIR). The results of heating TBA showed that the curing process consisted of two stages: The first stage was the deblocking and crosslinking period—the major period of the curing process. The second stage was the deep-curing period. At the end of this stage, a tighter crosslinking network was obtained. In addition, the detecting results of heating *in situ* FTIR proved that the reaction occurring in the second stage concerned the reaction of the deblocked isocyanate group and the NH group which came from urethane. In the end, the results of isothermal *in situ* FTIR showed that the curing temperature affected the extent of crosslinking. The higher the curing temperature, the deeper the curing extent. From the synthetical consideration of the curing temperature and curing time, the optimum curing condition was 170°C/10 min. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1599–1606, 1998

INTRODUCTION

Polyacrylate is an excellent material when it is applied as an electrodeposition coating. It can provide paint film with a light color, high-gloss retention, and outstanding weathering resistance.^{1,2} A self-crosslinkable polyacrylate system is superior because it avoids the compatibility problem of the resin and crosslinker and makes it easier to prepare a stable emulsion. For the thermosetting paint, the properties of paint film, such as hardness and toughness, depend to a large extent on the curing behavior of the coating system. So, it is very significant to study the curing mechanism. However, there has not been much work in this field. Previous reports usually emphasized the effect of different blocking agents on the curing condition and paid little attention to the detailed curing mechanism.^{3,4} Particularly, there are a few reports on the *in situ* FTIR technology that is used to detect the curing process of a coating system.

In present article, a self-crosslinkable polyacrylate containing blocked isocyanate groups was synthesized.^{5,6} The changes of the dynamic parameter and the molecular structure during the curing course were studied by torsion braid analysis (TBA), thermogravimetric analysis (TGA), and *in situ* Fourier transform infrared (FTIR). The results showed that the curing process consisted of two stages: In the first stage, the blocked isocyanate thermally dissociated and regenerated free isocyanate groups and hydroxyl groups. Then, the free isocyanate groups reacted with the hydroxyl groups on the chain of the acrylic resin to form a network. In the second stage, the blocking agent evaporated and the deblocked isocyanate group continued to react with the NH group of urethane and a tighter network was obtained. The curing extent was also shown to be influenced by the curing temperature. The higher the curing temperature, the deeper the curing extent.

EXPERIMENTAL

Materials

The monomers used in the preparation of polyacrylate (A) included butyl acrylate (BA), *N,N*-di-

Correspondence to: D. Chen.

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Table I Ratio of the Materials of the TBA Solution

Specimen	Polyacrylate (g)	Dibutyltin Dilaurate (g)	Acetone (g)
A ₁	4	—	15
A ₂	4	0.1	15

methylaminoethyl methacrylate (DM), styrene (S), 2-hydroxypropyl methacrylate (HPA), 2-ethylhexanol (2EH), and toluene-2,4-diisocyanate (TDI). The solvent was *n*-butanol and the inducer was 2,2'-azobisisobutyronitrile (AIBN). All the chemicals above were chemical pure (Beijing Chemical Co., Beijing, China).

Instruments

A GDP-2 polymer material dynamic TBA apparatus, a DuPont 1090 TGA apparatus, a Nicolet-170SX-FTIR, and a Ycc-16 computer temperature programmer-controller were employed.

Synthesis

In a three-necked reaction vessel, a half-blocked TDI was prepared by slowly adding 2EH (12.6 g, 0.2 mol) to TDI (34.8 g, 0.2 mol) over a period of 40 min below 10°C. Then, the batch was kept below 20°C for an additional 40 min and, after that, heated to 40°C and held for 1 h; HPA (29 g, 0.2 mol) was then added into the flask. The whole mixture was kept at 40°C for about 1.5 h until no free isocyanate groups were evident to give monomer I containing blocked TDI.

n-Butanol (50 g) was charged into another reactor equipped with a condenser, stirrer, thermometer, and dropping funnel. Monomer I, BA (76.8 g, 0.6 mol), DM (31.4 g, 0.2 mol), S (20.8 g, 0.2 mol), *n*-butanol (50 g), and AIBN (2 g) were well mixed in a flask. The reactor-charged *n*-butanol was heated to 100°C, and then the whole mixture of monomers was added using the dropping funnel over a 2-h period. At completion of the addition, the reaction was allowed to continue at 110°C. Over 5 h was required to make the resultant product's conversion approach 100%.

Study of Curing Behavior

Torsion Braid Analysis (TBA)

As shown in Table I, polyacrylate (A) was combined at room temperature with and without the

dibutyltin dilaurate catalyst. Acetone was used to reduce the viscosity of the mixture. The mixture was used to prepare specimens for TBA. The polymer-braid composite specimens were prepared by impregnation of multifilament fiber-glass braids with the mixture and dried at 50°C for 5 h. The specimen was then mounted in the fully automated TBA apparatus which was being maintained at a predetermined condition. In the heating TBA test, the heating rate was 2°C/min.

Thermogravimetric Analysis (TGA)

A DuPont 1090 TGA apparatus was employed. Samples were heated from 30 to 300°C with a heating rate of 5°C/min in a N₂ atmosphere.

In Situ Fourier Transform Infrared (FTIR)

A Nicolet-170SX-FTIR and temperature controller were employed. The samples were analyzed in an absorption mode at a resolution of 4 cm⁻¹ by signal averaging 15 scans. In the heating analysis, the heating rate was 2°C/min in the temperature range of 140–250°C. In the isothermal analysis, the temperature was kept at 160 and at 190°C. The analytical wavelength range was between 400 and 4000 cm⁻¹.

RESULTS AND DISCUSSION

Synthesis

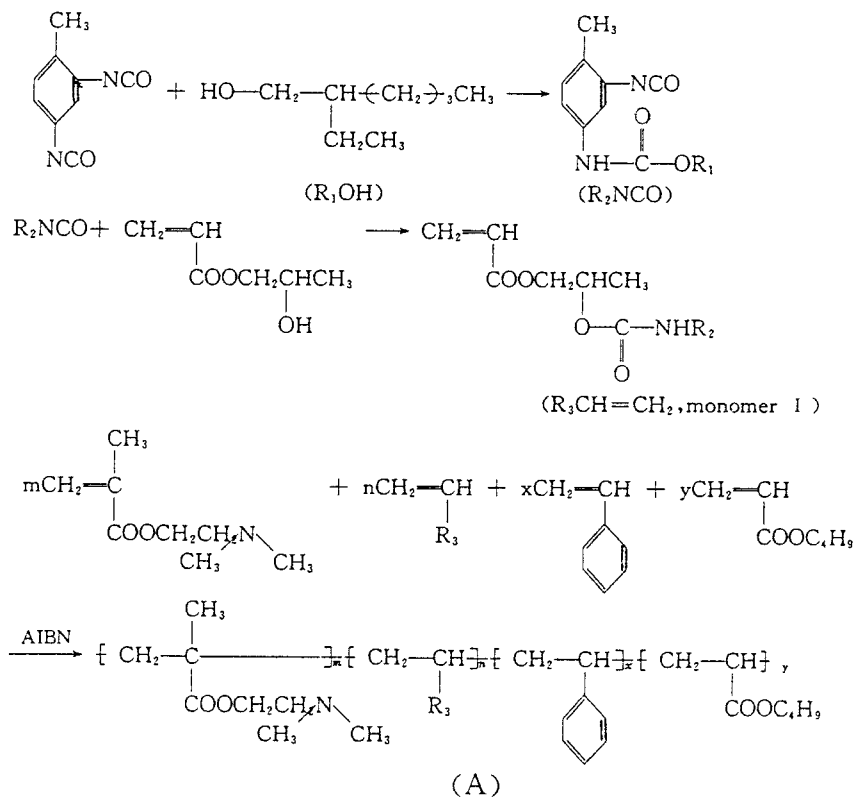
The synthetic route of polyacrylate (A) is shown in Scheme 1. It should be noted that the introduction of monomer I made it possible to cure it without adding another crosslinker for the coating system.

Heating TBA

As shown in Figure 1, the heating-curing process of the coating system was investigated by a heating TBA test. TBA is a very simple and effective method in the research of polymer curing behavior. During the curing process, the dynamic mechanic properties of the polymer would change greatly. Also, the changes could be reflected by the changes of relative rigidity ($1/p^2$) and logarithmic decrement, from which the curing temperature could be obtained.

From the spectra, four factors could be noted:

1. The heating TBA test spectra showed precisely and sensitively that the curing process



Scheme 1

- was divided into two stages. The curing temperature in each stage is shown in Table II.
- The changes of the relative rigidity and logarithmic decrement in the first curing stage were much greater than in the second stage. So, it can be deduced that the first stage is the major period of the curing process, and a crosslinked network was formed to some extent at the end of this stage. We called the

- first curing stage the deblocking and cross-linking period, and the second, the deep-curing period.
- A dibutyltin dilaurate catalyst could lower the curing temperature of the first stage efficiently and have little effect on the second stage. As we know, dibutyltin dilaurate is a special catalyst of the reaction of the NCO group and the OH group. So, it could be in-

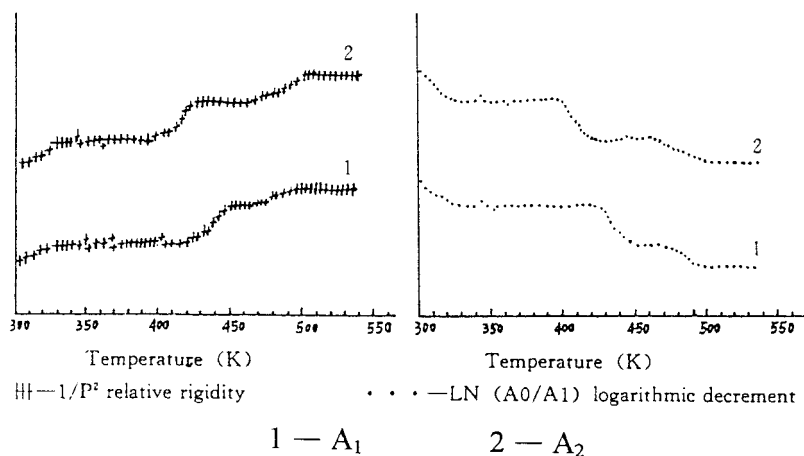


Figure 1 Heating TBA spectra for coating system.

Table II Curing Temperature Range of Two Samples

Sample	First Curing Stage	Second Curing Stage
A ₁	148–180°C	190–227°C
A ₂	120–152°C	190–227°C

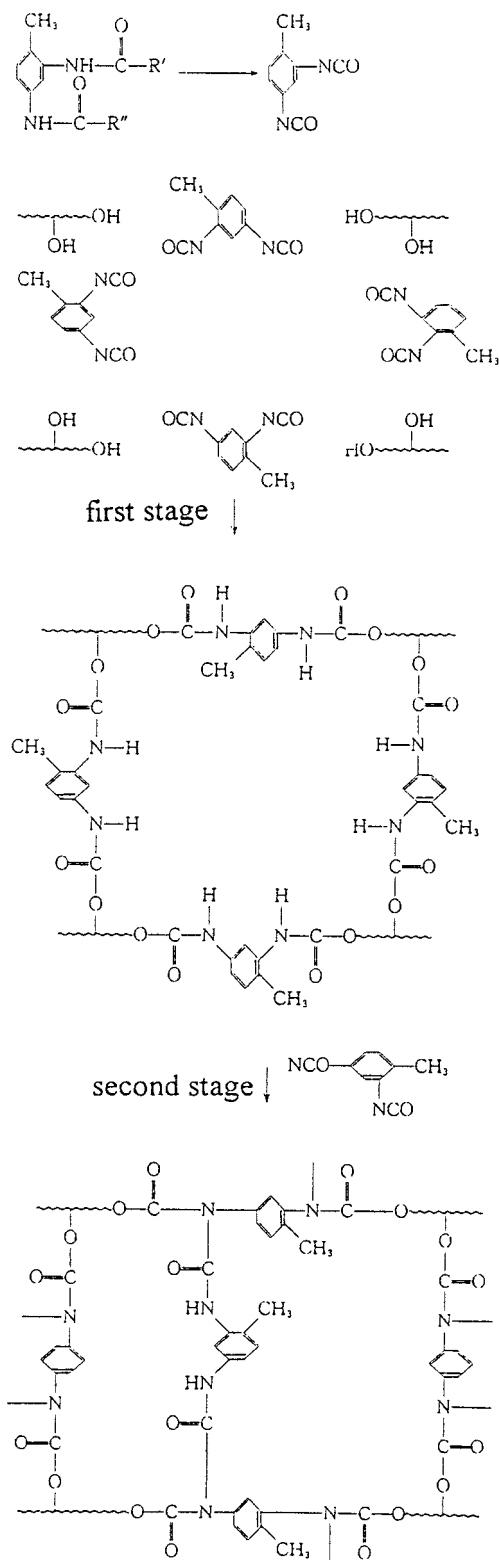
ferred that the reaction in the second stage is not that of the NCO and OH groups. Also, since there was only reactive hydrogen from the NH group except from the OH group, we concluded that the reaction of the second stage is that of the NCO group and the NH group.⁷

- In respect of the properties of the paint film after thermosetting, the hardness, toughness, and outward appearance of the film were very good and met the demands of paint film after the first curing stage. But the film became hard, brittle, and dark yellow in the second stage. Obviously, it does not improve the practical application and should be avoided.

From the above, the following could be inferred: The coating system's curing process consists of two stages: The first stage is the deblocking and cross-linking period. In this period, the blocked isocyanates dissociate gradually and the blocking agents are released. Then, the free isocyanate group reacts with the hydroxy group in the resin to form a cross-linked network to some extent. This stage is an ester-exchange course and includes some reorganization of the molecular structure. The second stage is the deep-curing period. In this period, the blocking agents evaporate and deblocked isocyanate groups proceed to react with NH groups in urethane and form ureidoformate. It increases the extent of crosslinking and the network becomes tighter. The transformation of the structure is shown in Scheme 2.

The mechanism can explain all the test results and four points should be noted:

- Since the reactivity of the NH group of urethane is much lower than that of the OH group, it is reasonable that the isocyanate group reacts with the OH group first and then proceeds to react with urethane at a higher temperature.
- It is impossible that only a branch structure was obtained at the end of the first curing stage. A certain crosslinked network must be formed; otherwise, the changes of relative ri-



gidity and logarithmic decrement in this period cannot be so great.

- In the curing process, the system changes

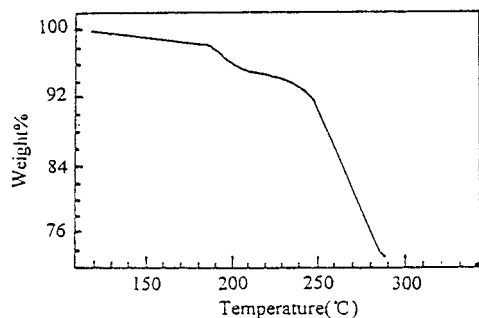


Figure 2 Thermogravimetric curve for degradation of system.

from a linear structure to a crosslinking network through ester exchange and reorganization. This change is favorable as far as the overall energy of the system is concerned. So, the change of the molecular structure in the above mechanism is feasible.

- The boiling point of the blocking agent (2EH) is 185°C. In the first stage, 2EH was released and still stayed in the system since the temperature was lower than the boiling point. In the second stage, the temperature became higher than the boiling point and 2EH evaporated. Obviously, the evaporation of the blocking agent is conducive to the reaction of the NCO and NH groups in the second stage. To confirm the evaporation process of the blocking agent, the curing system was analyzed using TGA. The TGA spectra are shown in Figure 2. The result shows that a part weight loss occurred between 190 and 210°C. This verified the above hypothesis.

Heating *in situ* FTIR

In the mechanism deduced above, it is the urethane that reacts with isocyanate in the second curing stage. But it cannot be verified in that case, because from the catalytic effect, we can only ensure that it is not the reaction of the NCO and OH groups that occurred in the second stage and it cannot be certain that it is the reaction of the NCO and NH groups and the NH group comes from urethane. To make this problem clear, it is necessary to study the change of the molecular structure. By using *in situ* FTIR, the heating-curing process was detected.

Figure 3 shows the IR spectra of polyacrylate (A), and the attribution of the IR characteristic vibration peaks⁸ are shown in Table III. Figure 4 shows the heating *in situ* FTIR spectra.

From Table III, we know that 1534 cm⁻¹ is the

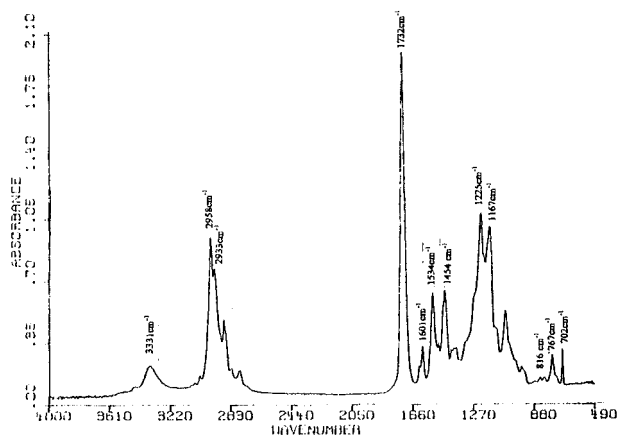


Figure 3 IR spectra of polyacrylate (A).

characteristic peak of NH in urethane. So, the change of the NH group could be investigated during the curing process. Since the characteristic CH group belonging to the monosubstituted benzene, at about 702 cm⁻¹ on the FTIR spectrum, had no change in the curing process, it could be chosen as the reference group. We chose the range 682–720 cm⁻¹ in the calculation of the absorbance area of the CH group. In the calculation of the

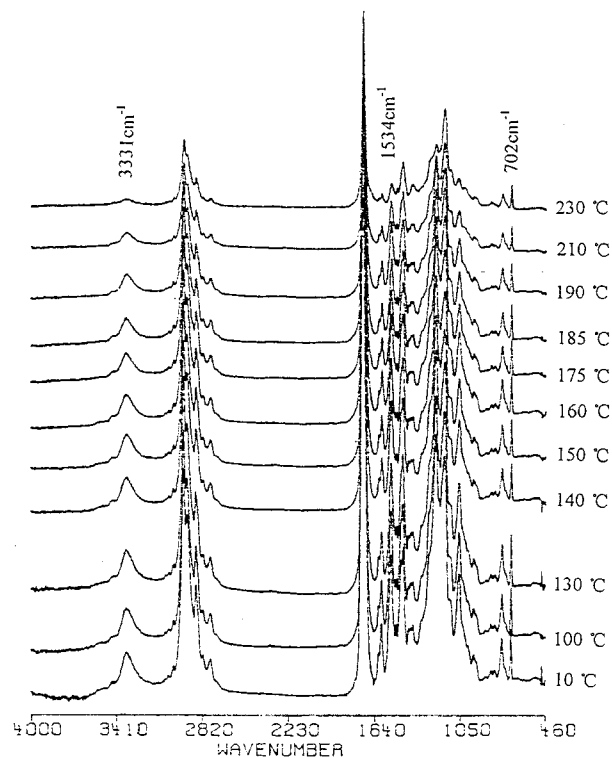


Figure 4 *In situ* FTIR spectra of the curing system at various temperatures during the heating-curing process.

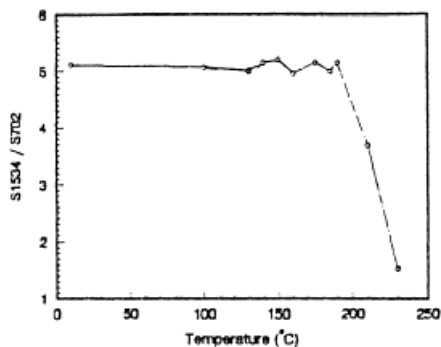
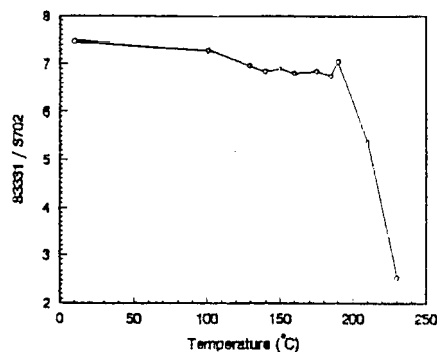
Table III Attribution of the IR Vibration Peaks

Polyacrylate (A) (cm^{-1})	Vibration Mode
3520–3438	ν (O—H)
3331	ν (N—H)
2958, 2933	ν (C—H)
1732	ν (C=O)
1601	δ (N—H) (amide I band)
1534	δ (N—H) (amide II band)
1454	ν (C—H) (methyl)
1225	δ (N—H) (amide III band)
1167	ν (C—O) (fatty ester)
816, 767	δ (C—H) (1,2,4-substituted benzene)
702	δ (C—H) (mono-substituted benzene)

NH group, the range 1506–1575 cm^{-1} was chosen to observe its change. The S_{1534}/S_{702} absorbance area ratios (Abs. ratio) were plotted against the temperatures to derive Figure 5, in which the relation between the change of the NH group and the temperature was obvious.

From Figure 5 we know that when the system was heated to 140–190°C the Abs. ratio of S_{1534}/S_{702} had no significant change. This is in accord with the deduced mechanism above. The mechanism that occurred at 140–190°C was the first curing stage, in which ester-exchange reaction occurred and the amount of the NH group had little change. However, when the temperature reached 190°C and higher, the Abs. ratio of S_{1534}/S_{702} decreased sharply. This phenomenon showed that in the second curing stage the NH group took part in the reaction. Also, since the peak at 1534 cm^{-1} is the characteristic vibration of NH belonging to urethane, it was also proved that the NH group came from urethane.

In addition, from Table III, we know that 3331 cm^{-1} is also a characteristic peak of the NH group.

**Figure 5** Change of S_{1534}/S_{702} during the heating-curing process.**Figure 6** Change of S_{3331}/S_{702} during the heating-curing process.

Also, the change of the NH group can be obtained by observing the change of the 3331 cm^{-1} peak. However, there were some weak peaks between 3438 and 3520 cm^{-1} belonging to the OH group, which meant that a small amount of solvent (*n*-butanol) still stayed in the system. Also, it is difficult to separate the peaks. Since the amount of the OH group is much lower than that of the NH group, from the change of the 3140–3520 cm^{-1} peaks, a rough change of the NH group could be achieved. The peak at 702 cm^{-1} (682–720 cm^{-1}) was also chosen as a reference peak. The S_{3331}/S_{702} Abs. area ratios were plotted against the temperatures to derive Figure 6. As shown in Figure 6, the Abs. area ratio decreased slightly in the early period of the curing process. This phenomenon was due to the volatilization of the small amount of solvent, the boiling point of which is 118°C. According to the change of the 1534 cm^{-1} peak, the curve decreased sharply when the curing temperature reached 190°C. The results confirmed the curing mechanism described above.

Isothermal *in situ* FTIR

To study the isothermal curing behavior, the curing process was investigated by *in situ* FTIR. Figures 7 and 8 show the isothermal *in situ* FTIR spectra at 160 and 190°C, respectively. Also, the change of the characteristic peaks were plotted to derive Figures 9 and 10. The calculated range of the peaks were the same as above.

From the results, three factors could be noted:

1. For the isothermal curing at 160°C, it was found that the peak at 1534 cm^{-1} changed little in the whole process. Also, the slight decrement of the peak at 3331 cm^{-1} was due to the volatilization of the solvent (*n*-buta-

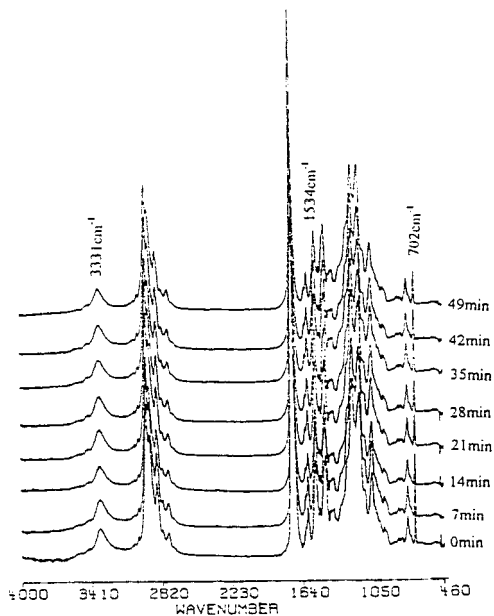


Figure 7 *In situ* FTIR spectra of curing system during isothermal curing process at 160°C.

mol). These phenomena showed that the curing occurred only in the first curing stage.

- For the isothermal curing at 190°C, it is evident that the regularity of the change in this process is very similar to the heating-curing process. It showed that both stages of the curing existed and illustrated that the curing temperature affected the curing extent. The

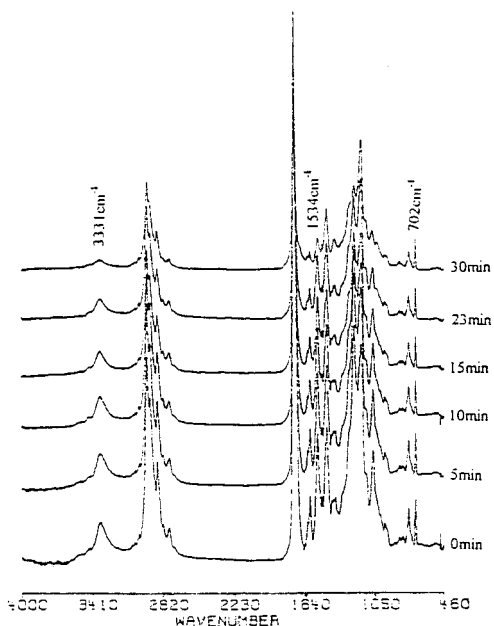


Figure 8 *In situ* FTIR spectra of curing system during isothermal curing process at 190°C.

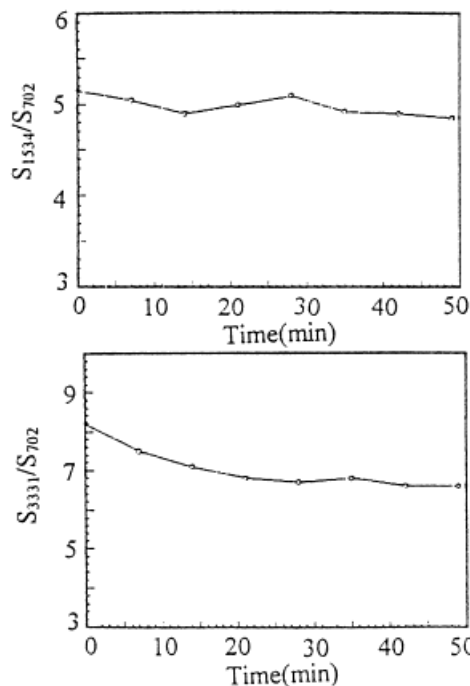


Figure 9 Changes of two characteristic peaks during the isothermal curing process at 190°C.

higher the curing temperature, the deeper the curing extent.

- From the results of the TBA, we know the

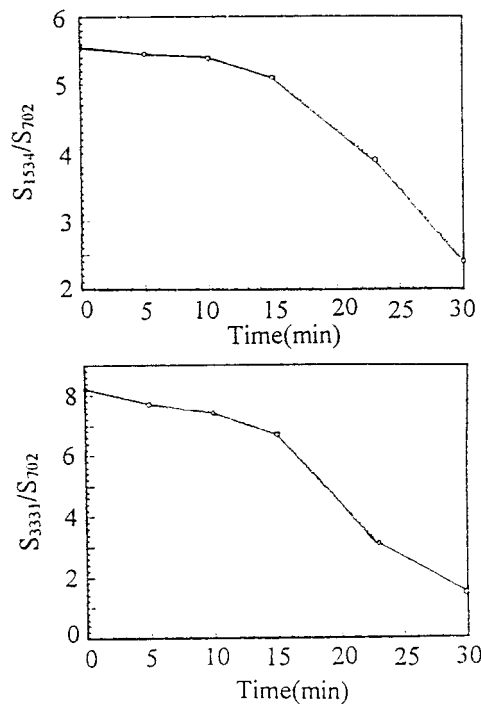


Figure 10 Changes of two characteristic peaks during the isothermal curing process at 190°C.

curing should be controlled within the first curing stage, or the practical value of the paint film would be destroyed. Since the curing extent is influenced by the temperature, the curing temperature could not be too high. After many repeated tests, 170°C/10 min was thought to be the optimum curing condition when both the curing temperature and time were taken into account.

CONCLUSION

1. The results of the heating TBA test showed that the curing process of the self-cross-linkable polyacrylate coating consisted of two stages: The first stage was the deblocking and crosslinking period. It was the major period of the curing process. The second stage was the deep-curing period. This period did not improve the properties of paint film and should be avoided. The mechanism could explain all the phenomena in the curing process and could be further proved by TGA and *in situ* FTIR.
2. The results of the TGA proved that in the second curing stage an evaporation of the blocking agent (2EH) existed.
3. The results of the heating *in situ* FTIR veri-

fied that the reaction occurring in the second curing stage concerned the reaction of the NCO and NH groups. Also, the NH group came from urethane.

4. The results of the isothermal *in situ* FTIR indicated that the curing temperature affected the curing extent. The higher the temperature, the deeper the curing extent. The optimum curing condition was 170°C/10 min.

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