

STUDY ON THE POST-CURE KINETICS OF EPOXY RESIN IRRADIATED BY AN ELECTRON BEAM*

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Abstract The post-cure kinetics of electron beam (EB) curing of epoxy resin initiated by diaryliodonium was investigated. The post-cure reaction fits first order reaction kinetics. The reaction rate constant increases with increasing treatment temperature of post-cure. The reaction rate of post-cure is much lower than the rate of its reaction on electron beam treatment.

Keywords Epoxy, Reaction kinetics, Electron beam curing, Post-cure

INTRODUCTION

Electron Beam (EB) curing of polymer matrix composites is a novel green manufacturing process. EB curing of composites offers significant advantages over traditional thermal curing^[1–3], including shorter curing time, low energy consumption, low curing temperature, good dimensional stability, better processing character, and so on.

According to the curing reaction mechanism of epoxy resin initiated by onium salt, the curing reaction includes three reaction steps of chain initiation, chain propagation, and chain termination or chain transfer. This reaction mechanism differs from the radical reaction mechanism in that the center of cationic polymerization introduces positive charge, so the cationic polymerization would not be terminated through double molecules, and the polymerization is terminated by chain transfer or single molecule^[4, 5].

For cationic polymerization of epoxy resin, the chain termination is achieved through the reaction between the cationic reactive center and the group that contains active hydrogen (such as the hydroxyl in the epoxy resin). During the chain termination, the hydroxyl loses its proton, which is transferred to the counteranion, so strong proton acid is regenerated. The regenerated proton acid initiates the polymerization of epoxy resin again. During the chain termination reaction, the reactive center is transferred, but the kinetic chain is not terminated during the whole polymerization^[6]. So the epoxy resin radiated by EB will continue to polymerize after the radiation is stopped. This is the post-cure effect of epoxy resin cured by EB.

The post-cure effect that was used to complete the curing of epoxy resin with cationic initiator could save more energy than complete EB curing, and it can be used to achieve some special purposes^[7, 8]. This effect is beneficial in decreasing residual stress and in improving the properties of the materials.

In this paper, the post-cure kinetics of epoxy resin with diaryl iodonium hexafluoroantimonate as initiator cured by electron beam was investigated.

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EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A epoxy resin (E54) was supplied by Wuxi Resin Factory. CD1012 (4-(2-hydroxy-tetradecyloxy)-phenyl-phenyl iodonium hexafluoroantimonate) was supplied by Sartomer Company (U.S.A). Hydrochloric acid (36%), acetone, sodium hydroxide, and potassium acid phthalate was obtained from Beijing Chemical Plant.

Methods

The electron beam accelerator was supplied by Beijing Normal University. Experimental conditions used in the measurements were: energy = 3–5 MeV, current > 200 μA, power = 0.7 kW, radiation dose rate = 10 Gy/s, total radiation dose = 2 kGy.

Preparation of EB Curable Resin

The catalyst (CD1012) (2 parts) was added to the epoxy resin E54 (100 parts) that had been heated to 80–100°C, and the resin system (E54-CD1012) was stirred to dissolve the catalyst in the in resin. The epoxy resin was stored under ambient environment for a definite time, and then the resin was dissolved in hydrochloric acid-acetone solution. The epoxy value was measured according to HG 2-741-72 (chemical industry standard of China).

RESULT AND DISCUSSION

According to the curing reaction mechanism of cationic epoxy, the chemical reaction between the epoxy group and proton acid generated by onium is the dominating chemical reaction during the post-cure stage after EB radiation was stopped, which resemble the chain initiation, chain propagation and regeneration of proton acid during the curing reaction by EB radiation. The initiator would not decompose to generate strong proton acid again after the EB radiation was stopped, so the summation (c_{X^-}) of proton acid and oxyonium ion is invariant.

According to the theory of reaction kinetics, the post-cure reaction rate of cationic epoxy irradiated by EB can be described by Eq. (1).

$$R = -\frac{dc_E}{dt} = k'c_E^n c_{X^-}^m \tag{1}$$

Because c_{X^-} is invariant, $c_{X^-}^m$ also is invariant. Supposing $k'c_{X^-}^m = k$, then we have:

$$R = -\frac{dc_E}{dt} = kc_E^n \tag{2}$$

where n is the reaction order of the curing reaction kinetics, c_E is the concentration of epoxy group, and k is the apparent rate constant of the curing reaction.

The post-cure kinetics of E54-CD1012 (2.0%) resin system at 12°C was investigated (Table 1 shows the experimental data). The relationship between the concentration of epoxy group and the placement time (reaction time) follows Eq. (3)

$$c_E = 0.09873 \times \exp(-t/2146.0989) + 0.3936 \tag{3}$$

Table 1. The data of post-cure effect of E54-CD12 (2.0%) at 12°C*

No.	Placement time (min)	Concentration of epoxide group (mol/100 g)	Dissolvability in acetone
1	0	0.492	Easy
2	10	0.470	Easy
3	22	0.447	Easy
4	40	0.428	Easy
5	50	0.415	Medium
6	60	0.412	Difficult
7	70	0.408	More difficult
8	120	Unmeasured	Insoluble

*Radiation dose: 2 kGy

The curve of the concentration of epoxide group versus time of placement shows that their relationship was a decaying exponential function; the curve was fitted (as shown in Fig. 1). The curve in Fig. 1 was differentiated, and the data of dc_E/dt (reaction rate) were obtained. The curve of dc_E/dt versus c_E was plotted and fitted (as shown in Fig. 2), and the equation of post-cure reaction rate of E54-CD1012 system is obtained:

$$R = -dc_E/dt = -1.8341 \times 10^{-4} + 4.6595 \times 10^{-4} c_E \quad (4)$$

It is shown that the kinetics of the post-cure of E54-CD1012 follows a first order reaction. Namely, the rate of post-cure reaction of the resin system is direct proportional to the concentration of the epoxy group. This equation is correct during the initial period of the post-cure reaction, when the reaction is not controlled by the diffusion of the reactive molecule. As the reaction continues, especially when the resin turns solid, diffusibility becomes the main factor that controls the reaction, and the kinetics no longer follows this equation.

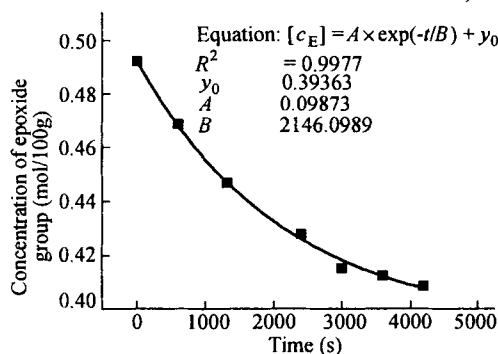


Fig. 1 Relation between the concentration of epoxy group and the time of post-cure (12°C)

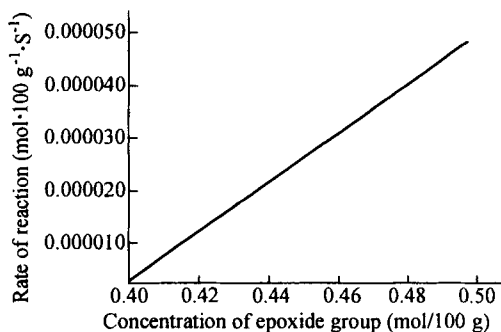


Fig. 2 Kinetics curve of post-cure effect (12°C)

The post-cure kinetics of the E54-CD12 (2.0%) resin system at 21°C was also investigated (as shown in Fig. 3 and Fig. 4). Its relationship between the concentration of epoxy group and placement time (reaction time) follows Eq. (5).

$$c_E = 0.1123 \times \exp(-t/1377.2022) + 0.3840 \quad (5)$$

The post-cure kinetics can be expressed by Eq. (6).

$$R = -dc_E/dt = -2.7815 \times 10^{-4} + 7.2462 \times 10^{-4} c_E \quad (6)$$

Compared with the rate constant of the post-cure kinetics equation of the E54-CD12 (2.0%) resin system, the rate constant ($7.2462 \times 10^{-4} \text{ s}^{-1}$) at 21°C is clearly higher than that at 12°C ($4.6595 \times 10^{-4} \text{ s}^{-1}$). This illustrates that the increase of reaction temperature can result in a clearly increasing reaction rate.

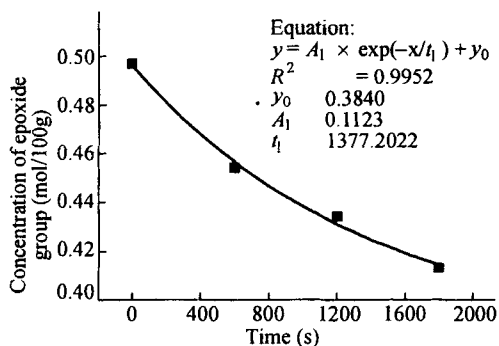


Fig. 3 Relationship between the concentration of epoxy group and the time of post-cure (21°C)

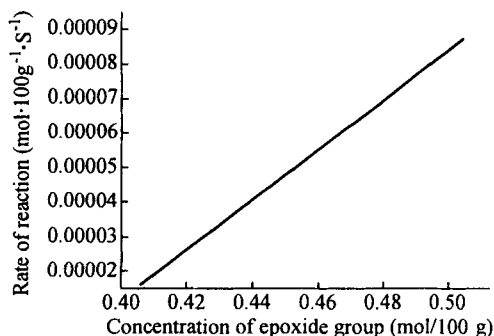


Fig. 4 Kinetics curve of post-cure effect (21°C)

Under the same condition, the rate constant of the EB curing reaction is approximately $0.01\text{--}0.02\text{ s}^{-1}$ ^[9], and the rate constant of post-cure reaction is about $0.00046\text{--}0.000725\text{ s}^{-1}$. This means that the rate of the EB curing reaction is correspondingly higher than that of the post-cure reaction of the same resin system. Because the reactive functional group absorbs the energy of the electron from the accelerator and is in an excitable state during EB curing, these reactive groups more easily participate in the curing reaction.

CONCLUSIONS

The kinetics of the post-cure of cationic epoxy irradiated by an electron beam follows a first order reaction. The post-cure reaction rate constant is elevated with the increase of post-cure temperature of the cationic epoxy. At the same time, the post-cure reaction rate constant is smaller than the electron beam curing reaction rate constant.

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