

CURING KINETICS AND PROPERTIES OF ACRYLIC RESIN CURED WITH AZIRIDINE CROSSLINKER

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Abstract A kind of aziridine crosslinkers was synthesized and used to crosslink acrylate copolymers. The crosslinking properties and curing kinetics of the resin were studied. It was found that with the increase of the content of crosslinker in the emulsion, the mechanical properties and solvent resistance of the resin will be apparently improved, but its glass transition temperature (T_g) is very low. The lowest amount of crosslinker used in the acrylic resin emulsion is 0.25%. Curing kinetics studied by DSC show that this curing reaction occurs readily because the apparent activation energy of the reaction is low (65.1 kJ/mol). These results demonstrate that the aziridine crosslinker is indeed a low temperature crosslinking agent and can be used at room temperature.

Keywords Aziridine, Acrylic resin, Crosslink, Curing kinetics, Differential scanning calorimetry (DSC)

INTRODUCTION

Polyfunctional aziridines have been shown to be useful as crosslinking agents in various types of coating systems such as carboxylated acrylics, vinyl acetate, carboxylated urethanes and styrene acrylics. When added to a coat system in amounts of 0.2 to 5% by weight of the total formula, they are effective low-temperature crosslinkers^[1]. The aziridine crosslinker has been considered as one of the most effective crosslinkers used in leather finishing. Compared with other crosslinkers used in acrylic resin finishing agents such as formaldehyde, epoxy crosslinkers, they provide improved physical properties of the crosslinked coating with respect to moisture resistance, adhesion, ultraviolet light stability, alkali resistance, corrosion resistance and gloss^[2]. So although expensive, they have been widely used in the leather-manufacturing industry.

Compared with the use of aziridine crosslinkers, studies on their curing behavior and curing kinetics are still rare. In this article, a kind of aziridine crosslinker was synthesized and used to cure acrylic resin. Its crosslinking properties and the influence of crosslinking on glass transition temperature were studied. The curing kinetics were also investigated by DSC. With regard to the curing behavior of polyacrylate, Ashraf^[3] used the torsion braid analysis (TBA) method to examine the curing reaction of diisocyanate and polyacrylate. Chu^[4] used DSC to analyze the kinetics of acrylic resin/epoxy resin system. Cheng used FT-IR to study the self-crosslinking reaction of acrylate containing epoxy^[5]. However, the studies on the curing kinetics of acrylate copolymers/aziridine crosslinker have never been reported. So the findings reported in this article may be of great significance to the use of aziridine crosslinker.

EXPERIMENTAL

Materials

All monomers, methyl acrylate (MA), ethyl acrylate (EA), acrylonitrile (AN), and acrylate acid (AA), were

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redistilled before use. The acrylic resin was prepared by emulsion polymerization in a four-necked glass reactor equipped with a condenser, a thermometer, four dropping funnels and a mechanical stirrer. Pre-dissolved emulsifier was added to a definite amount of distilled water with stirring. When the temperature of the solution approached 80°C, an aqueous solution of 2 g AA, aqueous K₂S₂O₈ solution and a mixture of 78 g EA, 10 g MA and 10 g AN were slowly dropped into the reactor. The reaction proceeded for 4 h. Upon cooling, acrylic emulsion was obtained.

Aziridine crosslinker was prepared by mixing ethanol amine and 95% sulfuric acid, both of which have previously been diluted with half their weight of water and cooled in an ice-bath. The amine was added slowly to the acid with constant stirring and also cooled in an ice-bath. The mixture was distilled under reduced pressure to remove water. Then pumping was stopped and the temperature was quickly raised to maintain vigorous boiling. When a definite turbidity appeared, heating was stopped. Crystallization suddenly happened, causing the temperature to rise sharply. After cooling, the cake was softened with ethanol and removed from the flask. The cake was ground to powder in ethanol medium followed by filtering and drying; 2-aminoethyl hydrogen sulfate was obtained.

A distillation flask containing 10 mL 14% aqueous NaOH was heated until distillation proceeded at a rapid rate. Then 42 g 2-aminoethyl hydrogen sulfate dissolved in 180 mL cool 12% NaOH solution was added to the distillation flask through the dropping funnel. The distillate was collected in a flask partially immersed in an ice-salt-bath.

After the distillation was complete, the receiving flask was fitted with a mechanical stirrer and two upright ice-water condensers to provide adequate cooling. The amine was salted out by adding solid sodium hydroxide to the distillate through one of the condensers. While salting out, the temperature of the distillate was kept below room temperature. Then ethylenimine was separated out with a separatory funnel^[6].

Trimethylolpropane triacrylate (TMP • TA) was weighed into a flask equipped with stirring rod, cooling means, and condenser. Ethyleneimine was slowly added to the flask which was kept below 10°C. After the reaction had proceeded for half an hour, aziridine crosslinker I was obtained.

Characterization

In this work, all measurements of the aziridine crosslinker were performed on samples in film form. The films for testing were prepared by diluting different amount of aziridine crosslinker with the same amount of distilled water, the resulting solution was mixed with acrylic resin emulsion to form several casting solutions. Each casting solution was poured into a shallow glass dish and kept at room temperature. When the emulsion systems became transparent, the films were dried under an infrared lamp for three days, followed by vacuum drying for 10 h, finally heated at 70°C for 6 h. The contents of the crosslinker in samples 1–6 were 0, 0.1, 0.25, 0.5, 0.75 and 1% (wt%), respectively.

Tensile properties of the films were examined at room temperature by using an Instron Universal Testing Machine, Model 5569. The tension speed was 500 mm/min.

To study the swelling properties of the films in various media, the dry-cured film with initial weight (W_0) was soaked in toluene, distilled water and 0.05 mol/L aqueous NaOH solution at room temperature, respectively. After 24 h, the films were taken out of the solvent, the surface of the films was blotted with filter paper and the films were weighed (W_1) again. The swelling ratio of the films was calculated as follows:

$$\text{Swelling ratio (\%)} = (W_1 - W_0) / W_0 \times 100\%$$

The crosslinking degree of coating film was determined by solvent extraction. The dry-cured coating film with initial weight (W_0) was extracted in a Soxhlet extractor with acetone for 11 h. The extracted film was dried under an infrared lamp to constant weight (W_1). The crosslinking degree of the coating films was calculated as follows:

$$\text{Crosslinking degree (\%)} = W_1 / W_0 \times 100\%$$

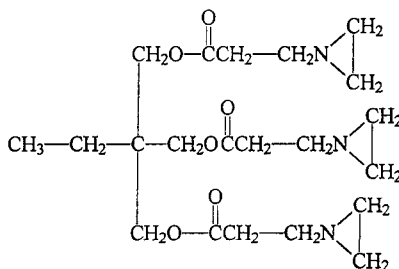
The glass transition temperatures of the film samples were recorded with a Du Pont 2100 DSC analyzer

from -50 – 100°C at a heating rate of 10 K/min under nitrogen atmosphere.

The curing kinetics study was carried out on a Du Pont 2100 DSC thermal analyzer from -50 to 200°C according to the dynamic method at a heating rate of 2.5 – 20 K/min . The samples for kinetic studies were prepared by the following procedure: A certain amount of acrylic resin film without crosslinker was dissolved in acetone. Excess crosslinker (about 10 percent of the resin) was also dissolved in acetone. The two solutions were mixed together at 0°C . The resulting solution was evaporated in vacuum at 0°C for 4 h and stored in dry ice until use.

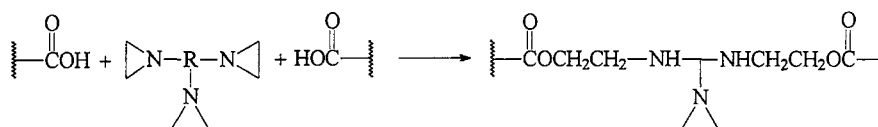
RESULTS AND DISCUSSION

The aziridine crosslinker belongs to a class of compounds which contain two or three ethylenimine cycles. The molecular formula of the crosslinker synthesized in this work is as follows:



Scheme 1 The formula of crosslinker trimethylolpropane tri[3-(1-aziridinyl) prionate]

Crosslinking of aziridine crosslinkers to acrylic resin is considered to proceed in the following fashion:



Scheme 2 Crosslinking of the aziridine crosslinker to acrylic resin

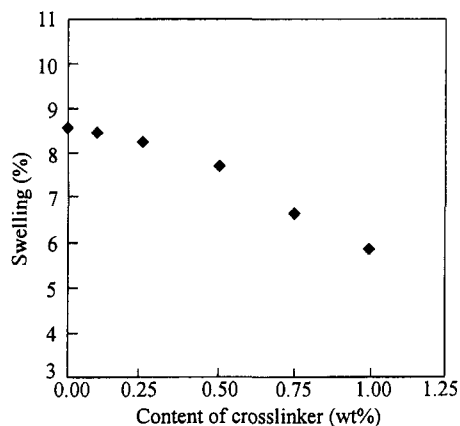


Fig. 1 Water resistance of the film
The acrylate copolymers is composed of 2 g AA, 78 g EA, 10 g MA and 10 g AN.

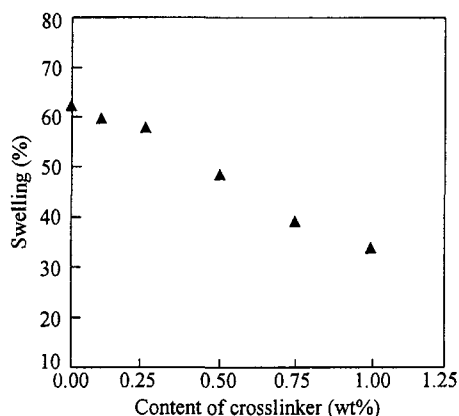


Fig. 2 Swelling of the films in 0.05 mol/L aqueous NaOH solution
The acrylate copolymers is composed of 2 g AA, 78 g EA, 10 g MA and 10 g AN.

The effects of crosslinker on swelling properties and crosslinking degree of the films in distilled water and 0.05 mol/L aqueous NaOH are illustrated in Figs. 1 and 2, respectively. Basically, the value of the swelling ratio was decreasing with increasing content of the crosslinker. The swelling ratio of the films in toluene was also

measured and it was found that sample 1 could dissolve in it. Samples 2, 3 and 4 could not be measured because they swelled fully into gel and the samples could not be handled. The more crosslinker was used, the higher the gel content. The swelling ratio of sample 5 was 1626%, and 6 was 1398%. Swelling was more prominent in toluene than in water. This is attributed to the low polarity of toluene.

The relation between crosslinking degree and the content of crosslinker is shown in Fig. 3. When the content of crosslinker is below 0.25%, the crosslinking degree is very small. But at 0.5%, the crosslinking degree rises abruptly to 40%. So the minimum amount of the crosslinker added to acrylic resin emulsion should not be less than 0.25%.

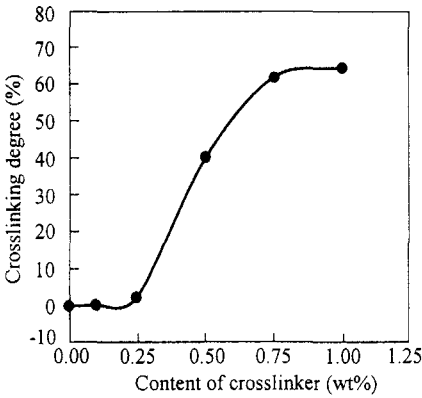


Fig. 3 Crosslinking degree of the films

The effect of the content of crosslinker on the tensile strength of the films is clearly shown in Table 1. The tensile strength and the elongation of the films exhibit an ascending and a descending trend, respectively, with the increase of crosslinker content. This implies that the crosslinking degree of the films having more crosslinker is higher than that with less crosslinker.

Table 1. Mechanical properties of the acrylate copolymer*

Sample	1	2	3	4	5	6
Content of crosslinker (wt%)	0	0.1	0.25	0.5	0.75	1
Tensile strength (Mpa)	1.19	1.31	1.38	1.64	1.86	2.50
Elongation (%)	1865	1580	1302	1180	1050	1011

* The acrylate copolymer is composed of 2 g AA, 78 g EA, 10 g MA and 10 g AN

The glass transition temperatures of the six film samples measured by DSC are listed in Table 2. The T_g of the six samples show no obvious difference. So the same conclusion as reached by others^[7] can be drawn that the influence of crosslinking on the glass transition temperature of acrylic films is very small, while its influence on the mechanical strength is large.

Table 2. Glass transition temperatures of the six films with different contents of crosslinker*

The content of the crosslinker (wt%)	0	0.1	0.25	0.5	0.75	1
$T_g(^{\circ}\text{C})$	-1.33	-1.19	-1.97	-1.84	-1.44	-1.33

* The acrylate copolymer is composed of 2 g AA, 78g EA, 10g MA and 10g AN

A curing kinetics study of acrylic resin crosslinked by aziridine crosslinkers has never been reported in the literature. The dynamic DSC method was used to study the crosslinking reaction of this system. Figures 4(a)–(d) and Table 3 show the heating scans of the acrylate copolymers at various heating rates. We can see that this aziridine crosslinker is indeed a low temperature crosslinking agent because the curing reaction starts at room

temperature. The broad and smooth shape of the curves indicates that the rate of the curing reaction is very low. That is one of the reasons why aziridine crosslinkers number among the most widely used crosslinkers in the leather-manufacturing industry.

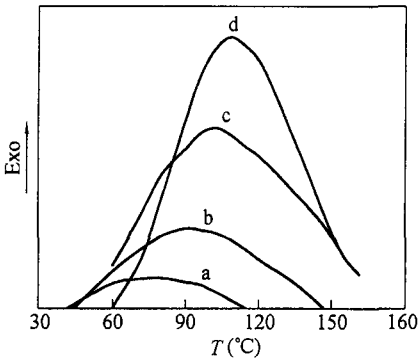


Fig. 4 DSC traces of acrylate/aziridine crosslinker system at various heating rates
a) 2.5 K/min; b) 5 K/min; c) 10 K/min; d) 20 K/min
Content of the crosslinker: 10 percent of the resin

Table 3. DSC of acrylic resin/aziridine crosslinker*					
Heating rate (K/min)	Sample weight (mg)	Exotherm			
		Onset (°C)	Max (°C)	Offset (°C)	ΔH (J/g)
2.54	6.39	29.6	74.99	125.3	16.7
5.10	5.22	31.7	90.66	146.7	15.9
10.25	7.16	43.6	98.30	150.4	16.3
20.55	7.58	53.4	107.01	169.9	15.6

* Content of the crosslinker: 10 percent of the resin

Equation (1) proposed by Ozawa^[8] was used to calculate the activation energy of the reaction and the calculated value was refined by the method of Doyle^[9] and Flynn^[10]. Pre-exponential factor Z was computed according to Eq. (2). The calculated activation energy and pre-exponential are 65.1 kJ/mol and 8.823 min⁻¹, respectively.

$$E = 2.19R \frac{d \lg \beta}{d(1/T)}$$

(1)

$$Z = \frac{\beta E e^{E/RT}}{RT^2}$$

(2)

CONCLUSION

From the above discussion, it can be concluded that the aziridine crosslinker is an effective curing agent for acrylate copolymers. The mechanical properties and solvent resistance will be improved, but the change of the glass transition temperature is very small.

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