Dynamic mechanical properties of cycloaliphatic epoxy resins cured by ultra-violet- and heat-initiated cationic polymerizations

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The dynamic mechanical properties and impact resistance of cycloaliphatic epoxy resins cured by ultra-violet- and heat-induced sulphonium salt initiators were found to depend on the type and concentration of initiator. The glass transition temperatures of both u.v.- and heat-cured samples decrease with increase in initiator concentration owing to the plasticization effect of initiator fragments remaining in the samples. The β relaxation, observed in all samples around −80°C at 1 Hz, was found to be due to molecular motions of the cyclohexyl rings. Slight suppression of this relaxation was observed only in the u.v.-cured system consisting of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate (ECC) and triphenylsulphonium hexafluoroantimonate (TPSHA), and was attributed to antiplasticization due to the decomposed TPSHA. The above findings lead to the conclusion that the u.v.-cured ECC system is more brittle than the heat-cured ECC system.

(Keywords: cycloaliphatic epoxy resin; latent curing agent; ultra-violet cure; dynamic mechanical properties; impact resistance; high-resolution solid-state ^{13}C nuclear magnetic resonance spectroscopy; plasticization)

INTRODUCTION

Latent curing agents have been developed that are mixed with epoxy resins beforehand, and the curing reaction is then triggered off by heat, light, humidity or pressure. In particular, u.v.-curable epoxy resin systems[1,2] have been investigated for use as rapidly curable coatings. Typical photoinitiators for cationic polymerization of epoxy resins are aromatic onium salts possessing a non-nucleophilic anion such as PF_6^-, SbF_6^-, AsF_6^- or BF_4^-. Triarylsulphonium salts[3–7] are considered to be one of the best photoinitiators because of their ability to absorb u.v. light over a wide wavelength range as well as their good heat stability and long shelf life.

Recently, aliphatic onium salts have been developed as a heat-induced initiator for epoxy cationic polymerization[8]. Carbenium ions are first produced from the thermal decomposition of these initiators and then initiate the ring-opening polymerization of epoxy groups. The epoxy resins cured by u.v.- and heat-initiated cationic polymerization consist of the epoxy homopolymers themselves, whereas conventional two-part epoxy resins consist of epoxy–hardener copolymers. Therefore, the molecular motions of the epoxy homopolymers can be characterized from the dynamic mechanical properties of the u.v.- or heat-cured epoxy resins.

A marked effect of initiator concentration on the cure rate of an epoxide has been reported[1–3]. The maximum u.v. cure rate of a cycloaliphatic epoxy resin is obtained with 2–3 wt% aromatic onium salts. The u.v. curing is relatively slow at concentrations below 1 wt%. At a concentration above 3 wt%, there is no further increase in the rate. The maximum rate of heat curing is also obtained with 1.5–3 wt% aliphatic sulphonium salts[8]. On the other hand, the effect of initiator concentration on the physical properties of the cured epoxy resins has not been investigated in detail. Fragments generated from initiator decomposition remain in the cured resins after curing, and thus the amount of the resulting ‘impurity’ should increase with increase in the concentration of initiator added. From a comparison of the physical properties of the u.v.- and heat-cured epoxy resins, we have characterized the effect of initiator fragments on the physical properties of cured epoxy resins.

In this report, several cycloaliphatic epoxy resins cured by u.v.- and heat-induced cationic polymerizations were investigated using dynamic mechanical and impact resistance measurements and high-resolution solid-state ^{13}C n.m.r. spectroscopy. The fragments generated from the decomposition of the sulphonium salt initiators used here were found to lower the glass transition temperature T_g of the epoxy resins. In particular, decomposed triphenylsulphonium salt was found to act as an antiplasticizer in the u.v.-cured system of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate and makes this cured epoxy resin more brittle than the corresponding heat-cured epoxy resin.

EXPERIMENTAL

Materials

The cycloaliphatic epoxy resins, 4-vinylcyclohexene

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oxide (VCO), 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexene carboxylate (ECC) and 3,4-epoxycyclohexyl adipate (EA), were supplied by Union Carbide and were used without further purification. The photoinitiator, triphenylsulphonium hexafluoroantimonate (TPSHA), and the heat-induced initiator, aliphatic sulphonium (CP66), were supplied by 3M and Asahi Denka, respectively. Mixtures of the epoxy resin and the photoinitiator or heat initiator were prepared in various initiator concentrations, 0.5–5 wt%.

U.v. curing procedures

A mixture of the epoxy resin 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 was then 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.

Heat curing procedures

A mixture of the epoxy resin and CP66 was poured into a mould consisting of a pair of Teflon-coated glass plates and a 1 mm thick silicone rubber spacer, and was cured in an oven at 120°C for 1 h and then at 150°C for 1 h.

Dynamic mechanical measurements

The complex Young's moduli E^* ($=E'+iE''$) of the cured samples were obtained with a Rheometrics RSA-2 solid analyser at 1 Hz at 5°C intervals in the temperature range from -150 to 250°C. Temperature was raised step by step, set to 5°C and 30 s for the temperature step and the soaking time at constant temperature, respectively. The bending test was carried out using bar-shaped samples, $50\times6\times1$ mm^3, set on the dual cantilever bending fixture with 0.1% strain. The T_g value was defined as the temperature of maximum $\tan\delta$ ($=E''/E'$).

D.s.c. measurements

Differential scanning calorimetry (d.s.c.) was carried out with a modified calorimeter. A modified d.s.c. system consisting of a Perkin Elmer DSC-4 differential scanning calorimeter and a Macam Photometrics Flexicure model UVLS102 u.v. light source (Philips HPA400 Hg lamp), referred to as photo-d.s.c.[9–14], was used for the measurements. U.v. light was guided through two light pipes leading to the sample and reference cells of the calorimeter. The light intensity at the cells was approximately 1 mW cm^{-2} at a wavelength of 350 nm. The photo-d.s.c. data were acquired for 25 min at 40°C under continuous u.v. irradiation. After the photo-d.s.c. measurement, a conventional thermal scan was carried out successively at a heating rate of 20°C min^{-1} in the temperature range from 40 to 250°C. Only the thermal scan was carried out for the heat-curable samples.

The integrated peak intensities of the photo-d.s.c. and the following d.s.c. thermograms were calculated with the DSC-4 data processor, and were represented as the heat of photoreaction, ΔH_P, and the heat of post-curing reaction, ΔH_{PC}, respectively. The total heat of reaction, ΔH_T, was calculated as the sum of the two terms: $\Delta H_T=\Delta H_P+\Delta H_{PC}$.

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

The ^{13}C cross-polarization[15,16]/magic-angle spinning[17,18] (c.p./m.a.s.) spectra were measured at the ^{13}C resonance frequency of 67.9 MHz on a JEOL GSX-270 spectrometer with a c.p./m.a.s. accessory. Typical spectra were obtained using 27 kHz spectral width, 8000 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. The spinning rate of 5.1–6.0 kHz was used for m.a.s. Typical 90° pulse width and spin-lock field 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.

Impact resistance measurements

Before the measurements, the sample was coated with a 0.3 mm applicator on a mild steel substrate (2 mm thick, JIS-G-3141, SPCC-B), which was treated with no. 320 sandpaper and cleaned with acetone, and was cured by the u.v./heat curing procedures. The impact resistance was measured by the falling-ball method according to ASTM-D-3451. A 4 lb ($\simeq$1.8 kg) weight with a round tip was dropped onto the coating sample from various heights, and the maximum height where the coating did not crack at all was recorded.

RESULTS AND DISCUSSION

Heat of reactions

The values of ΔH_P and ΔH_T obtained from the d.s.c. analyses are listed in *Table 1* for the u.v.- and heat-curable samples. Both ΔH_P and ΔH_T were found to be independent

Table 1 Heats of reaction and impact resistance of cycloaliphatic epoxy resins cured by u.v.- and heat-initiated cationic polymerizations

Epoxy resin	Initiator	Initiator composition (wt%)	ΔH_P (J g^{-1})	ΔH_T (J g^{-1})	Impact resistance[a] (cm)
VCO	TPSHA	2.0	37.8	50.5	–
ECC	TPSHA	2.0	13.1	27.5	5
EA	TPSHA	2.0	5.1	16.9	>100
VCO	CP66	1.5	–	54.6	–
ECC	CP66	1.5	–	34.0	40
EA	CP66	1.5	–	23.6	>100

[a] According to ASTM-D-3451

of initiator concentration above 1 wt% (results not shown); thus a typical composition was chosen in each epoxy/initiator system. The order of increasing ΔH_T values is VCO > ECC > EA in both u.v.- and heat-curable systems, and this order can be interpreted in terms of the epoxy equivalent weights of the samples (75, 137 and 205 for VCO, ECC and EA, respectively). The ΔH_T values of the heat-curable samples are always larger than those of the corresponding u.v.-curable samples in spite of the full cure of both samples confirmed by the c.p./m.a.s. spectra (results not shown). This may be attributed, to some extent, to loss of heat through the light pipes during the photo-d.s.c. measurements. The ratios $\Delta H_P/\Delta H_T$ are 0.75, 0.48 and 0.30 for VCO, ECC and EA in the u.v.-curable samples, respectively, indicating not only the highest photoreactivity of the VCO/TPSHA system but also the important role of the post-curing process for complete curing of u.v.-curable epoxy resin systems.

Cure characteristics

All samples of VCO/CP66 and most samples of VCO/TPSHA were cracked during the curing process. These are general observations for epoxy resins because of their brittleness and their contraction on polymerization. Consequently, only VCO/TPSHA = 100/2 among all the VCO samples prepared can be used for the dynamic mechanical measurements. On the contrary, all samples of ECC and EA were uncracked.

Dynamic mechanical properties of u.v.-cured epoxy resins

In *Figure 1* are shown curves of the storage moduli (E') and loss tangents ($\tan\delta$) of the u.v.-cured samples in the temperature range from −150 to 250°C. The modulus of the VCO/TPSHA system falls gradually with temperature during the glass transition, while that of the EA/TPSHA system drops steeply. The VCO molecule possesses two different epoxy groups, i.e. ethylene oxide and cyclohexene oxide moieties, while the EA molecule possesses two identical epoxy groups owing to its symmetrical molecular structure. The difference in molecular structure may cause a wider distribution of molecular weight between crosslinks (M_c) for the former epoxy resin than for the latter. Since a broader temperature range of the glass transition has been reported[19] to reflect a wider distribution of M_c, the difference in the temperature range of the glass transition observed for these epoxy samples is interpretable in terms of a difference in their M_c distributions.

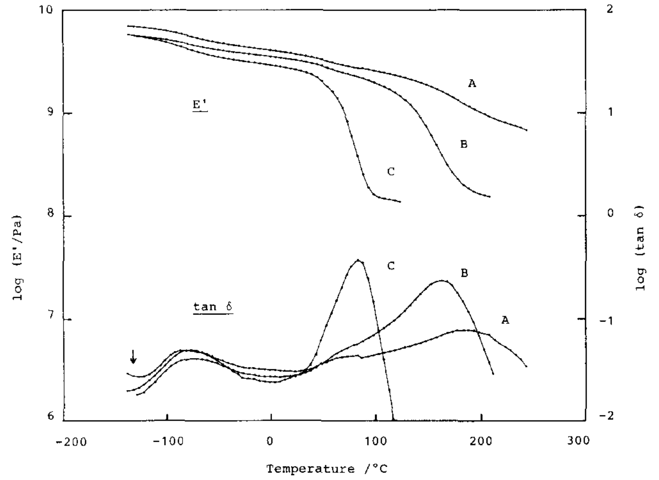

Figure 1 Temperature dependence of the Young's storage moduli (E') and loss tangents ($\tan\delta$) for cycloaliphatic epoxy resins cured by u.v.-initiated cationic polymerizations: A, VCO/TPSHA = 100/2; B, ECC/TPSHA = 100/2; C, EA/TPSHA = 100/2

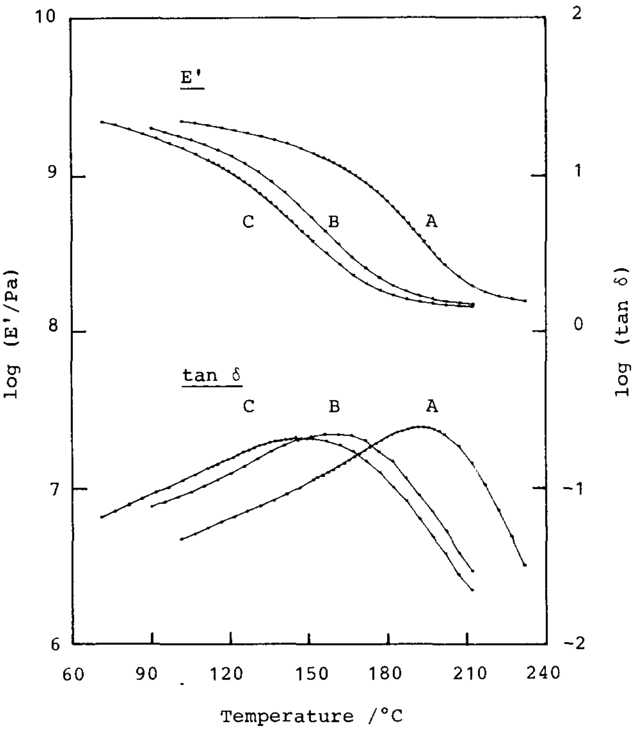

Figure 2 Temperature dependence of the Young's storage moduli (E') and loss tangents ($\tan\delta$) for cycloaliphatic epoxy resins cured by u.v.-initiated cationic polymerizations: A, ECC/TPSHA = 100/0.5; B, ECC/TPSHA = 100/2; C, ECC/TPSHA = 100/5

The EA/TPSHA system exhibits the smallest E' value in the glassy state and also the lowest T_g among the u.v.-cured samples studied here. The softest network structure in the EA/TPSHA system is attributed to the flexible butyl chain in the EA molecule. The tail of the relaxation peak that has been attributed to molecular motion of the butyl moiety[19] is recognized in the $\tan\delta$ curve of the EA/TPSHA system around −140°C (marked with an arrow).

The β relaxations are observed around −80°C in the $\tan\delta$ curves in *Figure 1*. The $\tan\delta$ curves for the β relaxation are similar to each other in these three samples except for a slight suppression for the ECC/TPSHA system. The latter finding suggests antiplasticization due to decomposed TPSHA (see below). The β relaxation of cyclohexyl methacrylate observed around −80°C at 1 Hz has been attributed to the chair–chair inversion of the side-chain of the cyclohexyl ring[19–22]. This relaxation has also been observed even if the cyclohexyl ring was introduced in the main chain of polymers[23]. Therefore, we conclude that the β relaxation observed here is due to molecular motions of the cyclohexyl rings in the cycloaliphatic epoxy resins.

Plasticization effect of initiator fragments remaining in cured epoxy resins

Figure 2 shows curves of E' and $\tan\delta$ of the u.v.-cured ECC/TPSHA system in the temperature range encompassing the glass transition. The E' and $\tan\delta$ curves shift to lower temperatures with increase of initiator concentration, though no significant difference in the spectral

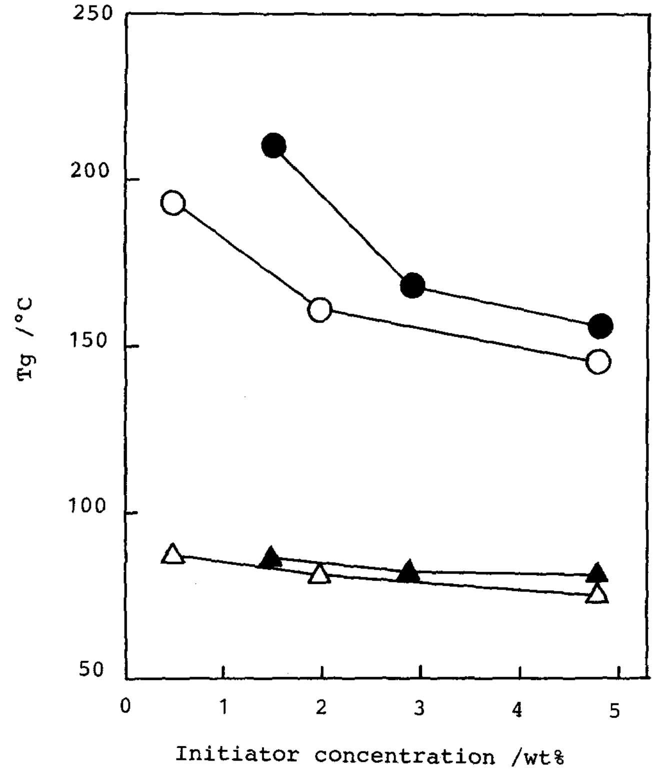

Figure 3 Initiator concentration dependence of the glass transition temperature for cycloaliphatic epoxy resins cured by u.v.- and heat-initiated cationic polymerizations: (○) ECC/TPSHA; (●) ECC/CP66; (△) EA/TPSHA; (▲) EA/CP66. The dynamic mechanical experiments were not carried out for the heat-cured samples with less than 1 wt% CP66 concentration owing to the incompleteness of curing

pattern was detected in the c.p./m.a.s. spectra for the cured samples with various initiator concentrations. In addition, the crosslink density calculated from the E' value in the rubbery state is almost constant irrespective of the initiator concentration. Therefore, this T_g shift is attributed to a plasticization effect due to initiator fragments remaining in the cured samples.

The T_g values of ECC/TPSHA, ECC/CP66, EA/TPSHA and EA/CP66 are plotted against initiator concentration in *Figure 3*. The T_g values decrease with increase in the initiator concentration, and hence the initiator fragments of TPSHA and CP66 act as plasticizers in the cycloaliphatic epoxy resins. In the u.v.-cured samples, the decomposed TPSHA, mainly $(C_6H_5)_2S$, acts as a plasticizer[24]. The chemical structure of CP66 has not been disclosed; however, aliphatic compounds containing a sulphur atom are candidates for the plasticizer in the heat-cured samples by analogy with TPSHA decomposition. The ECC samples exhibit a larger T_g depression than the EA samples in spite of a similarity in the chemical structures of ECC and EA. The cured EA samples are flexible in themselves, and thus are almost independent of the plasticization.

Comparison of u.v.- and heat-cured epoxy resins

The c.p./m.a.s. spectra of the u.v.- and heat-cured samples are shown in *Figure 4*. The broad resonances of the spectra were attributed to the heterogeneous chemical environments due to the crosslinked network structure of the cured epoxy polymers[25]. The signal assignments were done on the basis of solution ^{13}C n.m.r. assignments of ECC and EA[26]. No significant difference in the peak shapes and the chemical shifts was detected between the traces A and B, and between C and D, except for the resonance arising from initiator fragments. This indicates the identical chemical structure of the u.v.- and heat-cured epoxy polymers.

Figure 5 shows curves of E' and tan δ of the u.v.-cured ECC/TPSHA system and the heat-cured ECC/CP66 system in the temperature range from -150 to 250°C. The dynamic mechanical properties of these u.v.- and heat-cured samples are different from each other in spite of their identical chemical structure confirmed by the c.p./m.a.s. spectra. The T_g value of the ECC/TPSHA system is 40°C lower than that of the ECC/CP66 system, indicating a stronger influence of decomposed TPSHA than CP66.

The β relaxation in the ECC/TPSHA system is slightly suppressed compared with that in the ECC/CP66 system. The suppression of the local-mode relaxation of polymers by addition of a low-molecular-weight diluent is known as antiplasticization[27–29]. Since a diluent that is a planar molecule possessing ring moieties has been reported to act as a strong antiplasticizer[30], $(C_6H_5)_2S$ is considered

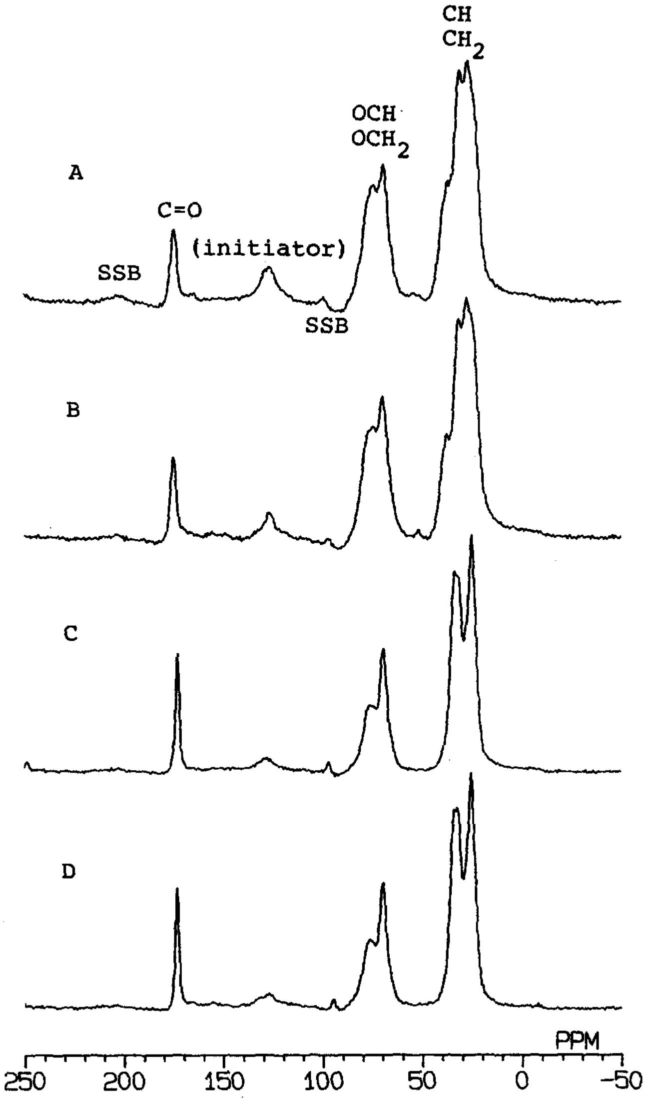

Figure 4 ^{13}C c.p./m.a.s. spectra of cycloaliphatic epoxy resins cured by u.v.- and heat-initiated cationic polymerizations: A, ECC/TPSHA = 100/2; B, ECC/CP66 = 100/1.5; C, EA/TPSHA = 100/2; D, EA/CP66 = 100/1.5

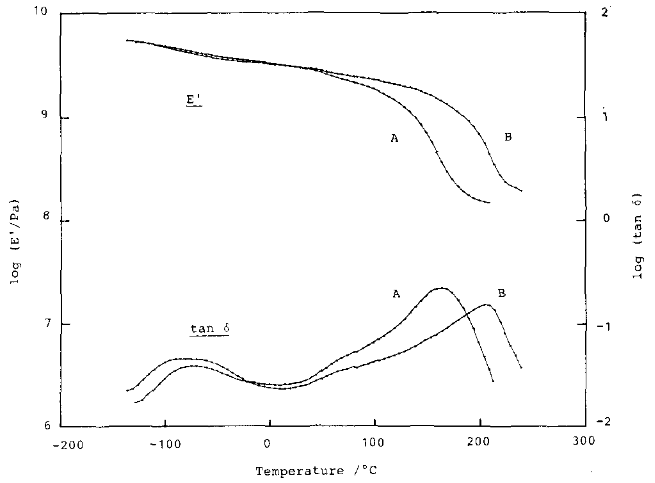

Figure 5 Temperature dependence of the Young's storage moduli (E') and loss tangents (tan δ) for cycloaliphatic epoxy resins cured by u.v.- and heat-initiated cationic polymerizations: A, ECC/TPSHA = 100/2; B, ECC/CP66 = 100/1.5

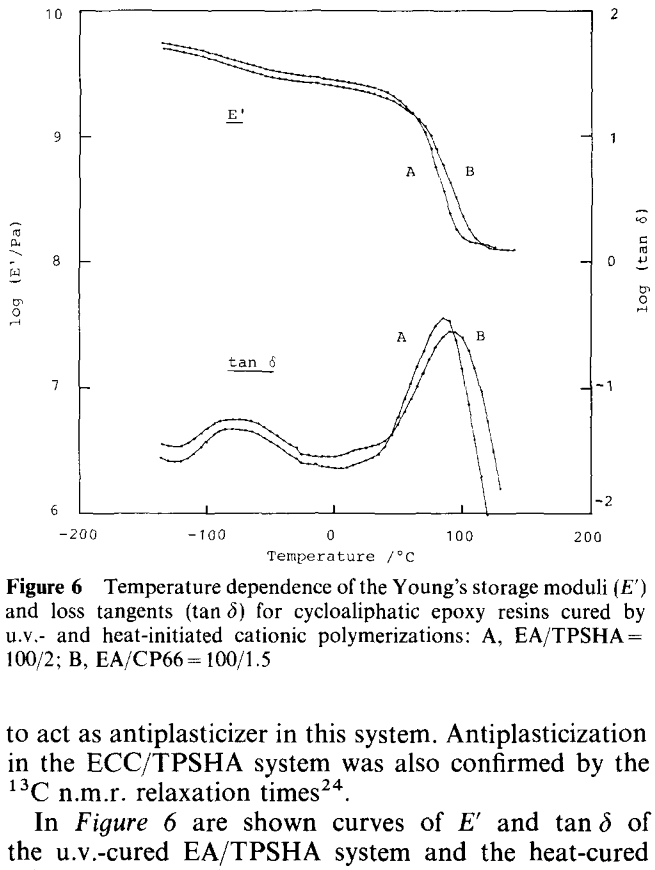

Figure 6 Temperature dependence of the Young's storage moduli (E') and loss tangents (tan δ) for cycloaliphatic epoxy resins cured by u.v.- and heat-initiated cationic polymerizations: A, EA/TPSHA = 100/2; B, EA/CP66 = 100/1.5

to act as antiplasticizer in this system. Antiplasticization in the ECC/TPSHA system was also confirmed by the ^{13}C n.m.r. relaxation times[24].

In *Figure 6* are shown curves of E' and tan δ of the u.v.-cured EA/TPSHA system and the heat-cured EA/CP66 system in the temperature range from −150 to 250°C. Contrary to the behaviour of the ECC samples described above, the dynamic mechanical properties of the two EA samples are almost identical. No suppression of the β relaxation is observed in both samples. However, the tan δ curve of EA/TPSHA shifts slightly towards lower temperature than that of EA/CP66 in the glass transition region, indicating a stronger influence of decomposed TPSHA.

The results of the impact resistance measurements of the u.v.- and heat-cured samples are listed in *Table 1*. The results for the VCO samples are missing in the table because all of them cracked during curing. Both EA samples exhibit such high impact resistance that the coatings were never broken in the experiments. The 'soft' butyl chain in the EA molecule should result in the flexibility of its cured samples. On the other hand, a significant difference in impact resistance is observed between the ECC/TPSHA and ECC/CP66 samples. The ECC/TPSHA sample is much more brittle than the ECC/CP66 sample in spite of no significant difference being detected in their c.p./m.a.s. spectra. Since the impact resistance of a polymer is known to depend on the intensity of the dynamic mechanical relaxation below room temperature[19], the suppression of the β relaxation should lead to the ECC/TPSHA sample being more brittle.

CONCLUSIONS

Cycloaliphatic epoxy resins cured by u.v.- and heat-induced initiators for cationic polymerization were investigated by d.s.c., dynamic mechanical and impact resistance measurements and by high-resolution solid-state ^{13}C n.m.r. spectroscopy. The d.s.c. analyses of the u.v.-curable samples indicate the important role of the post-curing process for complete curing.

The temperature range of the glass transition is in the order VCO > ECC > EA for the u.v.-cured samples, which is interpretable in terms of their M_c distributions. The EA sample possesses the softest network structure owing to the flexible butyl chain in the molecule. The β relaxation is found around −80°C at 1 Hz in all tan δ curves and is attributed to molecular motions of the cyclohexyl rings.

The T_g values of both u.v.- and heat-cured samples decrease with an increase in the initiator concentration owing to the plasticization effect of the initiator fragments remaining in the samples. The cured ECC samples exhibit larger T_g depression than do the EA samples.

The dynamic mechanical properties of the u.v.-cured ECC/TPSHA system are significantly different from those of the heat-cured ECC/CP66 system, but no significant difference in the spectral patterns was detected by their c.p./m.a.s. spectra. The T_g value of the ECC/TPSHA system is 40°C lower than that of the ECC/CP66 system. The β relaxation in the ECC/TPSHA system is slightly suppressed, indicating the antiplasticization effect of the decomposed TPSHA. Therefore, the ECC/TPSHA system is more brittle than the ECC/CP66 system.

In conclusion, the physical properties of the cycloaliphatic epoxy resins, particularly ECC, cured by u.v.- or heat-induced initiators are found to depend on, and thus may be controlled by, the type and concentration of the initiators.

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