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Dynamic mechanical and Fourier-transform infra-red analyses on the very late stage of the cure process in thermoset/thermoplastic blends: trifunctional epoxy/poly(ether sulfone)

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The changes in physical and chemical states with time at the very late stage of the cure process in a thermoset/thermoplastic blend, triglycidyl *p*-aminophenol (epoxy)/poly(ether sulfone) (PES)/4,4′-diaminodiphenylsulfone (curing agent), were investigated by dynamic mechanical analysis (d.m.a.) and Fourier-transform infra-red analysis (*FT*i.r.). D.m.a. showed the two-phase character: two-step decrease in the dynamic storage modulus E' *versus* temperature curve and two peaks in the dynamic loss $\tan\delta$ *versus* temperature curve, indicating phase separation via reaction-induced spinodal decomposition (which was confirmed by scanning electron microscopic observation). The low-temperature $\tan\delta$ peak assigned to the T_g of the PES-rich phase was elevated and the high-temperature peak assigned to the T_g of the epoxy-rich phase was depressed with increasing cure time. The inward shift of the two T_g values was quite strange. This strange shift was interpreted by taking account of the segregation of epoxy oligomer from crosslinked epoxy network in the neat epoxy system (probably by micro-gel formation) and the chain scission of the epoxy network established via etherification. That is, the low T_g of PES/epoxy oligomer mixture shifts to a higher temperature to attain the T_g of neat PES by converting the oligomer to the network, and the high T_g of the segregated pure epoxy network shifts to lower temperature by chain scission.

(Keywords: blend curing; epoxy resin; poly(ether sulfone))

INTRODUCTION

When epoxy resin is cured with amine, the chemistry consists of three principal reactions: epoxide–primary amine addition, epoxide–secondary amine reaction and epoxide–hydroxyl reaction (etherification)[1–3]; and the consequent chain extension, branching and crosslinking[4–7]. Such chemical reactions cause a complicated change in the physical state, from a viscous liquid to a gel and eventually to a vitrified material.

When thermoplastic polymers (e.g. poly(ether sulfone) (PES) and polycarbonate) are incorporated to improve the toughness of epoxy resin[8–13], the cure process becomes much more complicated. In a thermoset/thermoplastic blend, starting from a homogeneous mixture, the system is thrust into a two-phase regime by the increase in molecular weight of epoxy at the early stage of curing, and spinodal decomposition takes place to provide a regularly phase-separated structure[14]. The structure is fixed by gelation or vitrification at the late stage of curing. Thus, the cure process of a thermoplastic/thermoset system involves various transformations: the sol–gel transition, the liquid–liquid phase transition from single-phase to two-phase system, and vitrification by the increase of the glass transition temperature with increase of molecular weight and crosslink density. Such transformations can be monitored by combining time-resolved light scattering, dynamic viscoelastic analysis and torsional braid analysis. Actually, we recently established a new *TTT* (time–temperature–transformation) cure diagram for tetrafunctional epoxy/PES[15]. The *TTT* cure diagram describes the onset of phase decomposition, gelation, vitrification, the fixation of phase-separated structure and the end of phase separation as functions of cure temperature and cure time.

An example of the transformations in a thermoset/thermoplastic blend is shown in *Figure 1*. One can see a series of transformations on a time–conversion curve: onset of phase separation, gelation, fixation of phase-separated structure, end of phase separation and vitrification. Note here that vitrification takes place at a conversion of ca. 80%, i.e. less than 100%. This implies that some chemistry will go on after vitrification and it will impose some change in physical state with time after vitrification. [Vitrification is caused by the increase of the glass transition temperature (T_g), i.e. the system vitrifies when T_g reaches the cure temperature. Vitrification is assessed by the peak in t.b.a. (torsional braid analysis) damping–cure time curve at isothermal cure. Consequently, the system is frequently vitrified at a conversion less than 100%.]

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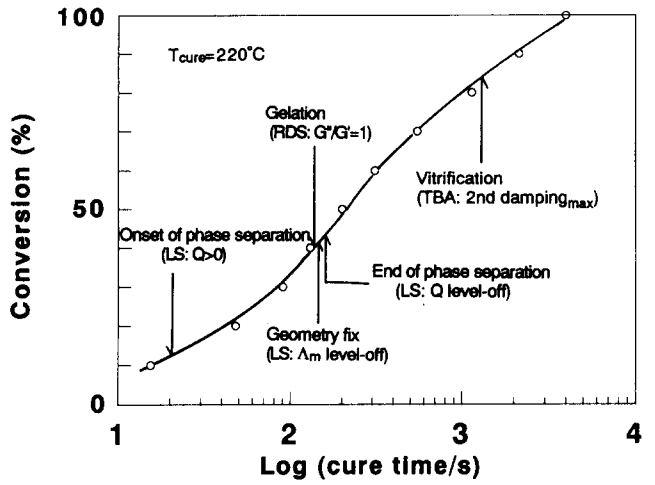


Figure 1 Various transformations during the cure process of a thermoset/thermoplastic blend, reproduced from the *TTT* cure diagram in the previous paper[15]. Tetraglycidyl 4,4'-diaminodiphenylmethane/PES/dicyandiamide (100/25/5) system cured at 220°C. Conversion is by d.s.c. exotherm peak area. Onset and end of phase separation are by the start-up and level-off of the increase in the light scattering invariant Q, respectively. Geometry fix is by the level-off of the increase in the Bragg spacing Λ_m by light scattering peak angle. Gelation is by the dynamic viscoelastic measurement, i.e. by the cross-over point ($G''/G'=1$) of the dynamic storage modulus G' and the loss modulus G'' by RDS (Rheometric Dynamic Spectrometer). Vitrification is by the damping maximum in t.b.a. (torsional braid analysis)

In this paper, we pay attention to this very late stage of the cure process in a thermoset/thermoplastic blend and investigate the reaction by *FT*i.r. spectroscopy and the change in physical state by dynamic mechanical analysis.

EXPERIMENTAL

A trifunctional epoxy resin, triglycidyl *p*-aminophenol, was supplied by Ciba-Geigy Co. (MY 0510). It has a low viscosity of ca. 600 cP at room temperature, an epoxy equivalent weight of 101 g mol^{-1} and a molecular weight of 300 g mol^{-1}. A 4,4'diaminodiphenylsulfone (DDS) supplied by Ciba-Geigy Co. (HT 976) was used as a curing agent. Epoxy and DDS were mixed at stoichiometric ratio (=43.5/26.5 in weight ratio) and non-stoichiometric ratio (epoxy/DDS=47/23 weight ratio). Poly(ether sulfone) (PES) was supplied by ICI Co. ($M_n=13.8\times10^3$).

A specimen for the dynamic mechanical analysis was prepared as follows. PES was dissolved in a mixed solvent of methylene chloride/methanol (=90/10 volume ratio) and epoxy was added to the solution. After the mixture was mixed thoroughly and concentrated to ca. 40% solid content, DDS was added. The mixture was poured into an open mould set at 145°C and degassed under vacuum for 30 min to remove residual solvent. The solvent-free mixture was inserted in a hot chamber and then cured at 180°C. After curing, the sample was allowed to cool slowly to room temperature. Then, the cured film (0.8 mm thick) was cut into a strip (6 mm × 20 mm) and was ready for the dynamic mechanical analysis. The dynamic mechanical properties were measured by a Rheolograph Solid (model 651, Toyo Seiki Co.). The frequency was fixed at 10 Hz and the scanning rate was 2°C min^{-1} over a wide range of temperature (100–350°C).

We also prepared a very thin film (50 μm thick) of the epoxy/DDS/PES mixture by solution-casting onto a silicone wafer for *FT*i.r. spectroscopy. After the cast film was dried under a vacuum of 10^{-4} mmHg for 12 h, it was cured in a hot chamber. *FT*i.r. spectra were measured at appropriate intervals during isothermal curing by an FT-IR 8100 (Shimadzu Co.).

Scanning electron mocrographs were obtained with a conventional secondary electron image for fractured and etched surfaces using a scanning electron microscope, JSM-T220 (JEOL Co.). Here the specimen was fractured at liquid-nitrogen temperature and was etched by immersing the fractured specimen in methylene chloride (preferential solvent for PES) at room temperature for 24 h.

RESULTS AND DISCUSSION

In *Figure 2* is shown the change in temperature dependence of the dynamic storage modulus E' and the loss tangent tan δ with curing at 180°C in a 47/23/30 epoxy/DDS/PES system. One can see the two-phase character—the two-step decrease in E' with increasing temperature and the two tan δ peaks—suggesting that phase separation has already taken place even after 30 min cure. So far, we have discussed the phase separation process by light scattering and shown that the separation is via the reaction-induced spinodal decomposition to yield a regularly phase-separated two-phase morphology[14,15]. Actually, one can see such morphology in the system cured for 24 h in *Figure 3*. A similar morphology was observed for the systems cured for 30 min and 3 h.

In *Figure 2*, the low tan δ peak temperature could be assigned to the glass transition temperature (T_g) of PES-rich phase and the high peak temperature to the T_g of epoxy-rich phase. However, note that the low T_g is

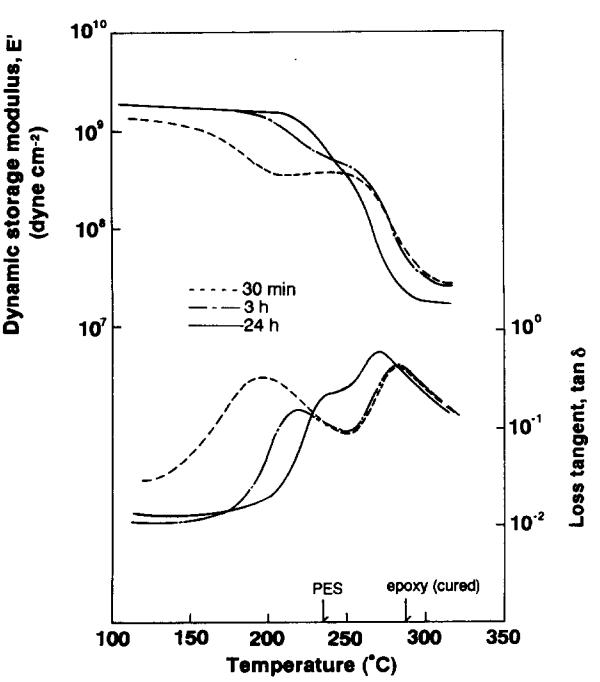


Figure 2 Temperature dependence of the dynamic storage modulus E' and the dynamic loss tan δ in 47/23/30 epoxy/DDS/PES system; cured at 180°C for 30 min, 3 h and 24 h

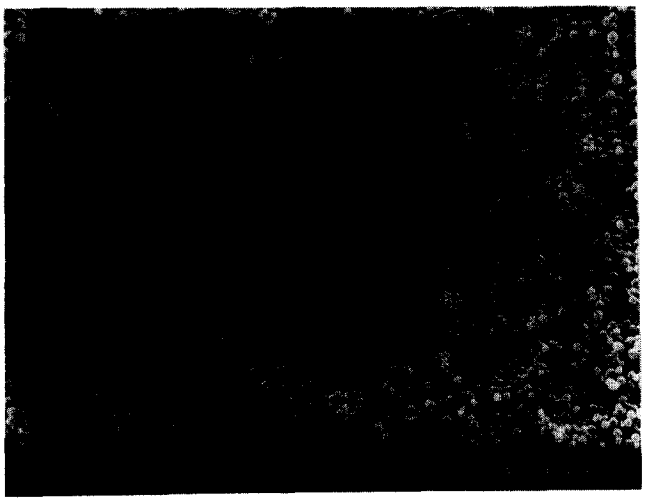


Figure 3 Scanning electron micrograph of 47/23/30 epoxy/DDS/PES cured at 180°C for 24 h

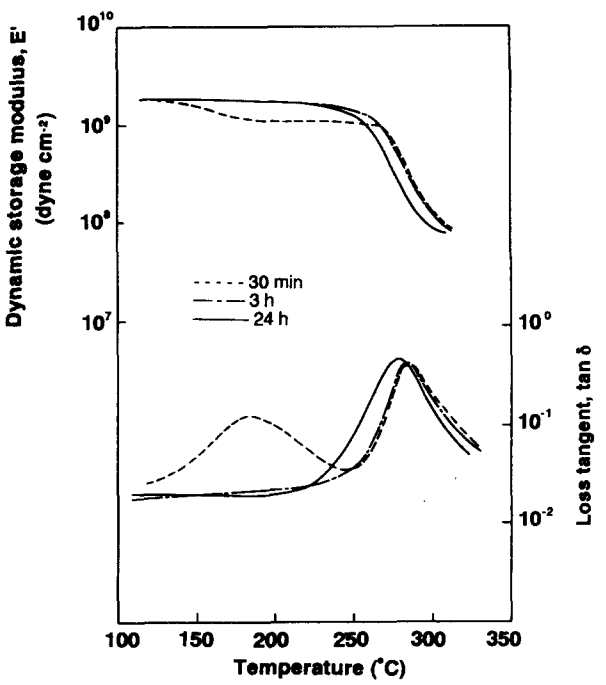


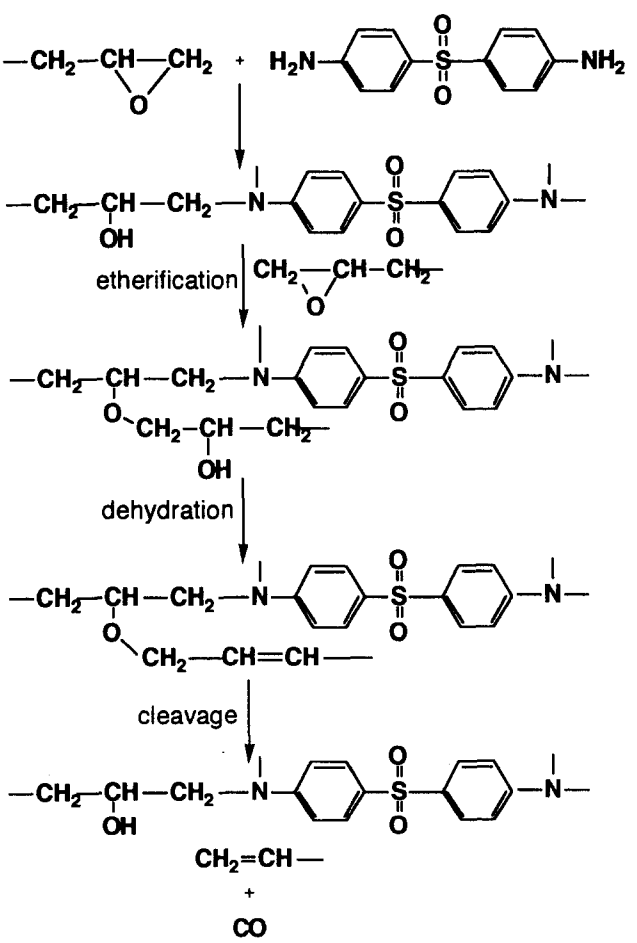
Figure 4 Temperature dependence of E' and tan δ in neat epoxy resin (47/23 epoxy/DDS); cured at 180°C for 30 min, 3 h and 24 h

elevated and the high T_g is depressed with increasing cure time. The inward shift of the two T_g values is quite strange, because the outward shift of T_g values is generally expected for two-phase systems generated by phase decomposition from a single-phase mixture; i.e. a homogeneous mixture of A and B decomposes to A-rich and B-rich regions and then to pure A and pure B regions so that T_g values usually shift outward. Therefore, the results in *Figure 2* give rise to two questions: (i) Why does the high T_g shift to lower temperature with curing? (ii) Why does the low T_g appear at a temperature lower than T_g of PES and shift to higher temperature with curing? One cannot answer the questions in the light of the ordinary scheme of phase separation.

An answer to the questions is provided by investigating the cure process of neat epoxy. *Figure 4* shows the change in temperature dependence of E' and tan δ with curing at 180°C in a neat epoxy system (47/23 epoxy/DDS). The resin cured for 30 min shows two tan δ peaks. The low-temperature peak disappears following cure. The results may imply that, after 30 min cure, the system is separated into crosslinked epoxy phase and epoxy oligomer phase and, at later stages, the latter is converted to the former phase to establish a homogeneous epoxy network. That is, segregation of epoxy oligomer seems to occur during curing in the neat epoxy system. Combining the results in *Figures 2* and *4*, the low-temperature tan δ peak in *Figure 2* can be assigned to the T_g of PES/epoxy oligomer mixture and the high-temperature peak to the T_g of neat epoxy network. Then the answer to equation (ii) is obtained.

Note that the high-temperature tan δ in *Figure 4* shifts to lower temperatures with curing, as in the case of the PES-loaded system in *Figure 2*. It implies that the T_g depression is a problem of epoxy resin itself; in other words, it is not related to the presence of PES. Judging from the rubbery plateau modulus (>300°C) in *Figure 4*, the three-dimensional network is already established in the resin after 30 min cure. The T_g depression after network formation could be caused by chain scission, which reduces the crosslink density. According to Lee[1], chain scission occurs via etherification and dehydration, as shown in *Scheme 1*.

The reactions in *Scheme 1* can be confirmed by *FT*i.r. analysis. *Figure 5* shows the change in *FT*i.r. spectrum with curing in the 47/23/30 epoxy/DDS/PES system. As the cure reaction proceeds, the epoxide band at 908 cm^{-1}



Scheme 1

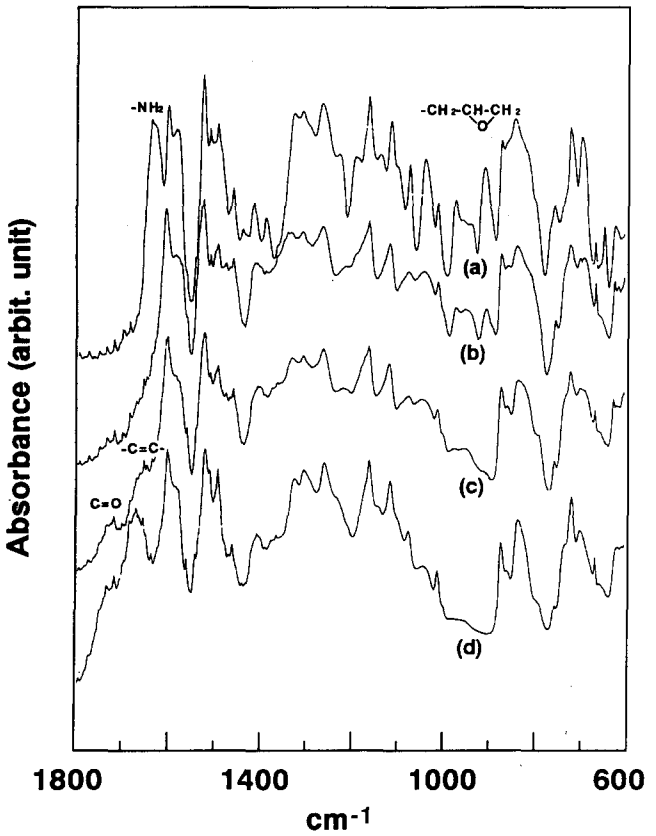


Figure 5 Change in *FTi.r.* spectrum with cure at 180°C: cure time (a) 0 (uncured), (b) 30 min, (c) 3 h and (d) 24 h; 47/23/30 epoxy/PES/DDS (epoxy excess system)

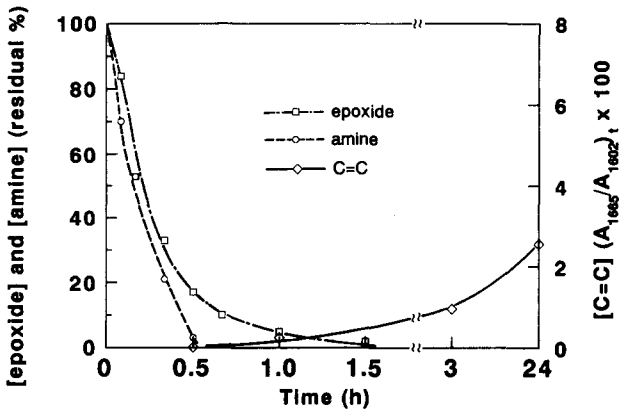


Figure 6 Residual epoxide and amine groups and evolution of C=C groups in 47/23/30 epoxy/DDS/PES (epoxy excess) system as a function of cure time at 180°C. Using A_{1602} (absorbance of phenyl group at 1602 cm^{-1}) as the internal standard, the residual percentage of epoxide and that of amine were estimated by $[(A_{908}/A_{1602})_t/(A_{908}/A_{1602})_{t=0}] \times 100$ and $[(A_{1620}/A_{1602})_t/(A_{1620}/A_{1602})_{t=0}] \times 100$, respectively. Amount of C=C groups was by $(A_{1685}/A_{1602}) \times 100$

and amine (N–H bending) band at 1620 cm^{-1} gradually decrease and then disappear. With decreasing epoxide and amine bands, a new band at 1665 cm^{-1} appears. The new band can be assigned to C=C stretching band. The results clearly support *Scheme 1*. The situation becomes more obvious by considering the plots of the decrease in the absorbance A of both amine and epoxy groups and the increase in that of C=C bond in *Figure 6*. One can see that the epoxy and amine groups are consumed and then the C=C group evolves.

One should note that the above results are for the epoxy excess system (47/23 epoxy/DDS), i.e. charge amount of epoxy is larger than the stoichiometric amount, 43.5/26.5 epoxy/DDS. Now, if the charge amount of epoxy is reduced to the stoichiometric level or less than that, the etherification in *Scheme 1* is expected to be restricted so that chain scission should be depressed. This was realized as shown in *Figures 7* and *8*. The epoxy and amine bands gradually decrease and eventually

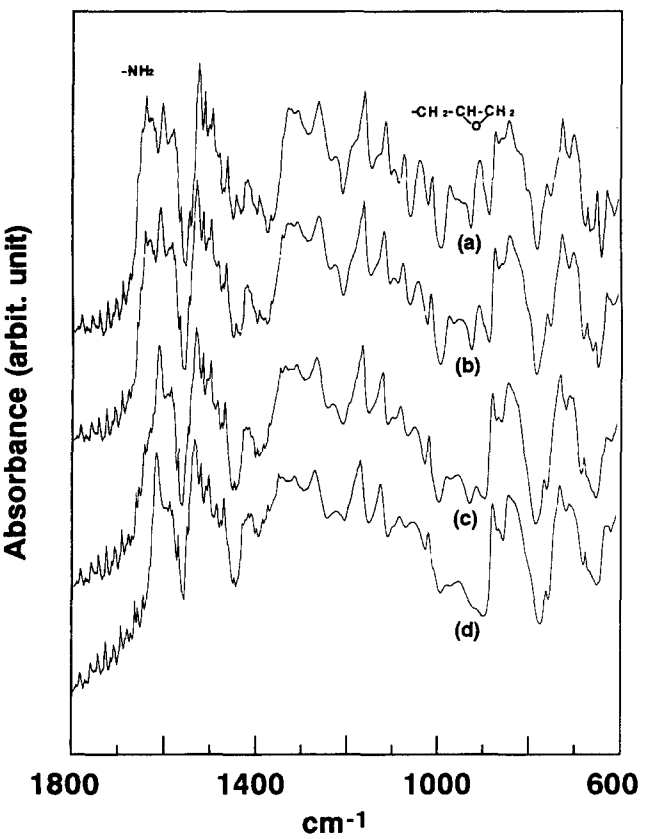


Figure 7 Change in *FTi.r.* spectrum with cure at 180°C: cure time (a) 0 (uncured), (b) 10 min, (c) 20 min and (d) 60 min; 43.5/26.5/30 epoxy/DDS/PES (stoichiometric system)

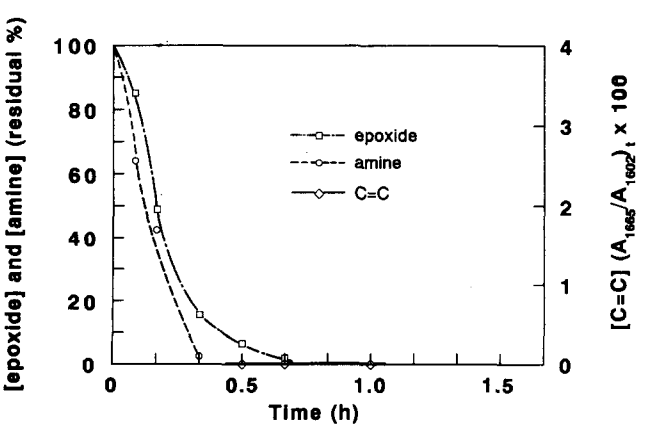


Figure 8 Residual epoxide and amine groups in 43.5/26.5/30 epoxy/DDS/PES (stoichiometric system) as a function of cure time at 180°C, showing no evolution of C=C group (see caption of *Figure 6*)

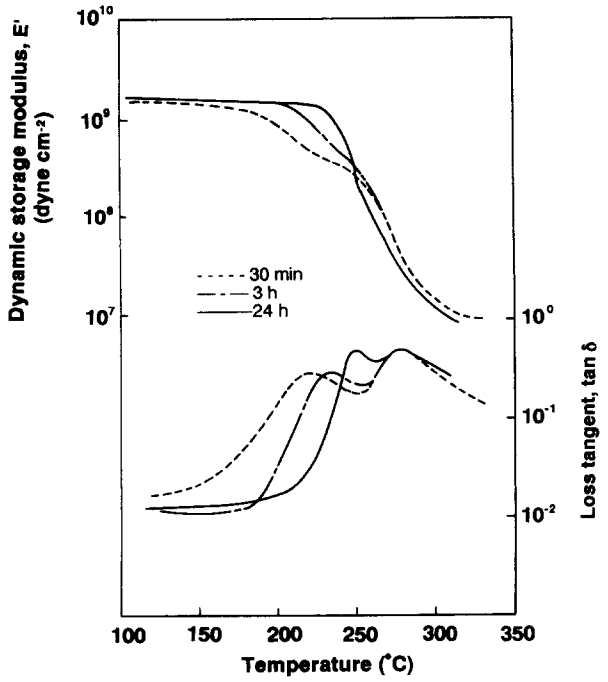


Figure 9 Temperature dependence of E' and $\tan\delta$ in 43.5/26.5/30 epoxy/DDS/PES (stoichiometric system); cured at 180°C for 30 min, 3 h and 24 h

disappear in the same way as in the epoxy excess system. However, the C=C bond never appears, suggesting that the reaction between epoxy and amine prevails over the etherification, and hence chain scission does not occur at the late stage of curing.

Then one can expect that the depression of high T_g will never happen in the stoichiometric system. As expected, the high-temperature $\tan\delta$ peak did not shift to low temperatures as shown in *Figure 9*. The results in *Figures 6–9* support the scenario for the inward shift of T_g values in *Figures 2* and *4*.

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