JOURNAL OF MATERIALS SCIENCE 25 (1990) 241–245

Phase separation mechanism of rubber-modified epoxy

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The phase separation mechanism during the cure reaction of a liquid rubber-modified epoxy resin was investigated by light scattering, light microscopy, torsional braid analysis, electron microscopy, and differential scanning calorimetry. The binary mixture of epoxy oligomer (diglycidyl ether of bisphenol A) and carboxyl-terminated butadiene–acrylonitrile copolymer (liquid rubber) exhibited the upper critical solution temperature-type phase behaviour. The mixture loaded with curing agent was a single-phase system in the early stage of curing. When the cure reaction proceeded, phase separation took place via the spinodal decomposition induced by the increase in the molecular weight of epoxy. This was supported by the characteristic change of light scattering profile with curing time. Electron microscopy revealed that, in cured resin, the spherical rubber domains are dispersed somewhat regularly in an epoxy matrix. The regular domain arrangement seems to result from a specific situation; the competitive progress of the spinodal decomposition and polymerization; i.e. the coarsening process to irregular domain structure seems to be suppressed by network formation in the epoxy phase. It was also shown that curing at higher temperatures resulted in the suppression at an earlier stage of spinodal decomposition, and hence, shorter interdomain spacing.

1. Introduction

Rubber-toughened epoxy resins are prepared by curing epoxy in the presence of liquid rubber, e.g. carboxyl-terminated butadiene–acrylonitrile liquid rubber (CTBN). It is well known that cured resin consists of the spherical domains of rubber-rich phase and a matrix of epoxy-rich phase. There are many studies on the relationship between the two-phase structure and the mechanical properties of the cured resins [1–8]. In this paper the structure development during the curing process is discussed. While the subject has been dealt with in several publications [9–11], no systematic study has been carried out. We investigated the phase separation behaviour in CTBN-modified epoxy resin during curing by light scattering and optical microscopy, until the system was completely vitrified. For the cured system, the results obtained by light scattering are compared with those obtained by transmission and scanning electron micrographies. Torsional braid analysis is carried out to monitor the gel point and the vitrification process. Analysis by differential scanning calorimetry (DSC) renders the time–conversion curve. From these results, we undertake a clarification of the mechanism of structure development.

2. Experimental details

The epoxy oligomer was a diglycidyl ether of bisphenol A, Epikote 828 (Yuka-Shell Epoxy Co.). The curing agent was 4-4′-diaminodiphenylmethane (DDM), and the liquid rubber was carboxyl-terminated butadiene–acrylonitrile random copolymer, Hycar CTBN 1300X8 ($M_n \simeq 3500$, 17 wt % bound acrylonitrile) (Ube Industries, Ltd–B.F. Goodrich Chemical Company).

First, CTBN was pre-reacted with an equal amount of the epoxy oligomer at 150° C for 2 h under a stream of nitrogen. The pre-reacted CTBN was used throughout this study.

To determine the phase diagram of the binary mixture of the epoxy oligomer and the pre-reacted CTBN, the two oligomers were thoroughly mixed in a mortar with a pestle at room temperature. The mixture was spread on to a cover glass (for microscopy). The thin layer of mixture on the cover glass was inserted in a heating–cooling stage (Linkam TH600) mounted on a light microscope. This stage can be programmed to provide a linear temperature rise and fall. First, the temperature was elevated to attain a single-phase mixture, and then the mixture was cooled. We selected four cooling rates; 5, 3, 2 and 1° C min^{-1}. During the linear temperature cooling, we observed an onset of phase separation under the light microscope. Based on these observations, we obtained the phase diagram of the epoxy oligomer/pre-reacted CTBN mixture.

We also prepared a mixture loaded with DDM in the same way. The ternary mixture (epoxy oligomer/pre-reacted CTBN/DDM) on the cover glass was placed in a hot chamber kept at a constant temperature and was cured. The chamber was set horizontally on the light scattering stage [12]. Radiation from a He–Ne

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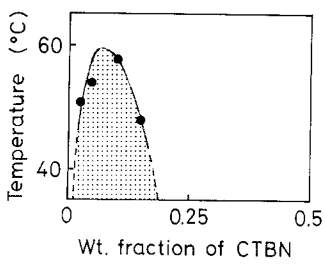

Figure 1 UCST-type phase diagram of the epoxy oligomer/pre-reacted CTBN mixture.

gas laser of 632.8 nm wavelength was applied vertically to the thin layer of mixture. The goniometer trace of the scattered light from the thin layer was given under a Vv (parallel polarized) optical alignment. Thus, the change in the light-scattering profile was recorded at appropriate intervals during isothermal curing. A light-scattering pattern was also observed using a photographic technique similar to that of Stein and Rhodes [13]. Structure development with curing was also observed under the light microscope.

The change in the relative modulus of the ternary mixture with curing was measured by the torsional braid analysis (Rheolograph TBA, Model 562, Toyoseiki Co.).

Two-phase morphology in the cured resin was observed by transmission and scanning electron microscopy (TEM and SEM). For TEM observation, the ultra-thin sections were microtomed from the cured resin stained with osmium tetraoxide. For SEM observation, the cured resin was fractured in liquid nitrogen and rinsed with tetrahydrofuran.

The conversion (degree of reaction) of epoxy was estimated by DSC (du Pont, model 910); from the area of the exotherm peak (temperature range: 75 to 275° C) evolving from the reaction during the DSC heating run at 20° C min^{-1}.

3. Results and discussion

3.1. Phase diagram of epoxy oligomer/pre-reacted CTBN mixture

The binary mixture of epoxy oligomer and the pre-reacted CTBN was heterogeneous at room temperature. When the temperature was elevated, e.g. up to 100° C, the mixture changed to an homogeneous system. During linear cooling from the homogeneous mixture, an onset of phase separation was observed under the light microscope when the temperature reached T_s. T_s varies with cooling rate; the higher rate yielded the lower T_s. Plotting T_s against heating rate, we obtained an intercept of T_s, at which the heating rate is zero. The intercept temperature may correspond to the binodal temperature. The binodal points thus estimated are shown by full circles in Fig. 1, indicating the upper critical solution temperature (UCST) type phase behaviour.

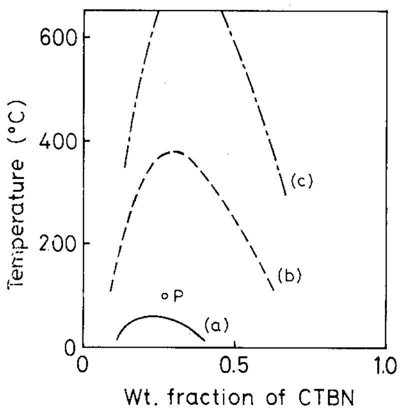

Figure 2 Variation of UCST-type phase diagram with increase in molecular weight of epoxy. (a) Calculated spinodal curve having the same critical point as that of Figs 1; $\chi = 0.041 + (500/RT)$, where R is the gas constant. (b) (c) Estimated spinodal curves for the systems having double and triple molecular weight of epoxy, respectively.

On the basis of current understanding of polymer–polymer miscibility, the UCST in Fig. 1 is expected to be elevated and the two-phase region would prevail in the phase diagram, as the molecular weight of epoxy increases with curing. This situation is demonstrated in Fig. 2.

Fig. 2 shows the spinodal curves which were estimated as follows. When the phase diagram is given as in Fig. 1, we can estimate the interaction parameter, χ_{12}, as a function of temperature, T, by assuming $\chi = A + (B/T)$, where A and B are constants to be selected by the best fitting of the critical temperature calculated on the basis of the Floly–Huggins equation

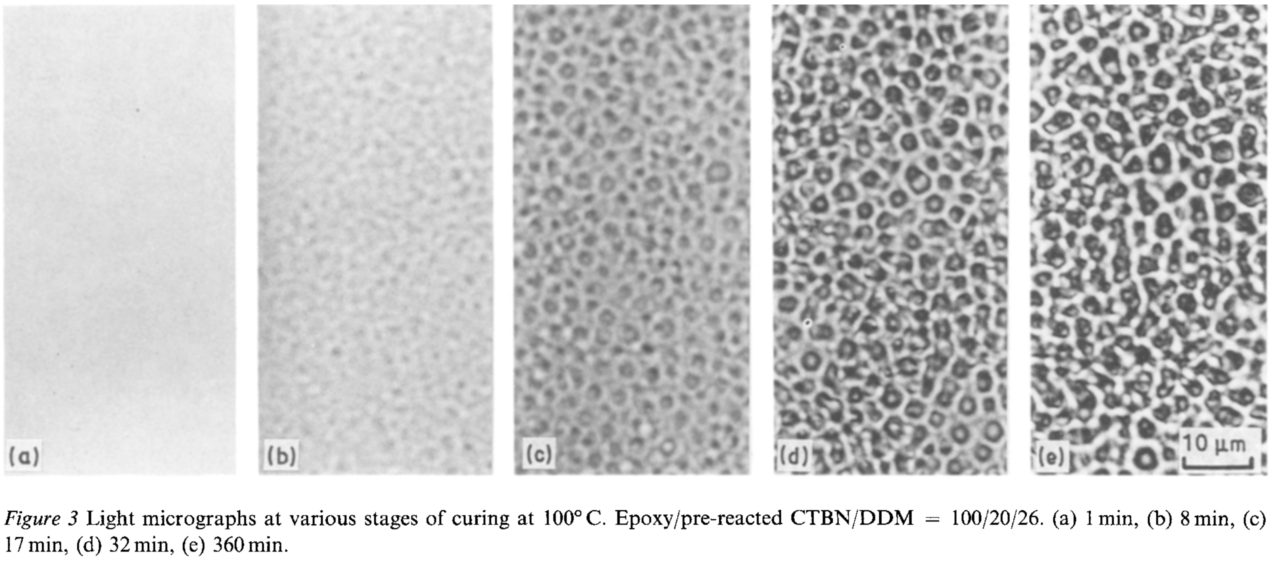

Figure 3 Light micrographs at various stages of curing at 100° C. Epoxy/pre-reacted CTBN/DDM = 100/20/26. (a) 1 min, (b) 8 min, (c) 17 min, (d) 32 min, (e) 360 min.

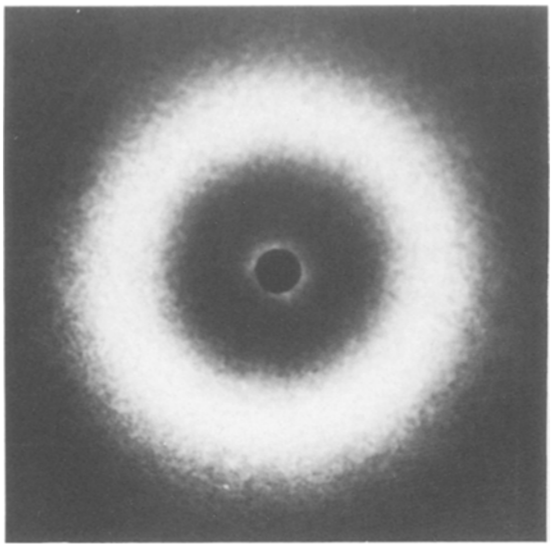

Figure 4 Light scattering pattern (Vv). Its goniometer trace is shown in Fig. 5 (24 min curve).

to the observed one [14]. Once $\chi(T)$ is given, one can easily obtain the spinodal curve when the molecular weights of component polymers vary. Curves (b) and (c) in Fig. 2 are those estimated when the molecular weight of epoxy doubles and triples respectively.

Fig. 2 implies that, if the curing proceeds at point P, the mixture is initially a homogeneous mixture and it will be thrust into a two-phase region after a certain curing time. Hence, the spinodal decomposition is expected to take place in the curing process.

3.2. Phase separation behaviour

Fig. 3 shows light micrographs observed at various stages of curing. Immediately after the temperature jump from room temperature to the curing temperature (100° C, above UCST), the system was homogeneous (Fig. 3a). After a certain time lag, phase separation took place, resulting in a fairly regular microscopic texture (Fig. 3b). Then, the image contrast of the texture became strong and the periodic distance decreased slightly with cure time (Figs 3c to e).

As expected from the micrographs in Fig. 3, a ring pattern of light scattering appeared after the time lag. A typical example is shown in Fig. 4. The ring pattern suggests the development of a regularly phase-separated structure. It also implies no preferred orientation of the structure. The ring pattern became brighter with cure time. This situation is demonstrated in terms of the change in the light-scattering profile given by the goniometer trace of scattered light (Fig. 5). The ring pattern and the characteristic change of scattering profile are the hallmarks of spinodal decomposition.

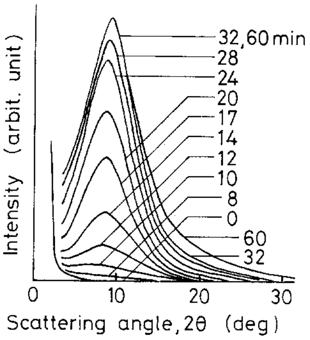

Figure 5 Change of light scattering profile with curing at 100° C. Compounding formula is the same as in Fig. 3.

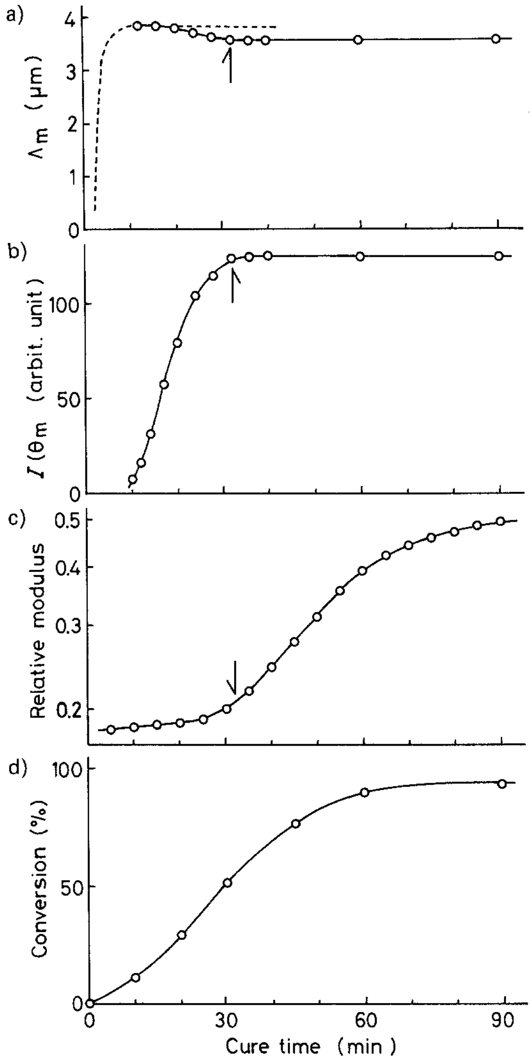

Figure 6 Time variations of (a) periodic distance by light scattering, (b) scattered intensity, I, at peak angle, θ_m, (c) the relative modulus by TBA and (d) conversion by DSC. Compounding formula and curing temperature are the same as in Fig. 3.

One can estimate the periodic distance (Λ_m) of the phase-separated structure as a Bragg spacing from the peak angle of scattering profile in Fig. 5. The variation of Λ_m with cure time is shown in Fig. 6a. The periodic distance decreases slightly with cure time and eventually levels off, suggesting that further structure development is suppressed by cross-linking and/or vitrification of the epoxy-rich phase. Consulting the time variations of the scattered intensity at peak angle $I(\theta_m)$ (Fig. 6b), TBA modulus (Fig. 6c), and the conversion estimated by DSC exotherm peak area (Fig. 6d), the overall two-phase structure seems to cease development as the polymerization approaches the gel point (at around 50% conversion; see arrow in Fig. 6c).

3.3. Two-phase morphology in cured resin

Fig. 7a is a transmission electron micrograph of the cured resin. One can see the two-phase structure in

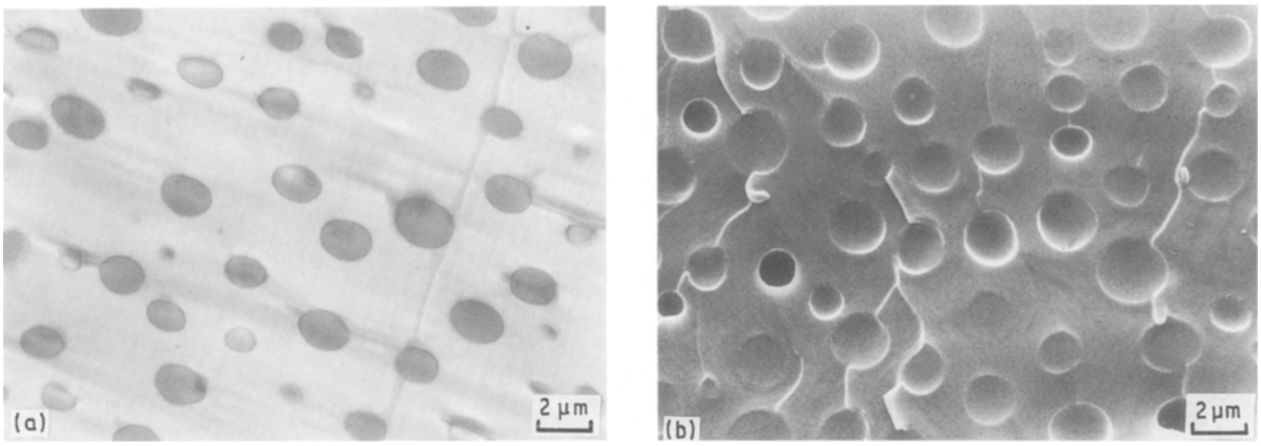

Figure 7 (a) TEM and (b) SEM of cured resin. Compounding formula and curing temperature are the same as in Fig. 3. Cure time 5 h.

which spherical rubber domains are dispersed in an epoxy matrix. Note here that the domain size is fairly uniform and the interdomain distance is approximately equal to the periodic distance estimated by light scattering profile in Fig. 6a.

Fig. 7b is a scanning electron micrograph of the same specimen. The two-phase structure here is almost identical to that of Fig. 7a. It suggests that the SEM observation is not an artefact. The SEM seems to suffice to investigate the two-phase morphology in our thermoset resin.

On the basis of the above results, a plausible scenario of the structure development in our rubber-modified epoxy resin may be as follows. After the temperature jump to curing temperature, the homogeneous mixture starts to phase-separate by spinodal decomposition (as already depicted in Fig. 2), resulting in the development of the co-continuous structure which is characteristic of spinodal decomposition, as shown schematically in Fig. 8a. When the phase separation proceeds, the structure grows self-similarly (Fig. 8b). At the same time, the thermodynamic quench depth $|\chi - \chi_s|$ (χ_s being the interaction parameter at the spinodal) increases, because the UCST-type phase boundary will be elevated by the increase in the molecular weight with curing (see Fig. 2). The higher quench depth takes the shorter periodic distance.* When the quench depth effect prevails over the coarsening process, the periodic distance may slightly decrease with cure time, in such a way as in Fig. 6a.

Now, at the late stage of spinodal decomposition, the phase connectivity will be interrupted to yield a droplet structure (Fig. 8c). Then, once an epoxy network has been established in the matrix, further curing will proceed without changing the loci of the droplets. Hence, the periodic distance will be maintained constant until the curing is completed. As a consequence, a regular arrangement of rubber domains is found in the cured resin (Fig. 8d).

3.4. Effect of cure temperature

From the above scenario, one may expect the domain structure with shorter interdomain distance (and a co-continuous structure, as an extreme case) in cured resin when the structure can be fixed by network formation in the earlier stage of phase separation. It could be realized by accelerating the cure rate. The simplest way may be to elevate the cure temperature. On the basis of this scheme, we investigated the effect of cure temperature on the development of structure.

As expected, the cure rate increased with increasing cure temperature, as shown in Fig. 9. Arrows in the figure represent the levelling off points in the $I(\theta_m)$ curves, which correspond to the TBA gel points. It can be seen that the mixture is gelled and loses mobility at an earlier stage for curing at higher temperature.

Fig. 10 shows the periodic distance obtained by light scattering in the cured resin as a function of the cure temperature. The periodic distance decreases with increasing cure temperature, as expected. This is confirmed by SEM observation, as demonstrated by the solid circles in Fig. 10. Scanning electron micrographs of the resins cured at the lowest temperature (100° C) and the highest one (180° C) are shown in Fig. 11. Fig. 11b suggests that, even by curing at the highest temperature, the two-phase morphology is still the

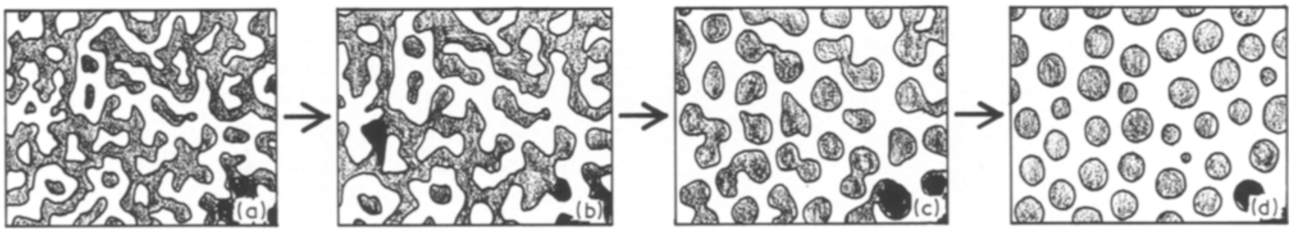

Figure 8 Schematic representation of phase separation scheme, resulting in a fairly regular domain structure.

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*According to the recent theory by Binder [15], the periodic distance, Λ_m, is expected to decrease as the quench depth increases: $\Lambda_m \sim |\chi - \chi_s|^{-1/2}$.

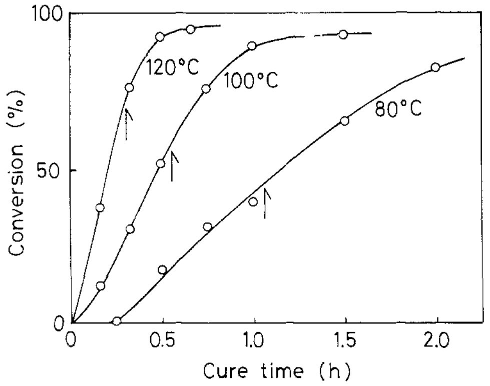

Figure 9 Time–conversion curves at various cure temperatures. Epoxy/pre-reacted CTBN/DDM = 100/10/26.

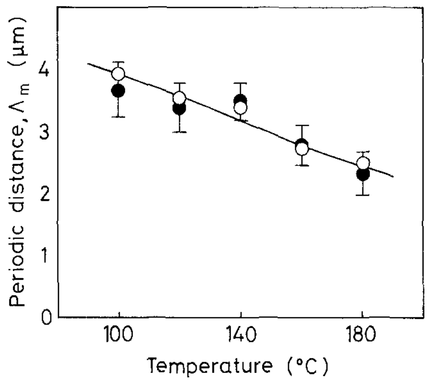

Figure 10 Periodic distances by (○) light scattering and (●) SEM in cured resins prepared at various temperatures compounding formula is the same as in Fig. 9.

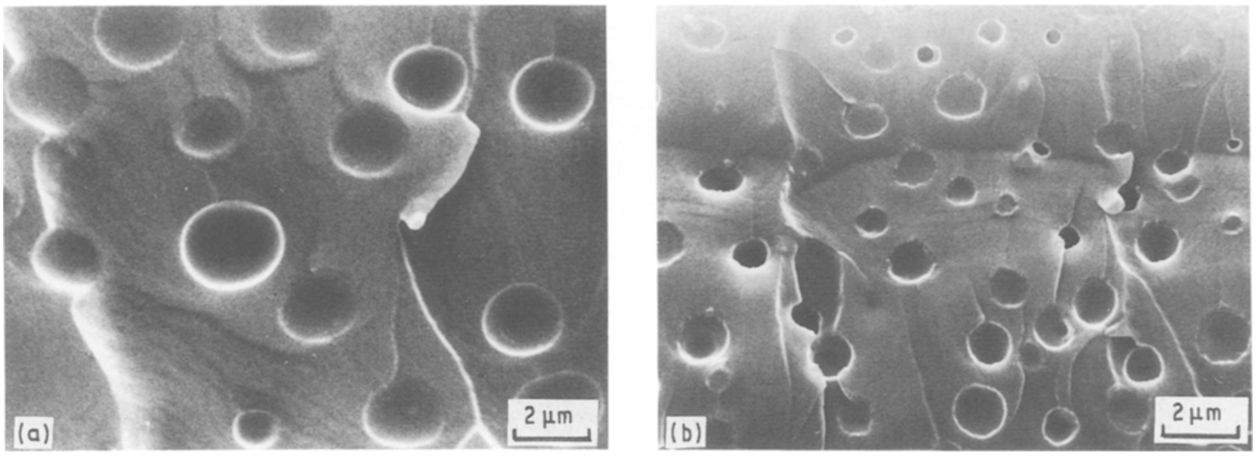

Figure 11 SEM of resin. Cured at (a) 100° C, (b) 180° C. Compounding formula is the same as in Fig. 9.

spherical domain structure; i.e. the co-continuous two-phase structure could not be obtained in the limited condition. It seems that, in order to prepare the co-continuous structure, we have to use another curing agent with a much higher reactivity.

4. Conclusion

The prevailing mechanism of phase separation during curing of the liquid-rubber modified epoxy resin seems to be spinodal decomposition under the successive increase of the thermodynamic quench depth. The chemical reaction during curing may be very complicated. It may involve chain extension, branching and cross-linking. The reaction induces phase separation in the early stage of curing and suppresses the separation at the late stage. That is, the complex chemical reaction causes the change in the physical state of the mixture and finally fixes the resulting state. A superposition of the chemical complexity on physical complexity makes it hard to understand and discuss in detail. However, if efforts are concentrated only on the competitive situation between the chemical and physical processes, we will be able to control the morphological development.

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Received 6 October 1988
and accepted 28 February 1989