

Preparation of low viscosity epoxy acrylic acid photopolymer prepolymer in light curing system

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Abstract. With the integration and development of materials engineering, applied mechanics, automatic control and bionics, light cured composite has become one of the most favourite research topics in the field of materials and engineering at home and abroad. In the UV curing system, the prepolymer and the reactive diluent form the backbone of the cured material together. And they account for more than 90% of the total mass. The basic properties of the cured product are mainly determined by the prepolymer. A low viscosity epoxy acrylate photosensitive prepolymer with a viscosity of 6800 mPa • s (25 °C) was obtained by esterification of 5 hours with bisphenol A epoxy resin with high epoxy value and low viscosity.

1. Introduction

The photocurable material is prepared on the basis of prepolymer, adding specific reactive diluents, photoinitiator and various additives. Under the irradiation of the curing light source, the photoinitiator in the liquid light-curing material is excited to become free radical or cation, which causes the material containing unsaturated double bond in the material to form a solidification reaction.

In the UV curing system, the prepolymer and the reactive diluent form the backbone of the cured material together. They account for more than 90% of the total mass [1]. The basic properties of the cured product are mainly determined by the prepolymer. According to the mechanism of light curing, the suitable prepolymer is also different [2].

(1) Free radical polymerization mechanism

The suitable prepolymers are resins with C=C unsaturated double bonds, such as propylene oxide (CH₂=CH-COO-), methacrylic oxide (CH₂=C (CH₃) -COO-), vinyl (C=C) and allyl (CH₂=CH-CH₂-) and so on.

Sort by the polymerization rate: CH₂=CH-COO- > CH₂=C (CH₃)-COO- > C=C > CH₂=CH-CH₂-.

(2) Cationic polymerization mechanism

The applicable prepolymer mainly includes epoxy resin, epoxy functionalized polysiloxane resin, and resin containing vinyl ether functional group.

Modern industrialized acrylated prepolymers are predominantly present: acrylated epoxy resins, acrylated urethanes, acrylated polyesters, and acrylated polyacrylates. And the former two are the most important. Table 1 lists the performance of common prepolymers [3].



Table 1. The performance of common prepolymers.

Type	Curing rate	Tensile strength	Flexibility	Strength	Chemical resistance	Anti-yellowing
Epoxy acrylate	Fast	High	Not good	High	Excellent	Middle to bad
Polyurethane acrylate	Fast	Adjustable	Good	Adjustable	Good	Adjustable
Polyester Acrylate	Adjustable	Medium	Adjustable	Medium	Good	Not good
Polyether acrylate	Adjustable	Low	Good	Low	Not good	Good
Acrylate resin	Fast	Low	Good	Low	Not good	Excellent
Unsaturated polyester resin	Slow	High	Not good	High	Not good	Not good

The selection of prepolymer in light curing system mainly takes the following factors into consideration: low viscosity, light curing speed, good physical and mechanical properties, glass transition temperature, curing shrinkage, low toxicity and low irritation [4].

Acrylic series resin is the second generation resin of light curing system. It is introduced into the functional group of the crosslinking reaction at the end of some prepolymer by introducing double bond into the acrylate [5]. Common polyester acrylate, polyether acrylate, epoxy acrylate, polyurethane acrylate, melamine acrylate. Among them, epoxy acrylate (EA) attracted much attention because of easy synthesis, strong adhesion, chemical resistance, high strength characteristics [6].

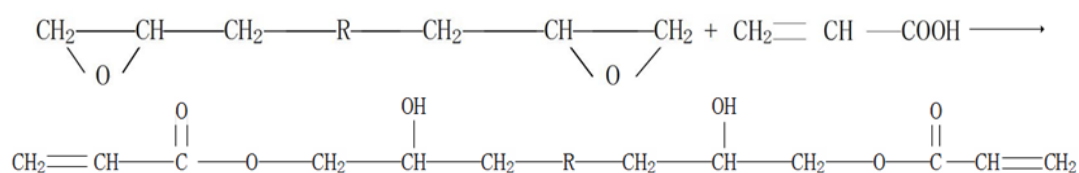
Epoxy acrylate can be divided into bisphenol A epoxy acrylate resin, novolac epoxy acrylate, epoxy acrylate and epoxy acrylate oil according to the structure. Among them, the bisphenol A type epoxy acrylate is the most stable [7]. Bisphenol A epoxy acrylate is obtained by reacting bisphenol A epoxy resin with (meth) acrylic acid [8]. Bisphenol A epoxy acrylate was prepared from resin and acrylic acid as prepolymer of light repairing agent [9].

2. Experimental approach

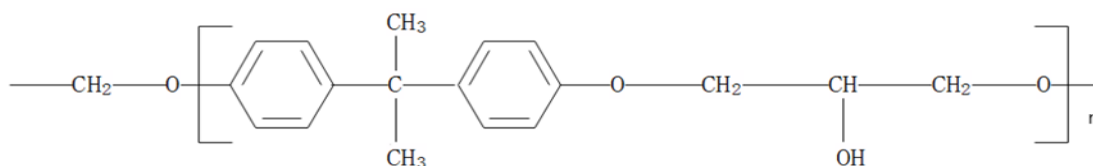
2.1. Reaction mechanism

Epoxy acrylates are formed by the reaction of epoxy resin and acrylic acid, and the preparation conditions vary depending on the type of EA. Catalysts that promote the reaction of epoxy groups and hydroxyl groups include strong bases and organic amines. The reaction between the epoxy group and the hydroxyl group is an exothermic reaction. It is very important to select a suitable polymerization inhibitor to prevent radical polymerization of unsaturated groups on acrylic acid during the preparation of epoxy acrylates. The common inhibitors are phenols (such as hydroquinone, etc.). The synthesis of epoxy acrylate is as follows [10].

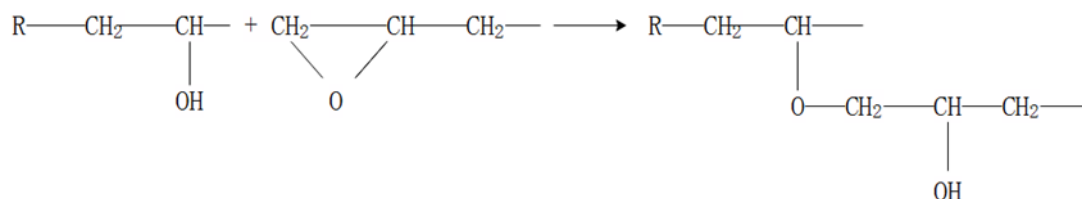
2.1.1. Main reaction.



Where R is:



2.1.2. *Side reaction.* The side reactions mainly include: The self - polymerization reaction occurs after epoxy ring – opening and reaction of epoxy groups with active hydrogen to form hydroxyl groups.



2.2. Evaluation of prepolymer quality

Measures to measure the quality of epoxy acrylate mainly consist of acidity value and viscosity [11]. In the reaction, the acidity value indicates the degree to which the reaction (esterification) proceeds (the conversion of the esterification reaction). The viscosity indicates the molecular size of the resin. In the experiment, a reasonable preparation process was selected by comparing the acidity value and viscosity of different reaction times [12].

2.2.1. *Determination of acidity value.* Weigh the quantitative samples dissolved in alcohol, adding phenolphthalein, titration with standard solution of potassium hydroxide; calculate the acidity value of the epoxy acrylic resin according to the following formula.

$$AV = \frac{C \times V \times 56.11}{m} \quad (1)$$

AV——acidity value V——the volume of KOH solution is consumed

C——concentration of KOH solution m——sample weight

The acidity value before reaction can be calculated according to formula (2)

$$AV_0 = \frac{K \times 56 \times 1000}{G} \quad (2)$$

AV₀——initial acidity value

G——the total mass of the reactants

K——molar number of acids

The reaction conversion P:

$$P = \left(1 - \frac{AV}{AV_0}\right) \times 100\% \quad (3)$$

2.2.2. *Determination of viscosity.* The reaction product (prepolymer) of epoxy resin with acrylic acid is Newton fluid. There are many methods for measuring viscosity of Newton fluid, such as capillary method, rotation method, etc. This experiment uses falling-ball method [13].

2.3. Experimental equipment

Experimental equipment is shown in figure 1. It includes: thermostat water bath, mixer, three-necked flask, thermometer, dropper, and so on.

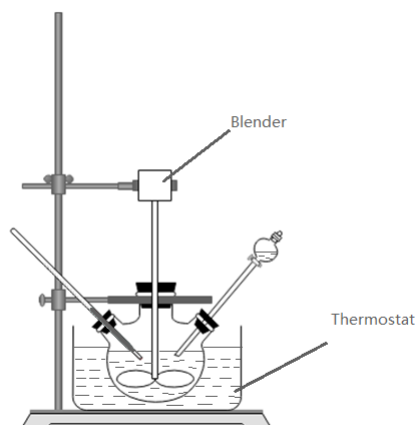


Figure 1. Experimental equipment.

2.4. Experimental material

Bisphenol A epoxy resin: E-51, acrylic acid (analytically pure), 95% ethanol (analytically pure), KOH (analytically pure), phenolphthalein (analytically pure)

2.5. Experimental method

- (1) Preparation of phenolphthalein indicator and concentration of 0.1 mol / L KOH-ethanol solution.
- (2) Heat the thermostat water bath at a temperature of 90 °C. Take proper amount of E-51, put it into three-necked flask, and heat three-necked flask in the thermostat water bath.
- (3) Add acrylic acid to the three-necked flask slowly and stir constantly during the drip process. After completion of the drop in the corresponding time, heat the thermostat water bath into 100 °C and continue stirring.
- (4) Measure the acidity value of the reactants in the three-necked flask at intervals of a certain time.
- (5) After two hours of reaction, take a certain amount of reactants at intervals of one hour and measure the viscosity of the reactants using falling-ball method.

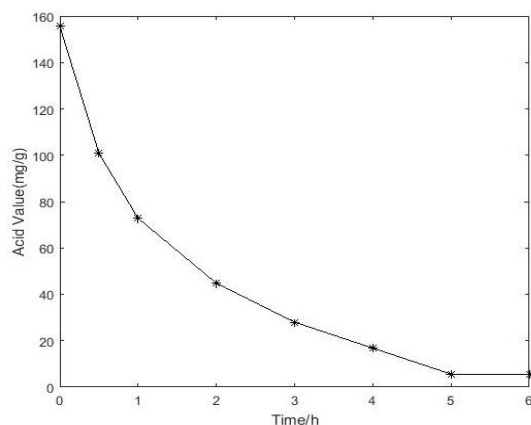
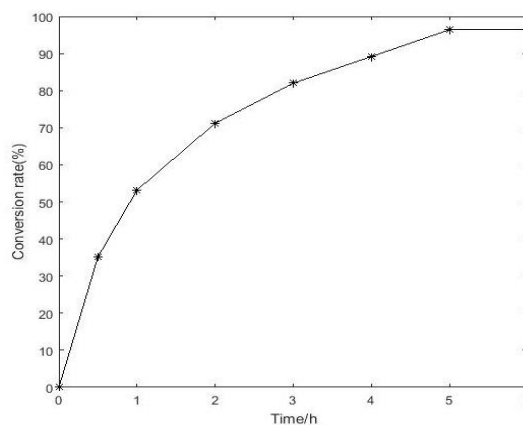
3. Experimental results

3.1. Acidity value and conversion rate in the reaction process

- (1) According to formula (2), the initial acidity value before reaction is 155.6mg/g.
- (2) In the process of reaction, the amount of acid was measured at regular time, and the acidity value and conversion rate were calculated according to formula (1) and formula (3). Table 2 shows the change of acidity value during the reaction. Figure 2 and figure 3 show the acidity value and conversion rate of reactants in different reaction stages.

Table 2. The acidity value changes during the reaction.

Reaction time	0.5h	1h	2h	3h	4h	5h	6h
Acidity value (mg/g)	100.8	72.8	44.8	28	16.8	5.6	5.6
Conversion rate (%)	35.2	53.2	71.2	82	89.2	96.4	96.4

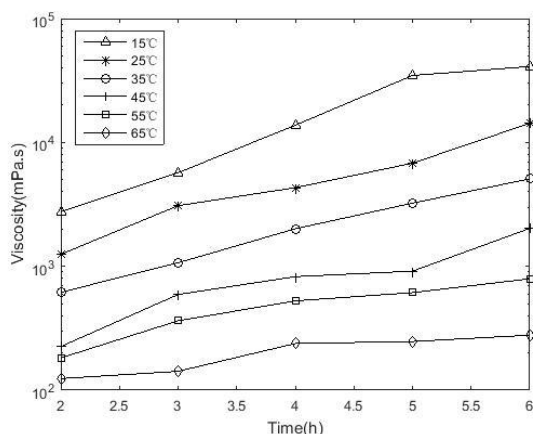
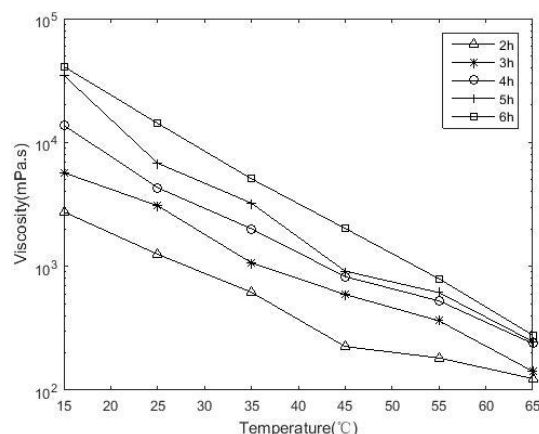
**Figure 2.** Acidity value-Reaction time.**Figure 3.** Conversion rate-Reaction time.

3.2. The change of viscosity during the reaction

In the reaction process, take proper amount of reactant and measure its viscosity at regular intervals by falling-ball method [14]. Then determine the change of viscosity under different temperature and reaction time. Table 3 shows the viscosity of prepolymer at different reaction time and environment temperature. Figure 4 and 5 show the viscosity and temperature-viscosity curves at different stages of esterification.

Table 3. The viscosity of prepolymer at different reaction time and environment temperature.

reaction time	viscosity of prepolymer (mPa s)					
	15°C	25°C	35°C	45°C	55°C	65°C
2h	2752	1250	617	225	182	124
3h	5692	3086	1067	592	363	142
4h	13783	4313	2009	825	526	238
5h	34727	6800	3236	914	613	247
6h	41000	14278	5086	2022	793	278

**Figure 4.** Viscosity-Reaction time.**Figure 5.** Viscosity-Temperature.

3.3. Experimental results

Experimental results show that:

(1) The initial esterification speed of epoxy resin and acrylic acid is faster. After 1 hour esterification, the conversion rate can reach 53.2%, and the corresponding acidity value is reduced to 72.8 mg/g.

(2) With the prolonging of esterification time, the conversion rate and acidity value gradually tend to be stable. When the reaction proceeds to 5 hours, the acidity value reaches a steady value of 5.6 mg/g. And the conversion rate of esterification is over 95%. As the reaction time increases, the conversion and the change of acidity value is no longer obvious. It indicates that the esterification reaction is basically over.

(3) As shown in figure 4, the viscosity of the reaction product of epoxy resin and acrylic acid increase with the progress of the reaction. The increase in viscosity is due to the fact that the macromolecule product is produced with the esterification reaction.

(4) As shown in figure 5, the viscosity of the reactants decreases with increasing temperature and the difference in viscosity of the reactants in the different esterification stages decreases as the temperature increases. When the temperature is 25 °C ~ 35 °C, the viscosity of each reactant is relatively stable. Thus, the use of a viscosity of 25 °C to characterize the reactant viscosity is comparable.

(5) When the esterification reaction was carried out for 5 hours, the acidity value and the conversion rate of the reactants had reached a stable value. At this point, the viscosity of the reactant is 6800 mPa•s(25°C).

4. Conclusion

(1) The reaction temperature was divided into two stages (low temperature dropping and constant temperature reaction). It can effectively prevent the self-polymerization of acrylic acid and gel of hydroxyl groups of epoxy resin and acrylic acid. It is beneficial to reduce the viscosity of prepolymer and guarantee its quality by dividing the reaction temperature into two stages (low temperature dropping and constant temperature reaction) and strictly controlling the reaction temperature and reaction time.

(2) A low viscosity epoxy acrylate photosensitive prepolymer with a viscosity of 6800 mPa•s(25°C) was obtained by esterification of 5 hours with bisphenol A epoxy resin with high epoxy value and low viscosity. Compared with the viscosity value of partially low viscosity epoxy acrylic acid, the viscosity of epoxy acrylic acid prepared in this study is greatly reduced, which can meet the requirement of viscosity of light-repair. Table 4 is the viscosity comparison of the different prepolymers [1].

Table 4. Viscosity comparison of the different prepolymers.

Company	Self-made	Sartomer	UCB s.a.	Cognis	Cognis
Product code	—	CN121	EB6040	3215	3660
Chemical Name	Low viscosity EA	Low viscosity EA	Low viscosity EA	Low viscosity EA	Low viscosity EA
Viscosity(mPa•s, 25°C)	6800	57500	25000	15000	7000

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