Plasticization and antiplasticization effects of sulphonium salt initiator fragments remaining in cycloaliphatic epoxy resins cured by electron beam and ultraviolet irradiation

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Molecular motions and the glass transition temperature (T_g) of electron beam (EB) cured cycloaliphatic epoxy resins were found to be significantly different from those of ultraviolet (u.v.) cured resins by using high-resolution solid-state nuclear magnetic resonance and dynamic mechanical measurements. The resins used were polymerized with an aromatic sulphonium salt initiator. Dependence of initiator concentration on spin-lattice relaxation time in the rotating frame revealed that the initiator fragments remaining in the EB cured samples act as antiplasticizer and plasticizer below and above 3 wt% initiator concentration, respectively. The dependence in the u.v. cured samples is also similar, but the critical initiator concentration is 1 wt%. This finding means that the unexpected effect, namely antiplasticization, is less in the EB cured samples than in the u.v. cured samples at the initiator concentration in commercially available samples ($\sim$1 wt%). In addition, the EB cured samples exhibit smaller T_g depression due to the antiplasticization–plasticization effect than the u.v. cured samples. Both the higher critical initiator concentration and the smaller T_g depression for the EB cured samples than for the u.v. cured samples are attributed to the lower concentration of the fragments remaining in the EB cured samples confirmed by their cross-polarization/magic angle spinning spectra.

(Keywords: solid-state ^{13}C n.m.r.; epoxy resin; EB cure; u.v. cure; plasticization; antiplasticization)

INTRODUCTION

Since ultraviolet (u.v.) irradiation induces cationic polymerization of epoxy resins by adding aromatic sulphonium salts possessing a non-nucleophilic anion, these sulphonium salts have been developed for photoinitiators of rapid curable epoxy resin systems[1–3]. Furthermore, electron beam (EB) irradiation has been reported to induce the epoxy polymerization with the sulphonium salts[4]. The starting materials (mixtures of epoxy resins and photoinitiators) of the EB cured epoxy resin systems are the same as those of the u.v. cured epoxy resin systems. Thus, the characterization of their cured resins should clarify the influence of the type of curing process on their chemical structures and physical properties.

We have reported previously that the dynamic mechanical properties and molecular motions of cycloaliphatic epoxy resins cured by u.v.-induced sulphonium salt initiator depend on the concentration of the initiator[5,6]. Glass transition temperatures (T_gs) of the u.v. cured samples decrease with an increase in the initiator concentration. In addition, the solid-state ^{13}C nuclear magnetic resonance (n.m.r.) relaxation data revealed that the cyclohexyl ring motion of the u.v. cured samples is suppressed as the initiator concentration increases in the range of 0.1–1 wt%, but is promoted with concentrations above 1 wt%, indicating the antiplasticization and plasticization effects, respectively, of the initiator fragments remaining in the samples. Therefore, our studies reported here are aimed at comparing the structures (both static and dynamic) of the EB cured epoxy resins with those of the well-characterized u.v. cured epoxy resins.

In this paper, the u.v. and EB cured cycloaliphatic epoxy resins are investigated in some detail using high-resolution solid-state ^{13}C n.m.r. and dynamic mechanical measurements. The T_g values and some solid-state ^{13}C n.m.r. relaxation times are measured for the u.v. and EB cured epoxy resins in order to study the dependence of the concentration of the photoinitiator added. In other words, plasticization and antiplasticization effects of the initiator fragments are discussed in terms of the curing procedures as well as the initiator concentration.

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EXPERIMENTAL

Materials

Cycloaliphatic epoxy monomer, 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate (ECC), and photoinitiator, triphenylsulphonium hexafluoroantimonate (TPSHA), were supplied from Union Carbide and 3M Company, respectively, and were used without further purification. Mixtures of the epoxy monomer and the photoinitiator were prepared with various initiator concentrations between 0.5 wt% and 5 wt%.

U.v. curing procedures

A mixture of ECC and TPSHA was poured into a u.v.-transparent mould consisting of a pair of 5 mm thick quartz glass plates and a 1 mm thick silicone rubber spacer, and then was irradiated with a 300 W high pressure Hg lamp for 1 h. The distance between the lamp and the sample was set to 15 cm. The u.v.-irradiated sample was post-cured in an oven at 120°C for 1 h and then at 150°C for 1 h.

EB curing procedures

A mixture of ECC and TPSHA was sandwiched between a pair of 100 μm thick poly(ethylene terephthalate) films. The thickness of the liquid sample was $\sim$150 μm. The sandwiched sample was irradiated with EB by a 60 cm wide multi-linear filament type accelerator (Cureton, Nissin High Voltage Co. Ltd) at an acceleration voltage of 300 kV and a beam current of 30 mA. The conveyor speed was set to 15 m min^{-1}. The dose per pass was 50 kGy under these irradiation conditions. The samples were passed under the EB irradiation 5, 6, 6, 8 and 10 times for TPSHA concentrations of 4.8, 2.9, 2.0, 1.0 and 0.5 wt%, respectively, in order to obtain tack-free cured films. The EB-irradiated sample was post-cured in an oven at 120°C for 1 h and then at 150°C for 1 h.

High-resolution solid-state ^{13}C n.m.r. measurements

The ^{13}C cross-polarization[7,8]/magic angle spinning[9,10] (CP/MAS) n.m.r. spectra were measured at a ^{13}C resonance frequency of 67.9 MHz on a Jeol GSX-270 spectrometer with a variable temperature CP/MAS accessory. Typical spectra were obtained using 27 kHz spectral width, 8 k data points, 1 ms contact time, 5 s pulse duration and 2000 accumulations at room temperature. The cured sample was packed in a cylindrical ceramic rotor. A spinning rate of 5.0–5.5 kHz was used for MAS. Typical 90° pulse widths and spin-lock fields were 4.1 μs and 60 kHz, respectively. Chemical shifts were calibrated through the methylene ^{13}C signal of adamantane (29.5 ppm) relative to tetramethylsilane.

The ^{13}C spin-lattice relaxation time (T_1^C) measurements were performed using Torchia's pulse sequence[11]. Delay times between ^{13}C 90° pulses ranged from 0.1 to 15 s. The ^{13}C spin-lattice relaxation time in the rotating frame ($T_{1\rho}^C$) was obtained using standard procedures[12]. Delay times after the ^1H radio-frequency field was removed ranged from 1 to 10 ms.

Dynamic mechanical measurements

The complex Young's moduli, E^* ($= E' + iE''$), of the cured samples were obtained with a Rheometrics RSA-2 solid analyzer at 1 Hz at 5°C intervals in a temperature range from 50 to 250°C. The temperature was raised stepwise, 5°C for every 30 s. The T_g value was defined as the temperature of maximum tan δ ($= E''/E'$).

RESULTS AND DISCUSSION

The ^{13}C CP/MAS n.m.r. spectra of the u.v. and EB cured samples are shown in *Figure 1*. The spectra of the u.v. cured samples at TPSHA concentrations of 2.0 and 4.8 wt% are given in *Figures 1a* and *b*, respectively, and are compared with those of the EB cured samples in *Figures 1c* and *d*, respectively. The n.m.r. signal assignments of the CP/MAS spectra were made on the basis of the solution ^{13}C n.m.r. resonance assignments for the corresponding monomer[13]. Broad resonances at 110–150 ppm, which are absent in the solution spectra of ECC, were attributed to the TPSHA fragments remaining in the cured samples. The main compounds produced by the photolysis of TPSHA are diphenylsulphide, benzene and Brønsted acid[14]. Both u.v.- and EB-irradiated samples were post-cured at 120°C and then at 150°C, hence volatile compounds are unlikely to remain in the sample. Non-volatile products, however, should remain even after post-curing, and thus their resonances appear in the CP/MAS spectra. As a result,

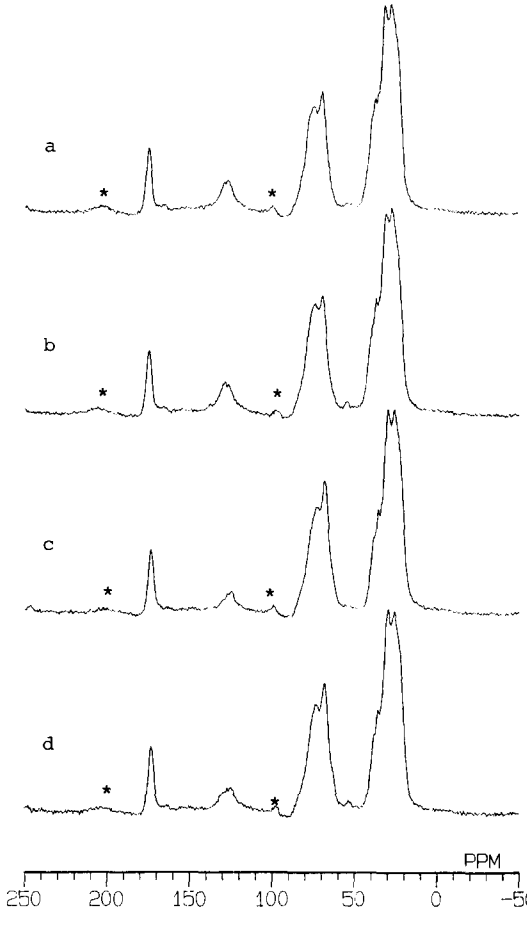

Figure 1 ^{13}C CP/MAS n.m.r. spectra of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate cured by u.v.- and EB-induced cationic polymerization: (a) u.v. cured sample of ECC/TPSHA = 100/2; (b) u.v. cured sample of ECC/TPSHA = 100/5; (c) EB cured sample of ECC/TPSHA = 100/2; (d) EB cured sample of ECC/TPSHA = 100/5. Spinning side bands are marked with asterisks

the resonances at 110–150 ppm are assigned to, mainly, the unsaturated carbons of diphenylsulphide.

The conversion of the samples calculated from the intensity ratio of the resonance at 55 ppm, which was assigned to unreacted epoxy carbons, to those at 60–90 ppm in the CP/MAS spectra[6] is >97% in all samples. Since no significant difference in the spectral features, except the signal intensity of the resonance arising from the TPSHA fragments, was detected among the traces in *Figure 1*, we concluded that there is no significant difference in the chemical structures of the epoxy polymers produced irrespective of the TPSHA concentration or the type of curing process.

The integral intensity ratios of the resonances at 110–150 ppm to those at 10–90 ppm are 0.074 and 0.052 in the CP/MAS spectra of the u.v. and EB cured samples, respectively, at a TPSHA concentration of 4.8 wt%. Since the irradiation energy of EB is considerably higher than that of u.v., secondary and tertiary photoproducts, which possess smaller molecular weights than the first photoproducts and consequently should diffuse out from the sample during post-curing, are likely to be formed by EB irradiation. Hence, for a given TPSHA concentration, the concentration of the TPSHA fragments remaining in the EB cured sample is expected to be smaller than that in the u.v. cured sample. Since the physical properties of the u.v. cured epoxy resins were previously found to depend on the concentration of the TPSHA fragments remaining in the sample[5], the physical properties of the samples should significantly depend on the type of the curing process.

The T_g values of the u.v. and EB cured samples are plotted against TPSHA concentration in *Figure 2*. The T_g value decreases with an increase in the TPSHA concentration in both u.v. and EB cured samples due to the diluent effect of the TPSHA fragments remaining in the samples. However, the EB cured samples exhibit smaller T_g depression than the u.v. cured samples. Additionally, for a given TPSHA concentration, the T_g value of the former is higher than that of the latter in spite of the same source and composition. The lower

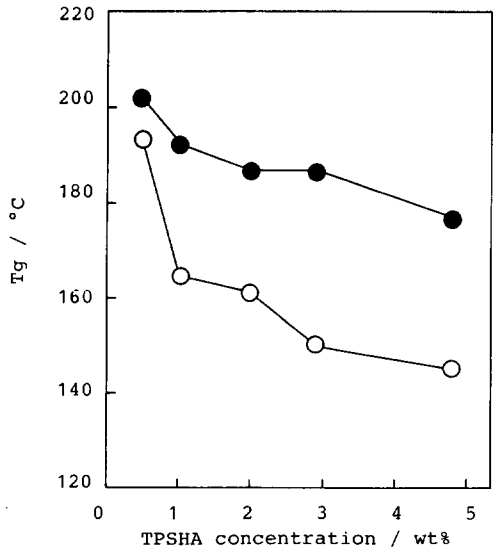

Figure 2 TPSHA concentration dependence of the T_g of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate cured by u.v. (○)- and EB (●)-induced cationic polymerization

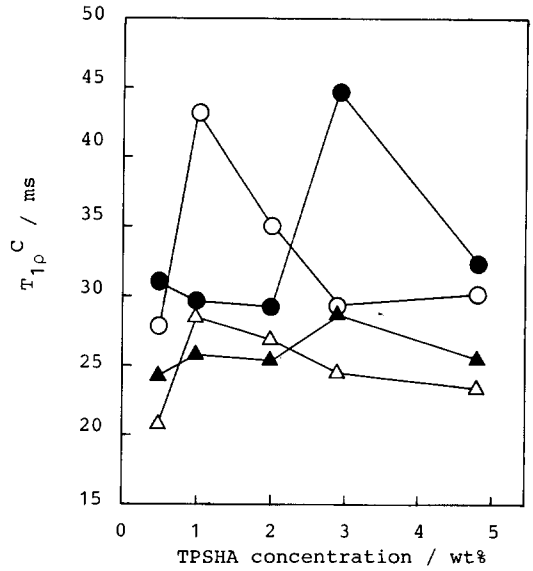

Figure 3 TPSHA concentration dependence of the ^{13}C spin-lattice relaxation time in the rotating frame ($T_{1\rho}^C$) of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate cured by u.v.- and EB-induced cationic polymerization: u.v. cured samples, 10–50 ppm (△); u.v. cured samples, 60–90 ppm (○); EB cured samples, 10–50 ppm (▲); EB cured samples, 60–90 ppm (●)

concentration of the TPSHA fragments remaining in the EB cured sample than in the corresponding u.v. cured sample, which was confirmed by the CP/MAS spectra, should lead to less depression of the T_g in the former.

Molecular motions in the u.v. and EB cured samples were investigated using T_1^C and $T_{1\rho}^C$ measurements. A mean relaxation time calculated from the variation of integral intensity of the whole resonance at 10–50 ppm or 60–90 ppm was found to reflect the molecular motions of the cyclohexyl ring moieties in the cured ECC samples[6]. We confirmed from $T_{1\rho}^C$ measurements using a variety of spin-lock field strengths[15] that the $T_{1\rho}^C$ values of the cured samples are dominated by the spin-lattice rather than the spin-spin relaxation process under a decoupling frequency of 60 kHz. In addition, variable temperature experiments indicated that molecular motions in the cured samples at room temperature are in the slow motion regime relative to both T_1 and $T_{1\rho}$ minima in the curves from Bloembergen–Purcell–Pound (BPP) theory[16]. Thus any increase in T_1^C or $T_{1\rho}^C$ indicates a decrease in mobility.

The $T_{1\rho}^C$ values of the u.v. and EB cured samples are plotted against TPSHA concentration in *Figure 3*. The increase and then decrease in $T_{1\rho}^C$, i.e. the decrease and then increase in the mobility of the cyclohexyl ring moieties, were observed with an increase in TPSHA concentration in both u.v. and EB cured samples. This TPSHA concentration dependence on $T_{1\rho}^C$, accompanied by a monotonous decrease in T_g, indicates the antiplasticization–plasticization effect of the TPSHA fragments remaining in the samples. The TPSHA fragments act as antiplasticizer below 1 wt% TPSHA concentration while they act as plasticizer above 1 wt% in the u.v. cured samples. The TPSHA fragments in the EB cured samples also exhibit a similar effect, but the critical initiator concentration is 3 wt%. The higher critical initiator concentration of the EB cured samples than for the u.v. cured samples should be attributed to the fact that the concentration of the TPSHA fragments,

which affects the molecular motions, is smaller in the former than in the latter. Maximum $T_{1\rho}^{C}$ values observed for the ether and ring moieties in the EB cured samples (3 wt% TPSHA) are almost equal to the corresponding values in the u.v. cured samples (1 wt%). Thus, the molecular motions in the EB cured sample being the most antiplasticized are suppressed to almost the same extent as those in the u.v. cured sample being the most antiplasticized. Note that the T_g of the former is 23°C higher than that of the latter in spite of exhibiting almost equal $T_{1\rho}^{C}$, suggesting that the effect of the TPSHA fragments on the micro Brownian motions of the epoxy networks may be, to some extent, different from that on the cooperative motions of the cyclohexyl rings in the mid-kilohertz region. This suggestion is supported by the fact that T_g decreases with an increase in TPSHA concentration in the range of 0.5–2 wt% in the EB cured sample in spite of almost constant values for $T_{1\rho}^{C}$.

The T_1^C values of the u.v. and EB cured samples are plotted against TPSHA concentration in *Figure 4*. In the u.v. cured samples, a decrease in the molecular motions in the megahertz region was observed as the TPSHA concentration increased in the range of 0.5–2 wt%, while a slight increase in the molecular motions was observed as the TPSHA concentration increased in the range of 2–5 wt%, indicating the antiplasticization–plasticization effect of the TPSHA fragments. On the other hand, a monotonous increase in T_1^C, thus a suppression of only the molecular motions, was observed with an increase in TPSHA concentration in the EB cured samples. The T_1^C and $T_{1\rho}^{C}$ results indicate that the molecular motions in the mid-kilohertz and megahertz regions are the most suppressed at TPSHA concentrations of 1 and 2 wt%, respectively, in the u.v. cured samples. This suggests that the diluent effect of the TPSHA fragments in the cured samples depends not only on the TPSHA concentration but also, to some extent, on the observation frequency of the motions. The u.v. cured sample at a TPSHA concentration of 2 wt% is plasticized from the viewpoint of molecular motions in the mid-kilohertz region, while it is antiplasticized in the megahertz regime. A similar phenomenon was observed in the EB cured sample at a TPSHA concentration of 5 wt%.

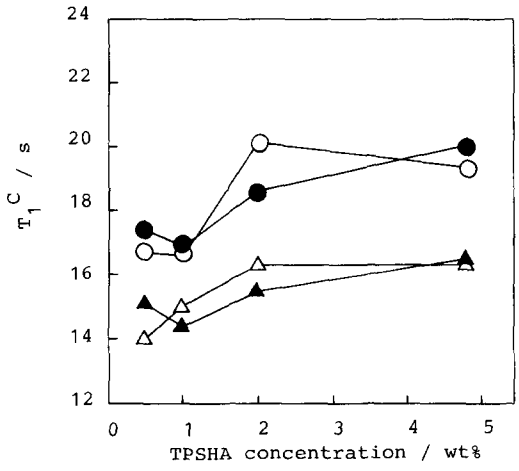

Figure 4 TPSHA concentration dependence of the ^{13}C spin-lattice relaxation time (T_1^C) of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate cured by u.v.- and EB-induced cationic polymerization: u.v. cured samples, 10–50 ppm (△); u.v. cured samples, 60–90 ppm (○); EB cured samples, 10–50 ppm (▲); EB cured samples, 60–90 ppm (●)

CONCLUSIONS

The EB and u.v. cured cycloaliphatic epoxy resins were investigated by high-resolution solid-state ^{13}C n.m.r. and dynamic mechanical measurements. The CP/MAS spectra of the cured samples indicate that their chemical structures are identical irrespective of the TPSHA concentration or the type of curing process used. However, for a given TPSHA concentration, the concentration of the TPSHA fragments remaining in the EB cured sample is smaller than in the u.v. cured sample. The T_g values decrease with an increase in TPSHA concentration in both u.v. and EB cured samples, however the EB cured samples exhibit a smaller T_g depression than the u.v. cured samples in spite of originating from the same source. The decrease and then increase in mobility of the cyclohexyl ring moieties accompanied by the monotonous decrease in T_g were observed with an increase in TPSHA concentration in both u.v. and EB cured samples, indicating the antiplasticization–plasticization effect of the TPSHA fragments remaining in the samples. The dependence of the TPSHA concentration on the $T_{1\rho}^{C}$ clarified that the TPSHA fragments act as antiplasticizer below 3 wt% TPSHA concentration and act as plasticizer above 3 wt% in the EB cured samples. The TPSHA fragments in the u.v. cured samples also exhibit a similar effect, but the critical initiator concentration is 1 wt%. This finding means that the unexpected effect, namely antiplasticization, is less in the EB cured samples than in the u.v. cured samples at the initiator concentration in commercially available samples (~1 wt%). In conclusion, the physical properties of the EB cured samples are found to be significantly different from those of the corresponding u.v. cured samples.

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