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Radical Formation through Curing Reaction of Epoxy Resins with 2,4,6-Trinitrophenol or 2,4,6-Trinitroresorcinol

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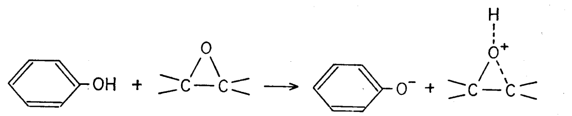
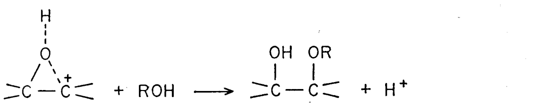
Radicals formed spontaneously during the cure reaction of epoxy resins with 2,4,6-trinitrophenol (TNP) or 2,4,6-trinitroresorcinol (TNR) have been investigated using electron spin resonance (ESR) technique. The ESR spectrum of the radicals stabilized in the epoxy resins cured with TNP was a triplet and the other spectrum of the radicals in the epoxy resins cured with TNR was a triplet with high anisotropy. The triplet splittings and *g*-values were attributed to radicals of the type $\rangle\mathrm{N{-}\dot{O}}$. The asymmetric line shapes of the triplet splittings caused by the ^{14}N coupling constant are induced by the slow motion of the radicals in the polymer. The presence of radicals of this type suggests the transfer of an oxygen of a nitro group of TNP or TNR during the cure reaction.

It has been known that phenols react with epoxy resins at elevated temperatures. The exact mechanism of the reaction has not been made sufficiently clear, but the reaction is likely to proceed through the formation of an intermediate oxonium ion:



(1)

The resultant phenoxide ion may then react with the epoxy group. The carbonium ion from the oxonium complex may react with a hydroxyl group.[1,2]



(2)

If polynitrophenols are used as the ring-opening agent of epoxy resins instead of phenols, reaction (1) may proceed easily because of the strong electron-attracting nature of nitro groups. In fact, the curing occurs by mixing TNP or TNR with the epoxy resins at room temperature.[3]

Recently it has been shown by ESR that radicals are generated during the cure reaction of the epoxy resins with TNP or TNR, and that they are stabilized in the cured resins. The process of radical formation through the cure reaction cannot be explained only from the ionic mechanism shown in the reactions (1) and (2). In the present study, we shall try to obtain some information about the radicals from ESR studies.

Experimental

Nitrophenols of extra pure commercial grade were purified by recrystallization. They were *o*-nitrophenol: mp 44—45 °C, *m*-nitrophenol: mp 96.5—97 °C, *p*-nitrophenol: mp 114—115 °C, 2,4-dinitrophenol: mp 113.0—113.5 °C, 2,6-dinitrophenol: mp 63—64 °C, and 2,4,6-trinitrophenol (TNP): mp 121.5—122.5 °C. 2,4,6-Trinitroresorcinol (TNR) was prepared by sulfonation and nitration of resorcinol: mp 174—175 °C. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) of extra pure commercial grade was purified by recrystallization twice from benzene, and it was dried under reduced pressure at 80 °C: mp 139—140 °C.[4,5]

The epoxy resin was Shell Chemical Company Epikote 828 (diglycidyl ether of bisphenol A, mol wt. approx. 380).[2] 1,2-Epoxypropane was dried with calcium hydride and purified by distillation: bp 35 °C. 1-Chloro-2,3-epoxypropane (a commercial guaranteed reagent grade) was used without further purification.

ESR measurements were carried out with a JEOL X-band spectrometer, model JES-PE-1X, using 100 KHz magnetic field modulation. The *g*-value was measured by comparison with $\mathrm{Mn^{2+}}$ in MgO placed in the cavity close to the sample position. The *g*-value of $\mathrm{Mn^{2+}}$ was determined beforehand by comparison with the value of DPPH ($g=2.0036$). The radical concentration of the sample was evaluated by the comparison of the double-integrated absorption intensity of the first-derivative spectrum with that of DPPH. Sample temperatures were controlled by a standard JES-VT-3A variable-temperature controller. The ESR measurements were made in air and in a vacuum. When the ESR was measured in a vacuum, the cured sample was ground and put into a standard sample-tube. The tube was sealed after evacuation by a vacuum-line system (10^{-4} Torr).

Results and Discussion

When 10—15 weight per cent of TNP or TNR was mixed with Epikote 828, the cure reaction proceeded at room temperature. ESR absorption was observed in these cure systems, as shown in Fig. 1. The Epikote 828–TNP system showed an asymmetrical triplet spectrum with an approximate 1:1:1 intensity distribution and centered at a position corresponding to $g=2.007$ (Fig. 1 (a)). The Epikote 828–TNR system also showed an asymmetrical triplet with $g=2.006$ (Fig. 1 (b)). These triplet spectra imply that the radicals formed have the odd electrons coupled strongly to the ^{14}N nuclei, and are most reasonably to be attributed to radicals of the type $\rangle\mathrm{N{-}\dot{O}}$. The change of the line shape and the *g*-value with temperature was examined for the cured sample having a TNP content of 15 per cent. The sample was cooled from room temperature to -170 °C and then heated to 70 °C progressively in a vacuum. The ESR spectra at 70 °C and at -170 °C are shown in Figs. 2 (a) and (b). The component of the triplet at -170 °C was broadened and showed a line width of 18 G† and $g=2.007$ at the central position, while the spectrum at 70 °C was almost the same as that at room temperature and showed a line width of 8 G and $g=2.007$. The difference in the line width is caused by the change of the motion of the radical molecules

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† $1\ \mathrm{G}=10^{-4}\ \mathrm{T}$.

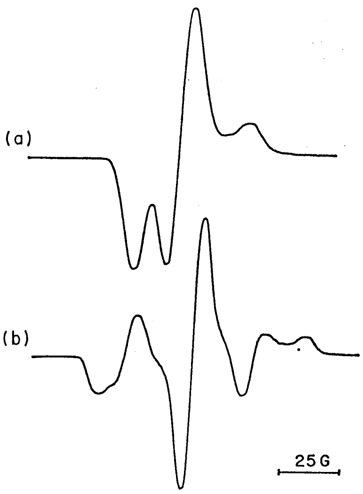


Fig. 1. ESR spectra of the radicals formed in the Epikoto 828–TNP system (a) and the Epikote 828–TNR system (b) at room temperature.

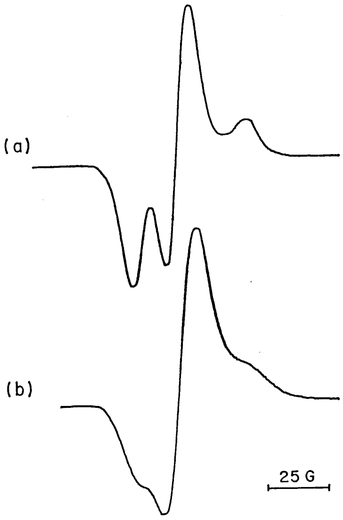


Fig. 2. Temperature dependence of ESR spectra of the radicals formed in the Epikote 828–TNP system. (a): 70 °C, (b): −170 °C.

in the cured resin. The same temperature dependence was seen on the Epikote 828–TNR system. The spectra shown in Figs. 1 and 2 agreed with the absorption pattern of nitroxide radicals when undergoing slow molecular motion, as has been investigated by the spin label technique.6–10) According to this technique, the outer side lines of the spectrum in Fig. 1 (b) show that the radicals are arranged in parallel, and the inner side ones show that the radicals are arranged parpendicularly to the magnetic field. The splitting shows that the rotational motion of the radicals in the epoxy resin–TNR system is more limited than that of the radicals in the epoxy resin–TNP system. Neither spectra in Fig. 1 are resolved completely. A slow rotational motion of the radicals in the cured resin causes the poorly resolved and asymmetrical line shapes.

When TNP or TNR was mixed with other epoxy resins such as Epikote 812 (triglycidyl ether of glycerol) or Epikote 871 (diglycidyl ester of dimeric linoleic acid),2) the cure reaction also proceeded at room temperature. In these cured resins the ESR spectra shown in Figs. 1 (a) and (b) were observed. However on adding TNP or TNR to monoepoxy compounds such as 1,2-epoxypropane or 1-chloro-2,3-epoxypropane, no ESR absorption occured. From these results, it is suggested that the radical formation and/or the accumulation result from a ring opening reaction of the epoxy resins which necessarily changes the resins to a high viscous state.

If mono- or dinitrophenol was mixed with Epikote 828 instead of TNP or TNR, the cure reaction scarcely proceeded at room temperature and these mixtures did not give the radicals. The mixtures were therefore heated in order to accelerate the cure reaction. The temperature was raised by 10 °C and left for 5 min. This process was repeated up to 300 °C. No ESR absorption was observed below 200 °C but a singlet spectrum due to carbonization appeared above 200 °C in each case. The result shows that not one or two but three nitro groups bonded to the benzene ring facilitate the radical formation.

The triplet spectra observed in the cure reactions of Epikote 828–TNP and Epikote 828–TNR systems may possibly be seen also in the nitrophenols alone. The ESR measurements of these nitrophenols were made under the same heating conditions as for the Epikote 828–nitrophenol mixtures. Mono- and dinitrophenols did not give the ESR absorption before carbonization, while TNP and TNR produced the radicals at 180—190 °C. Their ESR spectra are shown in Figs. 3 (a) and (b). These well resolved triplet spectra are observed both in a vacuum and in air. The spectra with an 1:1:1 intensity centered at a position corresponding to $g=2.006$ in Fig. 3 and an isotropic coupling constant of 28—30 G have been attributed to the radical $\rangle\mathrm{N{-}\dot{O}}$. This identification can be explained by the following facts: TNP decomposes slightly at 180 °C, and the g-value of the spectra almost agrees with the value of free spin. The intensity and the coupling constant of the spectra are the same as those of the radical $\rangle\mathrm{N{-}\dot{O}}$.11,12) Therefore, it is appropriate to conclude that the radicals formed in

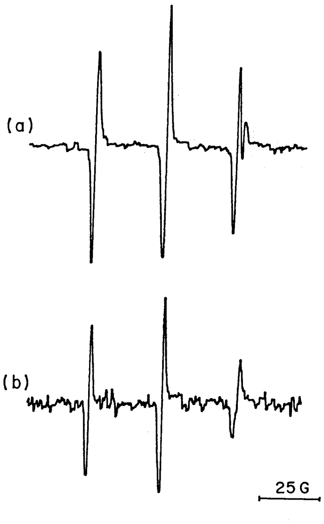


Fig. 3. ESR spectra of the radicals formed in TNP (a) and TNR (b) heated at 190 °C.

the epoxy resin cured with TNP or TNR coincide with those which appear by heating of TNP and TNR, although the radicals in the rigid state give the spectra in Fig. 1 and in the reverse case moving freely the radicals give the spectra in Fig. 3.

The changes in the absorption intensities (peak-to-peak height) of the center lines of the ESR spectra of the Epikote 828–TNP and Epikote 828–TNR systems as a function of time are shown in Figs. 4 and 5, respectively. The ESR absorption intensity of each system in Figs. 4 and 5 showed a maximum at 70 °C and the intensity changed little with time. The intensity curves above 70 °C in Fig. 4 clearly indicate a successive reaction A→B(radical)→C. On the other hand, the two steps-augmentation of the absorption intensity of the spectrum in Fig. 5 may imply that two hydroxyl groups of TNR take part in the ring-opening reaction of the epoxy groups.

More detailed investigations of the radicals formed in the Epikote 828–TNP system have been performed. Figure 6 shows the change of the absorption intensity of the center line of the triplet against the mixing ratio of TNP to the resin at 70 °C for 1 h. The ESR absorption appeared when the resin contains one per cent of TNP. When about 20 per cent of TNP was present, the ESR absorption showed a maximum. The absorption intensity of the cured resin which contained 15 per cent of TNP is equivalent to a radical concentration of 2×10^{17} spins/g.

The degree of cross-linking of Epikote 828 cured with TNP depends on the curing temperature, and is determined by the insolubility in acetone. The amount of the acetone-insoluble part of the cured resin which is mixed with 15 per cent of TNP is plotted against various temperatures as shown in Fig. 7. The absorption intensity of the ESR spectra of each cured resin is observed and plotted also in Fig. 7. As can be seen from the figure the change of these absorption intensities corresponds nicely to the amount of the acetone-insoluble part. That is, the more extensive the cross-linking is, the more the radicals are stabilized. At the temperature about 110 °C, the amount of acetone-insoluble part changes remarkably.

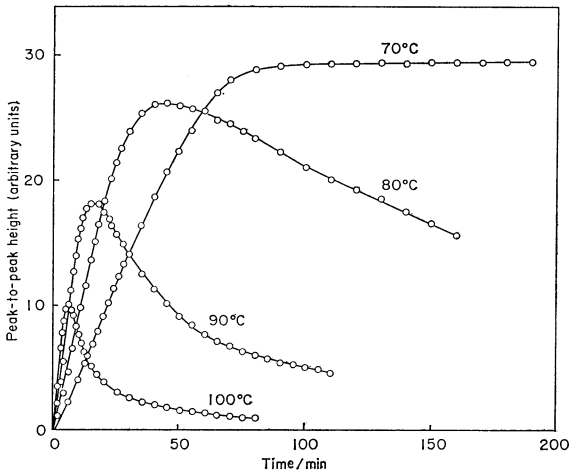


Fig. 4. Change in the intensities of ESR spectra of the radicals observed during the cure reaction of the Epikote 828–TNP system (Epikote 828/TNP=85/15) as a function of time.

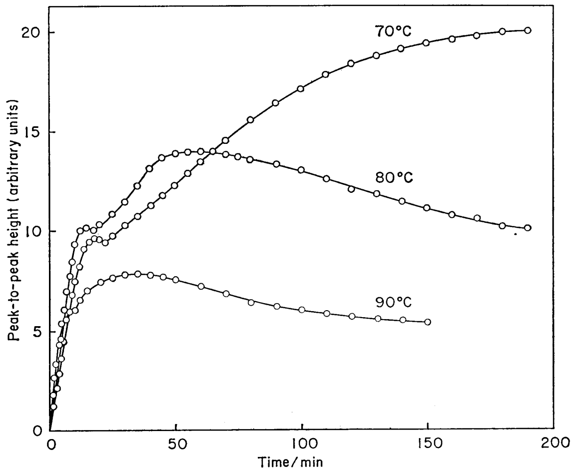


Fig. 5. Change in the intensities of ESR spectra of the radicals observed during the cure reaction of the Epikote 828–TNR system (Epikote 828/TNR=90/10) as a function of time.

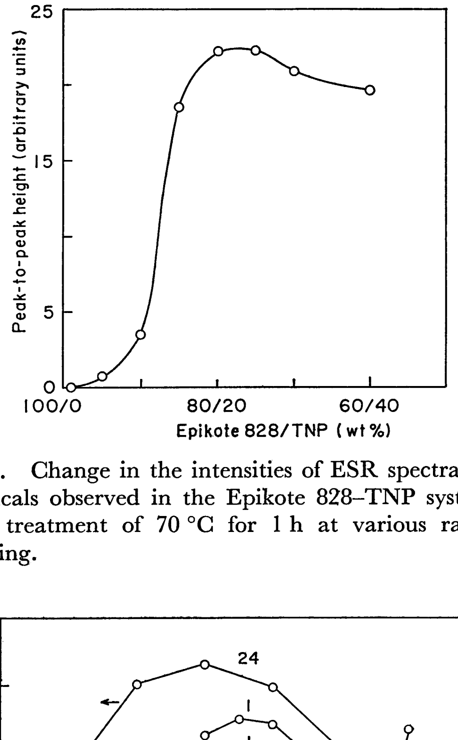


Fig. 6. Change in the intensities of ESR spectra of the radicals observed in the Epikote 828–TNP system by the treatment of 70 °C for 1 h at various ratios of mixing.

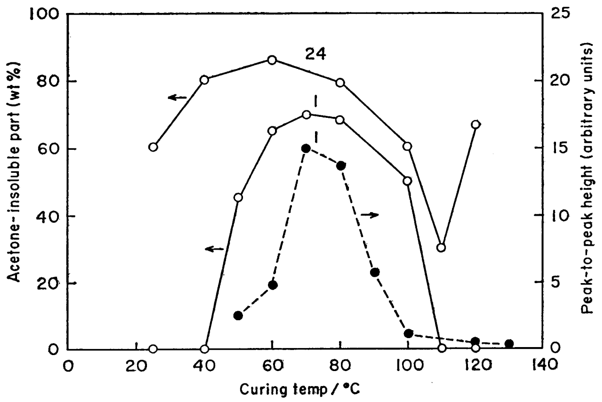
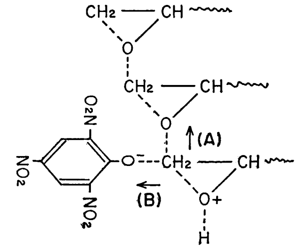


Fig. 7. Dependence of the acetone-insoluble parts and the ESR absorption intensities of Epikote 828 cured with 15 wt% of TNP at various temperatures. Numerals indicate cure time in hours.

This change of the acetone-insoluble part is caused by a ring-opening mechanism of Epikote 828 with TNP, and is explained by the following ring-opening reaction:



Scheme 1.

Scheme 1 implies that the ring-opening reaction has the character of a competitive reaction. When the reaction proceeds in the direction (A), more than to the direction (B), the cross-linked structure is formed directly. In the reverse case a linear product is formed at the first step, which is soluble in acetone. However many epoxy groups remain in this linear product and react with each other at elevated temperatures.[13] Finally the cross-linking occurs. It is considered that the reaction in the direction (A) proceeds at low temperature and the reaction in the direction (B) proceeds at high temperature. The latter mechanism can be supported by the fact that 2,4,6-trinitrophenyl propyl ether with hydroxyls was produced by the reaction of 1,2-epoxypropane with TNP.[14] However radical formation cannot be explained by this ionic mechanism in Scheme 1 which is almost the same as those of reactions (1) and (2). The radical formation during the cure reaction of the epoxy resins with TNP or TNR suggests that intermediate ions or radicals which appear in the high viscous reaction system promote transfer of the oxygen of a nitro group to an other position.

As the overall reaction under consideration is so complicated, the mechanism is not fully understood at present, but the ESR experiments show that the radical formation reaction must be taken into accout in interpreting the cure reaction discussed above.

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