A study of the structure of pre-gelled epoxy networks

King-Fu Lin* **and Wen-Yung Shu**
Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 10764, Republic of China

(Received 26 August 1993; revised 7 December 1993)

Ammonium salts of pre-gelled epoxy networks, in the form of spherical clusters, were prepared by the addition of hydrogen chloride in methanol solution to partially cured bisphenol A diglycidyl ether/ethylene diamine epoxy resins. The formation of ammonium salts resulted from the interaction of hydrogen chloride with the amine groups of the pre-gelled epoxy networks, as indicated by their infra-red and solid-state ^{13}C n.m.r. spectra and X-ray diffraction patterns. By increasing the time allowed for branching reactions or by increasing the concentration of branched molecular chains, the spherical clusters tended to form as agglomerations of ribbon textures, which were then demonstrated to be associated with the packing of the branched molecular chains. The packed networks could also be detected through X-ray diffraction studies of the post-gelled epoxy resins.

(Keywords: epoxy resins; two-dimensional networks; ammonium salts)

INTRODUCTION

The curing reaction of thermosetting polymers begins with linear growth of the chains, and then proceeds with two-dimensional branching reactions before the chains crosslink with each other to form three-dimensional networks[1]. It has been pointed out that branched molecular chains containing considerable numbers of highly polar groups, such as amine groups and hydroxy groups, might pack together during the curing reaction[2]. Evidence for the existence of packed, two-dimensional branched molecular chains has come from the discovery of packed networks in the etched fracture surfaces of post-gelled epoxy resins. In addition, the X-ray scattering patterns of post-gelled epoxy resins show a small diffraction peak for a scattering vector of 3.4–4.6 nm^{-1}, which has been associated with the local ordering structure in the epoxy network[3–5]. According to the Bragg equation, the d spacing of the corresponding local ordering structure is in the 14–19 Å range, the same order as the thickness of the packed network found in the etched fracture surface.

In this study, to investigate directly the existence of packed, branched molecular chains during the cure of bisphenol A diglycidyl ether/ethylene diamine (DGEBA/EDA) epoxy resins, the curing reaction was stopped by opening up the epoxy groups with hydrogen chloride (HCl) in methanol solution. Simultaneously, ammonium salts, in the form of spherical clusters, were precipitated. The ammonium salts from the pre-gelled epoxy networks tended to form as agglomerations of ribbon textures if the time allowed for branching reactions and the concentration of branched molecular chains were properly controlled. The objectives of this study were to elucidate the origin of these ribbon textures and investigate their relationship to the packing of two-dimensional branched molecular chains.

EXPERIMENTAL

Materials

Most of the DGEBA epoxy resins used were Epon 826 (Shell) with an epoxy equivalent weight (*EEW*) of 187 g mol^{-1}, measured by the hydrochloric acid/methyl ethyl ketone (MEK) method[6]. Epon 825 ($EEW = 175$ g mol^{-1}) was also used for comparison. However, unless otherwise specified, the DGEBA resin was Epon 826. Ethylene diamine (EDA; reagent grade, Osaka Chemicals) was used as the curing agent.

Sample preparation

Preparation of ammonium salts. The cured DGEBA/EDA resin systems were prepared using 50%, 100% and 200% stoichiometric quantities of the EDA curing agent with respect to the epoxy groups. In a typical experiment, DGEBA (5 g) was mixed with the required amount of EDA curing agent in a test tube at room temperature for at least 5 min to give a clear solution. Several solutions prepared in the same way were placed in a water bath controlled at a chosen temperature (20°C, 30°C or 40°C) to allow curing. The curing time was measured from the time when mixing was complete. A test tube was removed from the water bath after a chosen curing time and treated immediately with methanol (20 ml) containing 2 vol% concentrated HCl. The solution was stirred until it became clear, and then concentrated HCl (2 ml) was added. At this stage, a white precipitate was formed unless the curing time was such that crosslinking reactions were dominant. Blank tests were also performed using the same procedure by adding the HCl/methanol mixture and concentrated HCl to ethylene diamine which had been

---

*To whom correspondence should be addressed

0032-3861/94/16/3535-07

conditioned at 20°C, 30°C or 40°C for 30 min. In addition, to investigate solvent effects on the blank tests, HCl/acetone and HCl/MEK mixtures were also used to replace HCl/methanol. All the precipitates were filtered, washed with acetone several times and then dried under vacuum at room temperature.

Preparation of post-gelled epoxy resins. Post-gelled DGEBA/EDA epoxy resins were cured at 30°C for 24 h and then post-cured at 128°C for 10 h.

Analytical techniques

Curing exotherms of DGEBA/EDA epoxy resins were recorded on a Du Pont model 910 differential scanning calorimeter using isothermal scanning at 30°C for 200 min followed by dynamic scanning from 30°C to 300°C at a scanning rate of 5°C min^{-1}.

Chemical characterization of the precipitates was performed using infra-red (i.r.) and solid-state ^{13}C n.m.r. spectroscopy. The i.r. spectra were recorded on a Hitachi model 270-30 spectrometer with samples in the form of KBr discs. The solid-state ^{13}C n.m.r. spectra were recorded on a Bruker model MSL200 spectrometer equipped with a cross-polarization accessory by which a cross-contact time of 1 ms was set for transfer of proton polarization to carbon nuclei. Proton decoupling was achieved at a frequency of 50.4 MHz. A magic angle of 54.7° was set with a spin rate of 4 kHz at 25°C.

Wide-angle X-ray diffraction patterns of the precipitates and the post-gelled epoxy resins were recorded on a Philips model PW1710 X-ray diffractometer. Diffraction patterns were recorded by scanning at a rate of 3° min^{-1} over the angular range $3° < 2\theta < 50°$.

RESULTS AND DISCUSSION

Curing times for branching and crosslinking of molecular chains

The extent of curing for DGEBA cured with a stoichiometric amount of EDA as a function of curing time at 30°C was measured by differential scanning calorimetry (d.s.c.). *Figure 1* shows two d.s.c. scans: an isothermal scan at 30°C for 200 min, by which time the curing system had almost ceased reacting; and a dynamic scan from 30°C to 250°C at a scanning rate of 5°C min^{-1}. The latter scan measured the residual curing exotherm. The heat generated at the isothermal curing stage and the residual curing exotherm are 487.9 J g^{-1} and 345.1 J g^{-1}, respectively. The extent of curing X, plotted *versus* curing time in *Figure 2*, can be calculated from

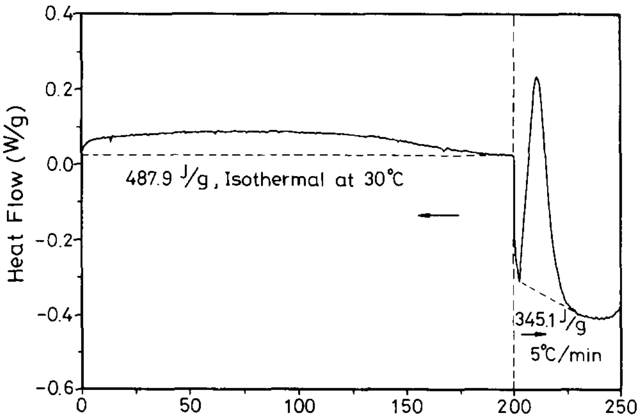

Figure 1 Isothermal d.s.c. scan at 30°C for 200 min followed by dynamic d.s.c. scan from 30°C to 250°C for DGEBA/EDA in the stoichiometric ratio

$$X = \frac{\Delta H(t)}{\Delta H(\mathrm{total})} \times 100\% \tag{1}$$

where $\Delta H(t)$ is the heat generated up to time t, measured from *Figure 1*, and $\Delta H(\mathrm{total})$ is 833 J g^{-1}, the total heat generated for complete curing of the epoxy resin.

The curing mechanism of DGEBA and EDA in the stoichiometric ratio prior to gelation has been well studied by Riccardi *et al.*[7]. For the suggested curing reactions it is assumed that the reactivities of primary and secondary amine hydrogens are the same and that part of the curing reaction is catalysed by the hydroxy groups initially present in the DGEBA epoxy resin and those generated during the reaction

$$\mathrm{E} + \mathrm{A} \xrightarrow{k_\mathrm{A}} \mathrm{R} + \mathrm{OH}$$

$$\mathrm{E} + \mathrm{A} + \mathrm{OH} \xrightarrow{k_\mathrm{B}} \mathrm{R} + 2\mathrm{OH} \tag{2}$$

where E is an epoxy group, A is an amine hydrogen and R is a reacted molecular chain. The curing rate can then be estimated from

$$\mathrm{d}X/\mathrm{d}t = (k_\mathrm{A}[\mathrm{E}]_0 + k_\mathrm{B}[\mathrm{E}]_0[\mathrm{OH}]_0 + k_\mathrm{B}[\mathrm{E}]_0^2 X)(1-X)^2 \tag{3}$$

where $[\mathrm{E}]_0$ and $[\mathrm{OH}]_0$ are the initial concentrations of epoxy and hydroxy groups, respectively. It has been indicated that the curing reactions (equations (2)) are competitive owing to their different activation energies; the reaction catalysed by hydroxy groups has a higher reaction rate at the commencement of curing when the curing temperature is lower than 50°C[7]. By integrating equation (3) for an isothermal cure we obtain

$$\int_0^{X_t} \frac{\mathrm{d}X}{(1-X)^2(X+b)} = k_\mathrm{B}[\mathrm{E}]_0^2 t \tag{4}$$

where

$$b = \frac{k_\mathrm{A}[\mathrm{E}]_0 + k_\mathrm{B}[\mathrm{E}]_0[\mathrm{OH}]_0}{k_\mathrm{B}[\mathrm{E}]_0^2}$$

and X_t is the extent of curing at time t. The analytical solution of equation (4) can be found elsewhere[8]. By using the kinetic rate constant provided in the literature[7], the extents of curing as a function of isothermal curing time t at 20°C, 30°C and 40°C can be calculated. The results shown in *Figure 2* agree well with the experimental data up to 70 min of curing at 30°C.

During the curing reaction, the molecular chains first grow linearly and then branch and crosslink by way of reactions between epoxy groups and amine hydrogens. The hydroxy groups only act as a catalyst, as indicated in equations (2). Therefore, the extents of curing at which the linear molecular chains begin to branch and the branched chains begin to crosslink depend on the number of amine groups in EDA that react. Each EDA molecule has four amine groups. According to combination theory, the combination number of n things taken r at a time can be calculated from

$$C(n, r) = \frac{n!}{r!(n-r)!} \tag{5}$$

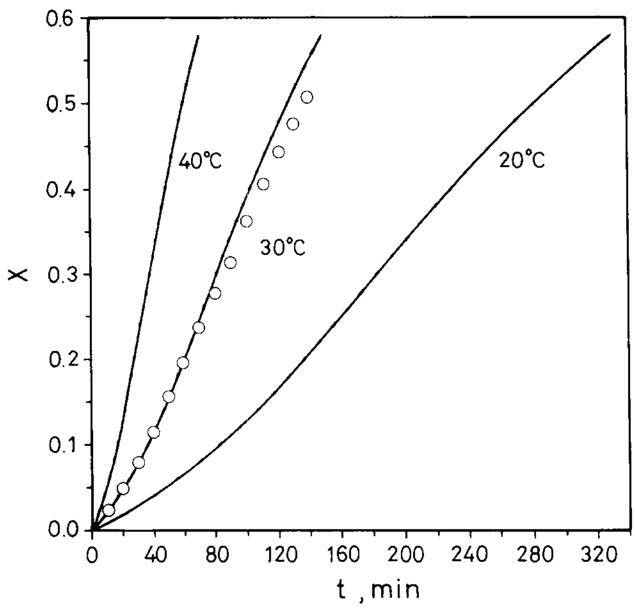

Figure 2 The extent of curing *versus* curing time for DGEBA/EDA epoxy resin in the stoichiometric ratio at various isothermal curing temperatures: (——) calculated results from equation (4); (○) calculated results from equation (1)

Thus, $C(n, r) = 6$ if any two of the four amine groups in EDA react. If these six combinations all contributed to the curing reaction, DGEBA resin mixed with a stoichiometric quantity of EDA would be fully cured. Only one combination is needed for linear growth of the molecular chains. More than one combination would lead to branching reactions. In other words, most of the linear growth of the chains proceeds in the initial stage of curing until the extent of curing reaches 16.7%.

By the same token, $C(n, r) = 4$ if any three of the four amine groups in EDA react. More than one combination would lead to crosslinking reactions. Thus, most of the branching reactions occur for a curing extent between 16.7% and 25%. Once the extent of curing exceeds 25%, crosslinking reactions will dominate. The times required for the extent of isothermal curing to reach 16.7% and 25% at 20°C, 30°C and 40°C are listed in *Table 1*, as are the times required to reach the gel point obtained from *Figure 2*. The extent of curing X_c at the gel point depends on the epoxy functionality f_E, i.e. the number of epoxy groups in an epoxy monomer, and the amine functionality f_A, i.e. the number of amine groups in an amine molecule. For the epoxy system in this study $X_c = 0.577$, as determined from the following equation

$$X_c = \frac{1}{\sqrt{(f_A - 1)(f_E - 1)}} \qquad (6)$$

Structure of pre-gelled DGEBA/EDA ammonium salts

The curing reactions of DGEBA/EDA epoxy resins in the pre-gelled stage were stopped by opening up the epoxy groups with HCl in methanol after the reactions had progressed for a given time at 30°C. Precipitation occurred upon further treatment of the solutions with an excess of HCl. To investigate how these precipitates are related to the pre-gelled epoxy networks, their chemical and physical structures were studied by i.r. and solid-state ^{13}C n.m.r. spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction. In the blank test of the EDA curing agent conditioned at 30°C for 30 min, the i.r. spectrum of the precipitate shown in *Figure 3a* suggests an ammonium salt, as indicated by the peaks[10] at 3000 cm^{-1}, 1600 cm^{-1}, 1580 cm^{-1} and 1500 cm^{-1}. The solid-state ^{13}C n.m.r. spectrum shown in *Figure 4a* has only one sharp peak at 36.6 ppm which represents carbon atoms attached to $H_2N{:}HCl$ groups. Both spectra indicate that the precipitate was an ammonium salt with the chemical structure $ClH{:}NH_2(C_2H_4)H_2N{:}HCl$. An SEM study of the precipitates also revealed that they were basically in flat platelet form with a thickness of about 10 μm (*Figure 5*). When the conditioning temperature of EDA prior to the preparation of the ammonium salt was changed from 20°C to 40°C, the platelets became smaller but their thickness apparently did not change. Upon changing the concentration and amount of the HCl/methanol mixture and its rate of addition for the preparation of the EDA ammonium salts, neither the thickness nor the basic form of the platelets was changed, although the platelet size was changed slightly. On the other hand, when methanol in the HCl/methanol mixture was replaced by acetone or methyl ethyl ketone (MEK), the precipitated EDA ammonium salts were produced in smaller quantities and the platelets present in the

Table 1 The isothermal curing times of DGEBA/EDA epoxy resins in the stoichiometric ratio for various extents of curing at 20°C, 30°C and 40°C

	Curing time (min)		
Extent of curing	20°C	30°C	40°C
$X = 16.7\%$	120	53	24
$X = 25\%$	160	71	33
$X_c = 0.577$	329	148	70

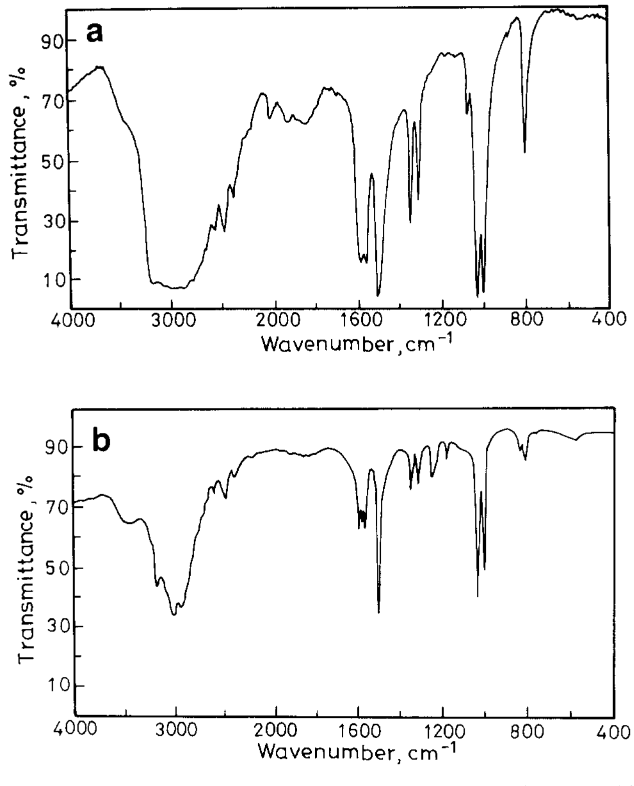

Figure 3 I.r. spectra of (a) the pure EDA ammonium salt prepared in the blank test and (b) the DGEBA/EDA (in the stoichiometric ratio) ammonium salt, both after curing at 30°C for 30 min

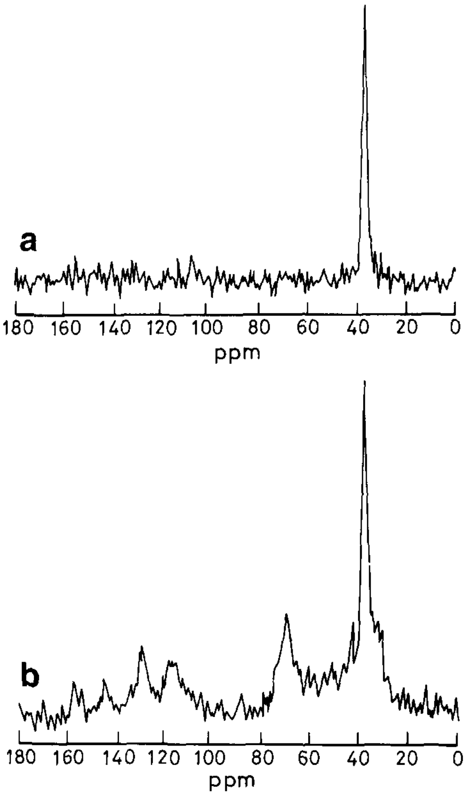

Figure 4 ^{13}C n.m.r. spectra of (a) the pure EDA ammonium salt prepared in the blank test and (b) the DGEBA/EDA (in the stoichiometric ratio) ammonium salt, both after curing at 30°C for 30 min

Figure 5 SEM photograph of the pure EDA ammonium salt prepared in the blank test

precipitates tended to fuse together. Obviously, the precipitated ammonium salts are more soluble in acetone and MEK than in methanol, and thus HCl/acetone and HCl/MEK mixtures were not such good precipitators as the HCl/methanol mixture in this study.

Figure 6 shows the SEM photographs of the precipitates prepared from DGEBA cured with a stoichiometric amount of EDA at 30°C for 30 min, 50 min and 65 min. According to the earlier analysis of the reaction in terms of the extent of curing, the DGEBA/EDA molecular chains after curing for 30 min are still at the stage of linear growth (see *Table 1*). The i.r. spectrum of the precipitate after 30 min (*Figure 3b*) suggests an ammonium salt in an epoxy resin, as indicated by the peaks for the ammonium salt at 3000 cm^{-1}, 1600 cm^{-1}, 1580 cm^{-1} and 1500 cm^{-1} and the additional peaks at 840 cm^{-1}, 1260 cm^{-1} and 3500 cm^{-1} from the substituted aromatic groups, ether groups and hydroxy groups in the DGEBA moiety, respectively[11]. The solid-state ^{13}C n.m.r. spectrum of the same precipitate (*Figure 4b*) confirms the i.r. results: the peak at 70 ppm represents methine carbons attached to hydroxy groups and methylene carbons attached to ether groups in the DGEBA moiety; the peak at 127 ppm represents aromatic carbons attached to hydrogen atoms; and the peaks at 144 ppm and 156 ppm represent aromatic carbons not attached to hydrogen atoms[12]. Moreover, the X-ray diffraction pattern is similar to that of the EDA

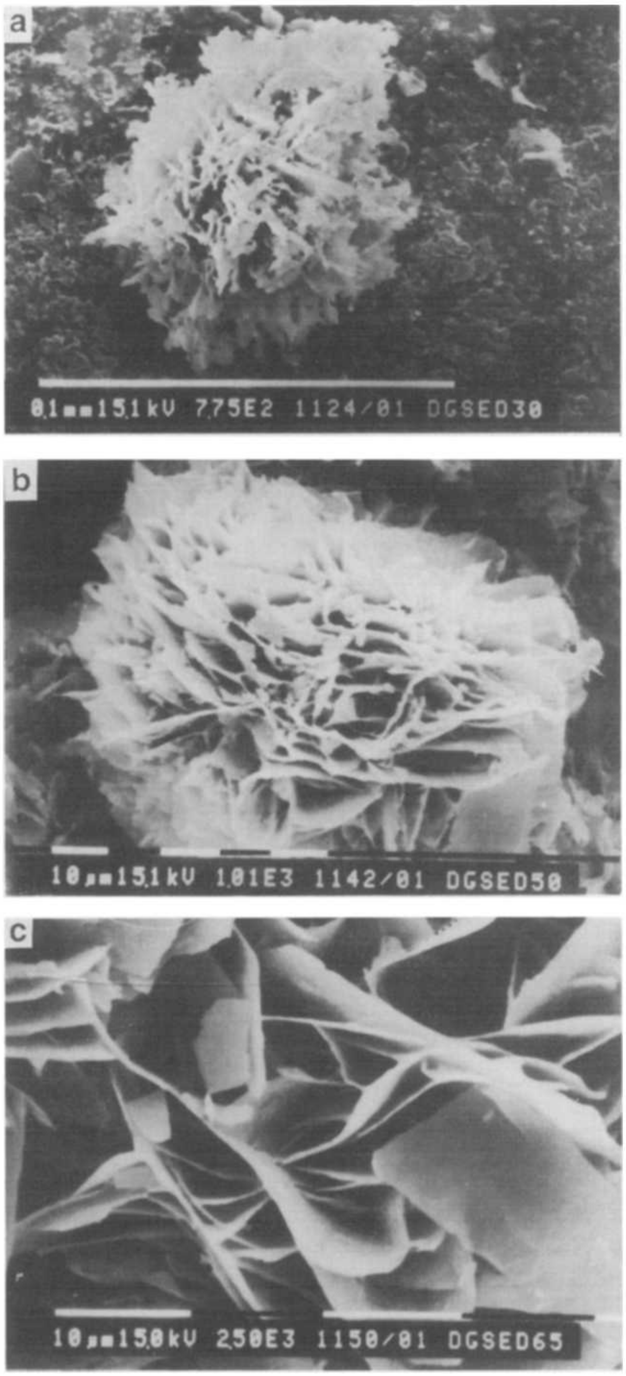

Figure 6 SEM photographs of DGEBA/EDA (in the stoichiometric ratio) ammonium salts after curing at 30°C for (a) 30 min, (b) 50 min and (c) 65 min

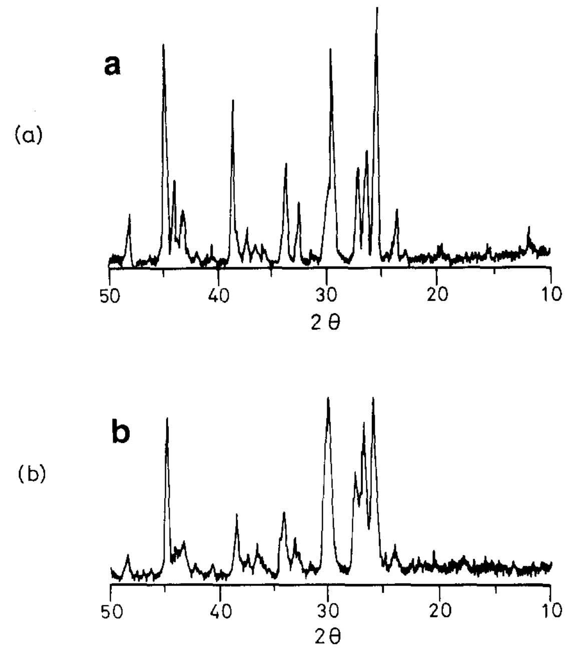

Figure 7 Wide-angle X-ray diffraction patterns of (a) the pure EDA ammonium salt prepared in the blank test and (b) the DGEBA/EDA (in the stoichiometric ratio) ammonium salt, both after curing at 30°C for 30 min

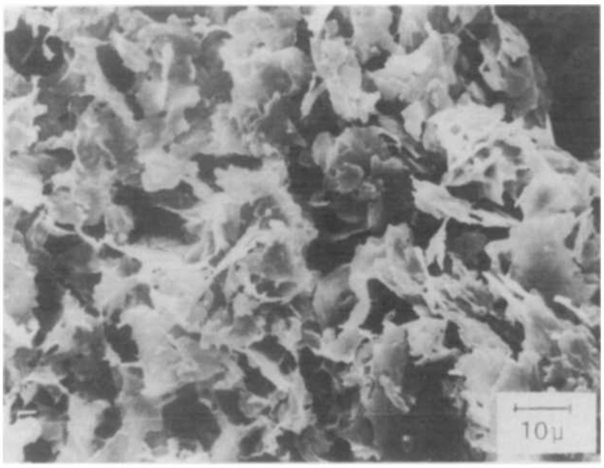

Figure 8 SEM photograph of the DGEBA/EDA ammonium salt prepared in a similar way to that in *Figure 5a* except that DGEBA here was Epon 825 ($EEW = 175$ g mol^{-1})

ammonium salt shown in *Figure 7*, except that the diffraction peaks are broader. The broader diffraction peaks resulted from the crystal imperfection known as the mosaic structure[13], which occurred because of interference in the crystallization of the ammonium salts by the DGEBA/EDA molecular chains.

The precipitates prepared from the 30 min cured DGEBA/EDA epoxy resin in the stoichiometric ratio were formed as spherical clusters coagulated in the radial direction with a size of 70–130 μm, as shown in *Figure 6a*. However, the precipitates prepared under the same conditions but with pure DGEBA epoxy resin (with $EEW = 175$ g mol^{-1}) did not show the coagulated structure, as shown in *Figure 8*. The DGEBA epoxy resin with $EEW = 187$ g mol^{-1} is a mixture of species with different molecular weights. The typical chemical structure of the resin is shown in *Figure 9*, and the molecules with $n > 0$ contain hydroxy groups. Thus, it is believed that the formation of spherical clusters was facilitated by the hydroxy groups in the molecules with $n > 0$ providing the hydrogen-bonding sites for coagulation in the mixture. We also found that if we used DGEBA with $EEW = 193$ g mol^{-1} rather than that with $EEW = 187$ g mol^{-1}, we obtained more, smaller spherical clusters in the precipitate, indicating that higher numbers of hydroxy groups provide more nuclei for coagulation[14].

For the epoxy resins cured for 50 min at 30°C, the spherical clusters in the precipitated ammonium salts had textures composed of ribbons, as shown in *Figure 6b*. The resins cured for 65 min had well-developed ribbon textures where the ribbons tended to connect with each other, as shown in *Figure 6c*. No precipitate was found when the resin was cured for longer than 70 min.

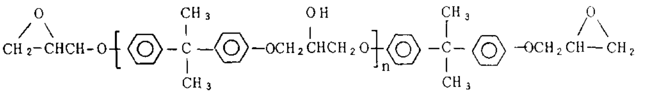

Figure 9 Typical chemical structure of DGEBA epoxy resin

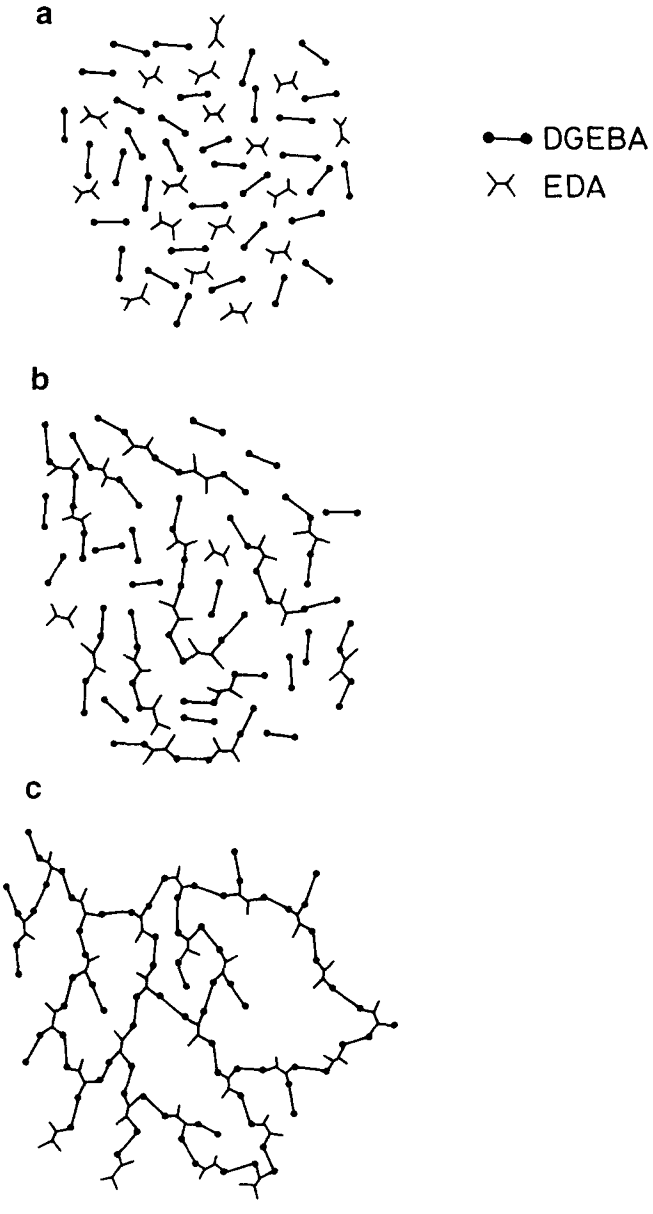

Figure 10 The process that forms a two-dimensional branched DGEBA/EDA (in the stoichiometric ratio) epoxy network: (a) mixing stage; (b) linear growth; (c) branching stage

According to the data in *Table 1* and our earlier analysis of the reaction in terms of the extent of curing, the molecular chains began to branch after 53 min and crosslink after 71 min. Thus, the formation of ribbons in the ammonium salts took place during the period of the branching reactions. After that, the crosslinked molecular chains were too big to be precipitated as an ammonium salt.

So far, we have demonstrated that the formation of the ribbon texture is related to the branching of the DGEBA/EDA molecular chains. The process that forms a two-dimensional branched DGEBA/EDA epoxy network cured in the stoichiometric ratio is shown schematically in *Figures 10a–c*. The chemical reactions of the mixed monomers begin with linear growth of the chains and then proceed with branching reactions, in which only three out of four amine groups in each EDA molecule react. It has been suggested that two-dimensional branched molecular chains containing considerable numbers of highly polar groups, such as amine groups and hydroxy groups, might pack together during the curing reaction[2]. In that case, packing might be facilitated by increasing either the time allowed for branching reactions or the concentration of branched molecular chains.

When the DGEBA/EDA epoxy resins in the stoichiometric ratio reached the branching reactions by curing at 20°C, the agglomerations of ribbon textures in the precipitates had a size of 110–210 μm, about twice as big as those prepared by curing at 30°C. *Figure 11a* shows a typical SEM photograph of the former precipitates. As the curing temperature was increased to 40°C, the ribbon texture was replaced by a tiny leaf-like texture, as shown in *Figure 11b*. According to *Table 1*, the times allowed for branching reactions are 40 min, 18 min and 9 min at 20°C, 30°C and 40°C, respectively. The results indicate that longer branching times cause the ribbon texture to grow, while shorter times prevent the formation of the ribbon texture. However, it should not be ruled out that the temperature during the preparation of the ammonium salt might affect the size of the precipitate. Nevertheless, since the branched molecular chains are assumed to have a tendency towards packing, the longer branching time should favour this. This hypothesis was further supported by the curing reactions of DGEBA/EDA in 50% and 200% stoichiometric ratios at 30°C.

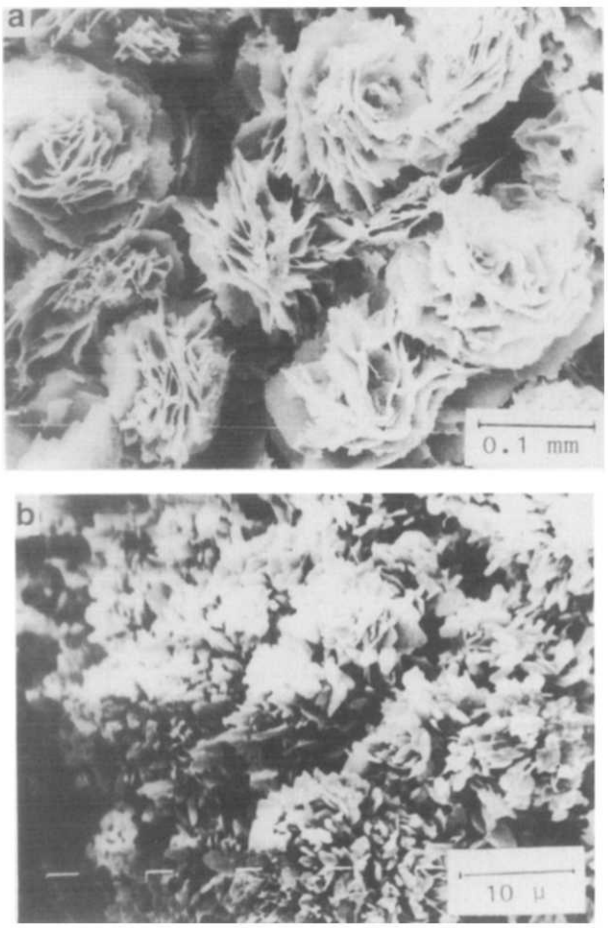

Figure 11 Typical SEM photographs of DGEBA/EDA (in the stoichiometric ratio) ammonium salts prepared after the curing reaction had reached the branching stage at (a) 20°C and (b) 40°C

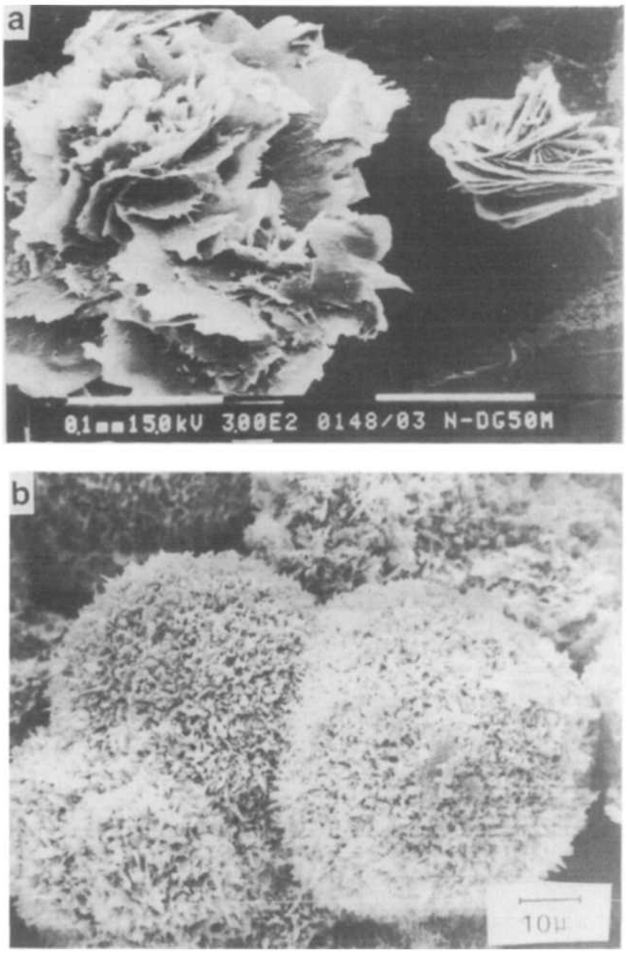

Figure 12 Typical SEM photographs of DGEBA/EDA ammonium salts prepared in (a) 200% and (b) 50% stoichiometric ratios after the curing reaction had reached the branching stage at 30°C

Figures 12a and *12b* show the typical textures of the precipitates prepared from the cured DGEBA/EDA in 200% and 50% stoichiometric ratio, respectively. The agglomeration of ribbon textures shown in *Figure 12a* have a size of 110–250 μm, bigger than those in the precipitate prepared from the cured DGEBA/EDA in the stoichiometric ratio. Apparently, this is because the concentration of branched molecular chains in the former curing system was higher than that in the latter. On the other hand, when DGEBA was cured with 50%

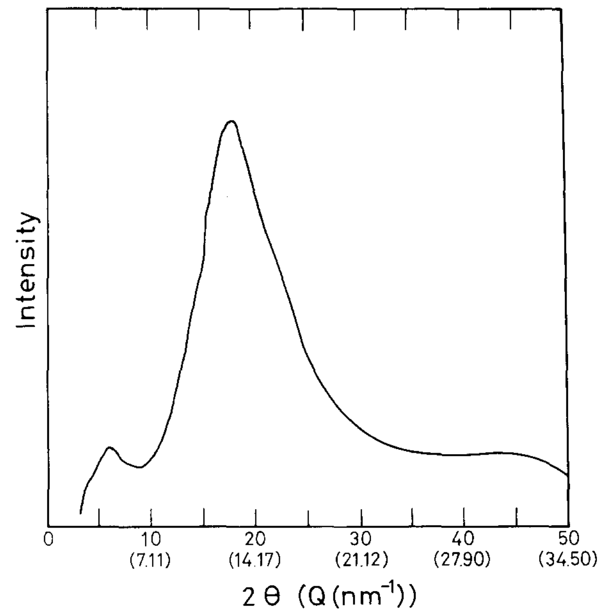

Figure 13 Wide-angle X-ray diffraction pattern of post-gelled DGEBA/EDA epoxy resin in the stoichiometric ratio

stoichiometric quantity of EDA, the concentration of branched molecular chains was lower. As a result, the packing of branched molecular chains was less significant, and thus no ribbon texture was found, as shown in *Figure 12b*. Therefore, packing of the branched molecular chains can also be facilitated by increasing the concentration of branched molecular chains.

Similar to the X-ray diffraction of post-gelled DGEBA/diethyltriamine (DETA) epoxy resin[2], the post-gelled DGEBA/EDA resin had a small diffraction peak at $Q = 4.1\ \mathrm{nm}^{-1}$, as shown in *Figure 13*, associated with a local ordering structure in the epoxy network. The d spacing of the local ordering structure in the epoxy network corresponding to this peak position is 15 Å, as calculated from the Bragg equation. Thus, the local ordering structure is believed to be composed of networks that are packed together at an average repeat thickness of 15 Å. Two other pieces of evidence were also observed in our laboratory[2]: one is that curing of the DGEBA/DETA epoxy resin under shear could facilitate the packing of the branched molecular chains in the shear direction; the other is that packed networks in post-gelled epoxy resins were directly observed in the fracture surfaces of chromium acetylacetonate toughened tetrafunctional epoxy resins and in the formic acid etched fracture surfaces of difunctional epoxy resins.

CONCLUSIONS

According to the statistical prediction for the curing of DGEBA/EDA epoxy resin in the stoichiometric ratio, most of the branching reactions of the growing linear chains occur at a curing extent between 16.7% and 25%. During the branching stage at 30°C, ammonium salts, prepared by the addition of an HCl/methanol mixture to the curing systems, were formed as agglomerations of ribbon textures. By increasing the time for branching reactions and decreasing the curing temperature, or by increasing the concentration of branched molecular chains with an amount of EDA over the stoichiometric ratio, the agglomeration of ribbon textures were encouraged to grow. After the curing reaction reached the crosslinking stage, no ammonium salts in epoxy networks were obtained. Since the wide-angle X-ray diffraction patterns of post-gelled epoxy resins indicated the existence of packed networks at an average repeat thickness of 15 Å, the ribbon texture was believed to be composed of packed networks, which turned out to be a structural element present after curing.

ACKNOWLEDGEMENT

Financial support for this work from the National Science Council of Taiwan through grant NSC-79-0405-E002-02 is gratefully acknowledged.

REFERENCES

1 Prime, R. B. in 'Thermal Characterization of Polymeric Materials' (Ed. E. A. Turi), Academic Press, New York, 1981, Ch. 5
2 Lin, K.-F., Shu, W.-Y. and Wey, T. L. *Polymer* 1993, **34**, 277
3 Kumar, S. and Adams. W. W. *Polymer* 1987, **28**, 1497
4 Lovell, R. and Windle, A. H. *Polymer* 1990, **31**, 593
5 Korkhov, V. P., Faitel'son, E. A. and Molchanov, Y. M. *Mekh. Kompoz. Mater.* 1989, **6**, 1103
6 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw-Hill, New York, 1972, p. 4-16
7 Riccardi, C. C., Adabbo, H. E. and Williams, R. J. J. *J. Appl. Polym. Sci.* 1984, **29**, 2481
8 Johnson, R. E. and Kiokemeister, F. L. 'Calculus with Analytical Geometry', Allyn and Bacon, Boston, 1969, p. 811
9 Riccardi, C. C. and Williams, R. J. J. *Polymer* 1992, **33**, 45
10 Nakanishi, K., Goto, T. and Ohashi, M. *Bull. Chem. Soc. Jpn* 1957, **30**, 403
11 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw-Hill, New York, 1972, p. 4-3
12 Cholli, A., Ritchey, W. M. and Koenig, J. L. *Am. Chem. Soc. Symp. Ser.* 1984, **243**, 233
13 Cullity, B. D. 'Elements of X-Ray Diffraction', Addison-Wesley, Massachusetts, 1972, p. 103
14 Shu, W.-Y. and Lin, K.-F. in 'Proceedings of the 13th ROC Polymer Symposium' (Ed. D. Hu), National Tsin-Hua University, Hsin-Chu, Taiwan, 1990, p. 472