Reaction-induced phase separation in rubber-modified epoxy resins

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A mixture of epoxy with liquid nitrile rubber (CTBN, ATBN) was cured under various conditions. Structure development during curing was investigated by light scattering, scanning electron microscopy and torsional braid analysis. High temperature cure above 100°C yielded a spherical domain structure with fairly uniform domain size; the higher cure rate, the smaller was the domain size. High temperature cure using a curing agent with extremely low reactivity yielded a spherical domain structure having a bimodal distribution in domain size. Low temperature cure (at room temperature) yielded a co-continuous two-phase structure. The variation in the two-phase structure of the cured resins was successfully interpreted by a phase separation scheme based on the spinodal decomposition which is induced by the increase of the molecular weight of epoxy in the curing process. The cured resin with co-continuous structure was found to exhibit excellent damping efficiency and high peel strength.

(Keywords: epoxy resin; CTBN; ATBN; light scattering; spinodal decomposition; co-continuous structure; vibrational damping)

INTRODUCTION

Rubber-modified epoxy resins are prepared by curing mixtures of epoxy with liquid rubbers, such as carboxyl-terminated butadiene–acrylonitrile liquid rubber (CTBN) and amine-terminated butadiene–acrylonitrile rubber (ATBN). It is well known that the cured resins are two-phase systems, in which the spherical rubber domains are dispersed in the matrix of epoxy[1–3]. In a previous article[4], we investigated the phase separation mechanism in the curing process by light scattering. The results suggested that phase separation proceeds via spinodal decomposition induced by the increase in the molecular weight of epoxy and that the spherical domain structure results from the fixation of the phase-separated structure at a late stage of spinodal decomposition by the network formation of epoxy. According to this mechanism, it is expected that the structure fixation at the early stage of spinodal decomposition should yield the co-continuous two-phase structure which is characteristic of spinodal decomposition. This theory is tested in this paper. If the co-continuous structure is available, it must be supplementary evidence for the structure development mechanism via spinodal decomposition. The co-continuous two-phase structure should be a new morphology of rubber-modified epoxy resins. Hence it is also interesting to deal with the structure–property problem.

BACKGROUND

A binary mixture of epoxy (diglycidyl ether of bisphenol A) and CTBN exhibits UCST (upper critical solution temperature) type phase behaviour[4]; see *Figure 4*. The mixture loaded with curing agent is a single-phase system at the very early stage of curing. Curing then induces phase decomposition, because the UCST is elevated by the increase in the molecular weight of epoxy with curing, and hence the system is thrust into a two-phase region at curing temperature (see, for example point P in *Figure 4*). The light scattering studies in our previous article[4] indicated that two-phase structure develops via spinodal decomposition, as schematically shown in *Figure 1*. The spherical domain structure, which has been frequently reported in the literature as the two-phase morphology in cured materials[1–3], was shown to result from the fixation of the fragmented structures (*Figure 1c, d*) by network formation in the matrix of epoxy-rich phase. That is, it seems that the structure formation is governed by the competitive progress of the phase separation with the chemical reaction, and the phase separation is allowed to proceed to attain stage (c) or (d) (*Figure 1*) under conventional curing conditions.

From the above scheme, one may expect that the co-continuous structure (*Figure 1a, b*) would be maintained in the cured resin when the structure can be fixed by network formation at an early stage of phase separation. This would be realized by using a curing agent with high reactivity. On the contrary, if we use a curing agent with extremely low reactivity, what happens? This is the motivation behind the studies described in this paper.

EXPERIMENTAL

The epoxy oligomer used in this study was a diglycidyl ether of bisphenol A, Epikote 828, supplied by Yuka-Shell Epoxy Co. Two liquid rubbers were supplied by Ube Industries Ltd – B.F. Goodrich Chemical Company: CTBN (carboxyl-terminated butadiene–acrylonitrile random copolymer, Hycar CTBN 1300X8, 17 wt% bound acrylonitrile, $M_n \approx 3500$) and ATBN (amine-terminated butadiene–acrylonitrile random copolymer,

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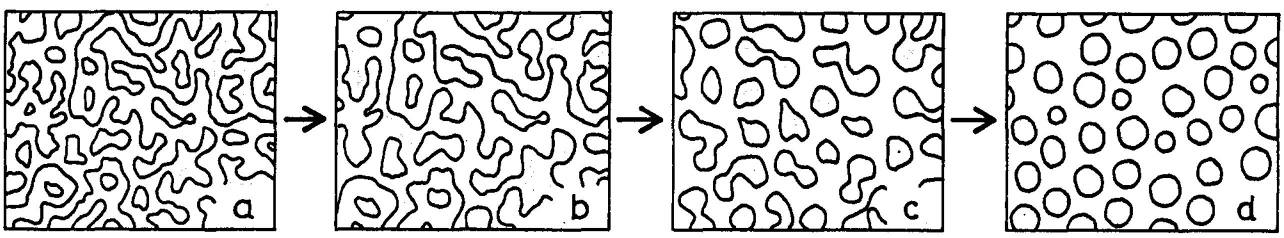
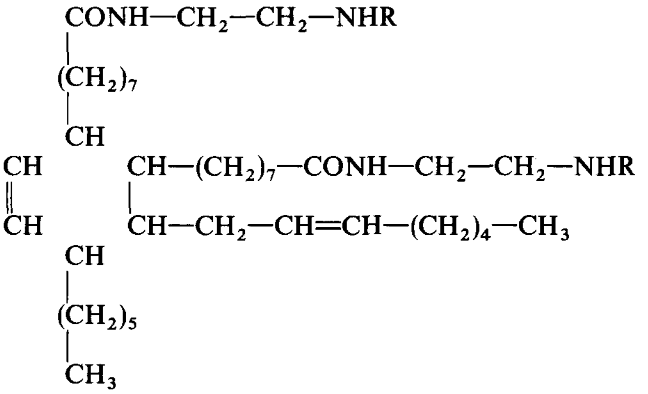


Figure 1 Schematic representation of phase separation scheme. Co-continuous structure, (a), develops at an early stage of spinodal decomposition and grows up self-similarly to yield a similar structure with longer periodic distance, (b). The phase connectivity is then interrupted to be converted to a fragmented structure, (c), and further to a spherical domain structure, (d)

Hycar ATBN 1300X16, 16.5 wt% bound acrylonitrile, $M_n \approx 3500$). Two curing agents were used: piperidine and Versamid® 125 (Henkel-Hakusui Co.). The structure of Versamid is reported to be



Before mixing, CTBN was pre-reacted with an equal amount of epoxy oligomer at 150°C for 2 h under a stream of nitrogen.

The phase diagram of the epoxy/ATBN mixture was determined by the cloud point method.

Epoxy oligomer, liquid rubber and curing agent were thoroughly mixed in a mortar with a pestle at room temperature. The mixture was cast onto a cover glass (for microscopy). The thin layer of mixture on the cover glass was placed in a hot chamber kept at a constant temperature and cured. The chamber was set horizontally on a light scattering stage[5]. Radiation from a He–Ne 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 of the light scattering profile was recorded at appropriate intervals during isothermal curing.

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

Two-phase morphology in the cured resin was observed under transmission and scanning electron microscopes (TEM and SEM). For TEM observation, 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.

Tensile stress–strain measurement of the cured resin was made on a Toyo Baldwin UTM-T-20 under a constant rate of elongation, 30% min^{-1}, at 24°C.

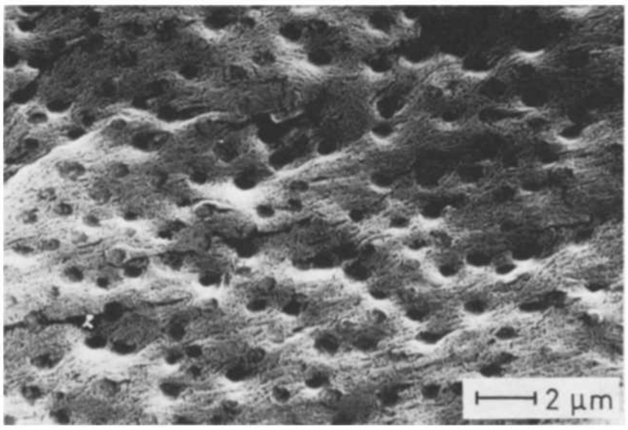


Figure 2 SEM of cured resin (epoxy/pre-reacted CTBN/Versamid = 100/20/50); cured at 100°C for 1 h

Vibrational damping efficiency was evaluated by the resonance frequency method[6] in terms of loss factor η, the normalized imaginary part of the complex bending stiffness. The measurement was made for a sandwich configuration: steel plate (0.8 mm thick), cured resin (0.2 mm thick), steel plate (0.8 mm thick); 250 mm length × 30 mm wide.

The T-peel strength and shear strength were measured according to ASTM D1876 and D1002, respectively.

RESULTS AND DISCUSSION

Fast curing

Figure 2 is a SEM of the epoxy/pre-reacted CTBN system cured with Versamid. Spherical domains with uniform size are dispersed quite regularly. Versamid is known to be a highly reactive curing agent. The interdomain spacing Λ_m of this system is compared with that of a similar system cured with a less reactive curing agent (DDM; 4,4′-diaminodiphenylmethane) in *Figure 3*. As expected, Versamid renders a two-phase system with a shorter interdomain spacing. However, the domain structure is still spherical. In other words, even with the aid of a highly reactive curing agent, we failed to obtain a co-continuous structure such as that schematically shown in *Figure 1a* and *b*.

The results in *Figures 2* and *3* may imply that the rate of phase separation is still fast compared with the rate of chemical reaction and hence the co-continuous structure cannot be fixed by network formation of epoxy-rich phase at an early stage of phase separation. Another conceivable way to obtain the co-continuous structure is to slow down the rate of phase separation by decreasing the chain mobility. This can be accomplished by decreasing the temperature, for instance, down to room temperature. However, at low temperature, the epoxy/pre-reacted CTBN system is at a two-phase region in the phase diagram, as indicated by point Q in *Figure 4*. It is not appropriate for our purpose*.

On the other hand, epoxy/ATBN mixture has a UCST well below room temperature, as shown in *Figure 4*. This is a favourable UCST system. It was cured with Versamid at room temperature (then post-cured at 100°C). *Figure 5a* shows the SEM of the cured resin. Fine globules, a few micrometres in diameter, are seen. This size is fairly uniform. Furthermore, globules seem to be connected with each other. Note here that the interconnected globule structure is a kind of co-continuous structure.

Figure 6 shows the change of light scattering profile with room temperature curing. After a certain time lag, a scattering peak appears, suggesting the development of a regularly phase-separated structure. The intensity of scattered light increases with time, the peak angle being almost constant. By post-curing at 100°C, the peak angle θ_m hardly changed. The periodic distance estimated by using the θ_m (using Bragg's law) is almost equal to the inter-globule distance in *Figure 5a*.

The time variation of $I(\theta_m)$ from *Figure 6* is plotted and compared with that of the TBA modulus in *Figure 7*. *Figure 7* suggests that, as expected, the gel point (indicated by the arrow) appears at an early stage of phase separation, and the periodic distance is maintained constant (see *Figure 6*) at the later stage at which the concentration contrast between two phase increases and levels off (as indicated by the variation of $I(\theta_m)$).

Figures 5–7 probably tell us that the network is already established in the epoxy-rich region of co-continuous structure and prevents the fragmentation of the structure,

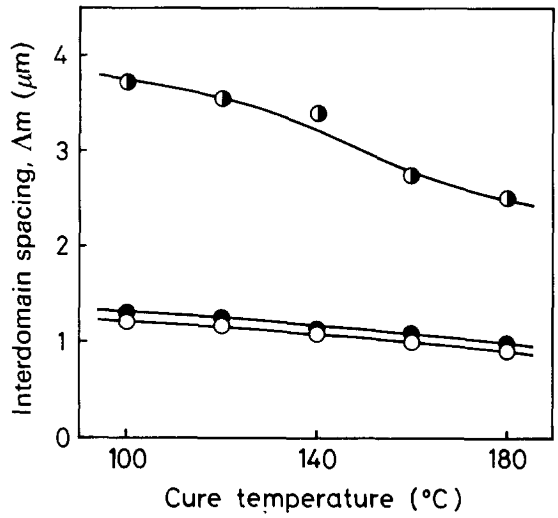


Figure 3 Interdomain spacing determined by light scattering in cured resins prepared at various temperatures: ●, ○, cured with Versamid (epoxy/pre-reacted CTBN/Versamid = 100/20/50, epoxy/pre-reacted CTBN/Versamid = 100/11.9/50, respectively); ◑, cured with DDM (epoxy/pre-reacted CTBN/DDM = 100/10/26): reproduced from previous paper[4]

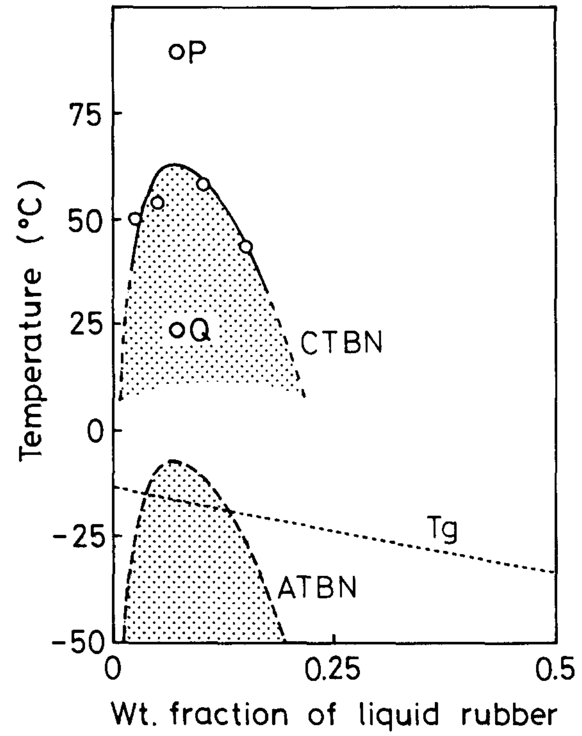


Figure 4 Phase diagrams of epoxy/liquid rubber mixtures: ——, epoxy/pre-reacted CTBN; ---, epoxy/ATBN. UCST of epoxy/ATBN system seems to be located just above the glass transition temperature of the mixture (straight dashed line, calculated by Fox equation)

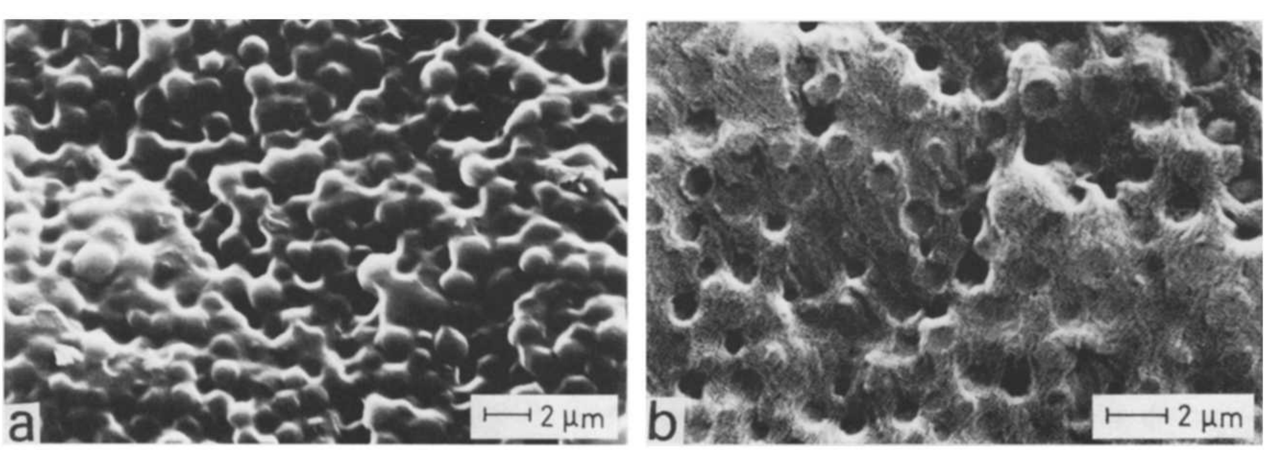


Figure 5 SEM of cured resin (epoxy/ATBN/Versamid = 100/45/50). (a) Cured at 24°C for 10 h and post-cured at 100°C for 1 h, showing the interconnected globule structure. (b) Cured at 100°C for 1 h, showing the spherical domain structure without room temperature cure (control)

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*Setting the curing temperature at the single-phase region is a prerequisite for the development of co-continuous structure via spinodal decomposition.

eventually resulting in the interconnected globule structure, as schematically shown in *Figure 8* (from (a) to (b)*). In any case, we successfully prepared the co-continuous two-phase system.

Slow curing

Piperidine is known to be a curing agent with low reactivity. It facilitates slow curing, as demonstrated by TBA curves in *Figure 9*.

Figure 10 is a TEM of the epoxy/pre-reacted CTBN system cured with piperidine. Large and small spherical domains are seen, suggesting a bimodal distribution of rubber domains. Note that the small domains are dispersed between the large ones.

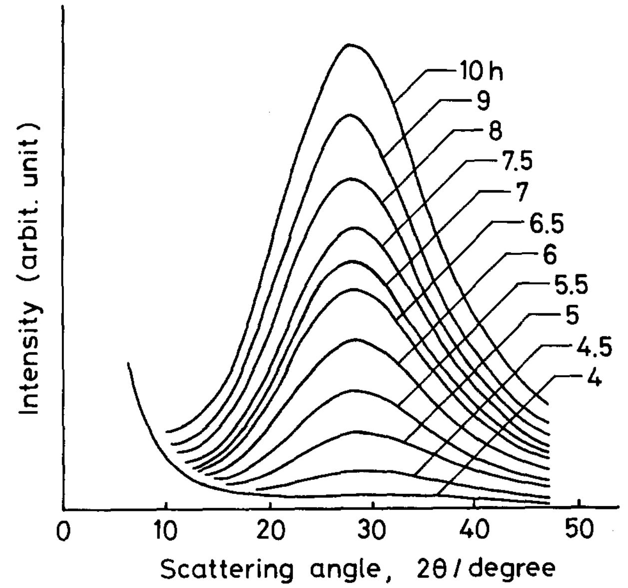

Figure 6 Change of light scattering profile with curing at 24°C. Compounding formula is the same as in *Figure 5*

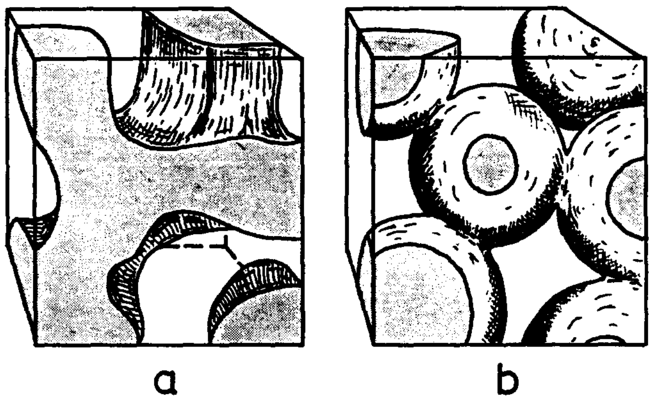

Figure 8 Schematic representation of structure change from (a) co-continuous structure by spinodal decomposition to (b) interconnected globule structure

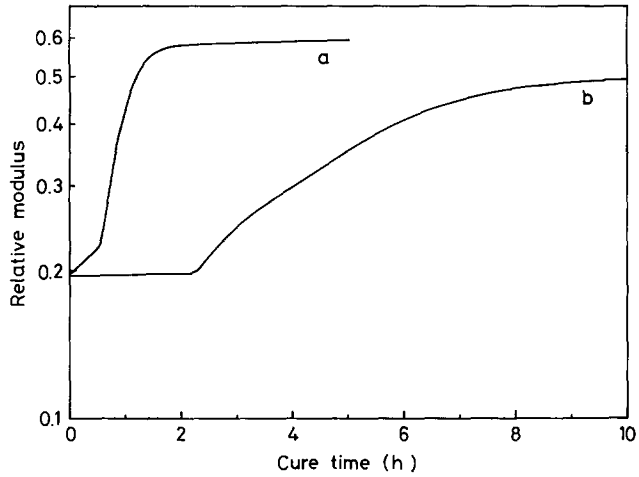

Figure 9 TBA curve for curing of epoxy/pre-reacted CTBN = 100/20 mixture with (a) DDM (26 phr) at 100°C and (b) piperidine (5 phr) at 90°C

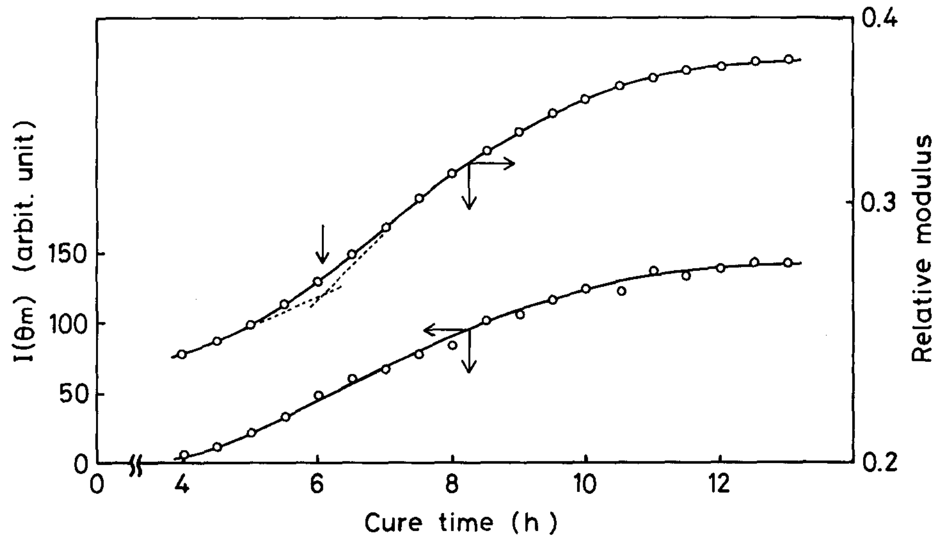

Figure 7 Time variation of relative modulus determined by TBA and scattered light intensity I at peak angle θ_m during room temperature cure. Compounding formula is the same as in *Figure 5*

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* This scenario is based upon the spinodal decomposition mechanism, as discussed in the caption to *Figure 1*. In contrast, one might argue that, during the curing process, the system has to pass through the metastable region before it is thrust into the unstable region, and hence phase decomposition by a nucleation-growth mechanism is expected to take place. However, this is not conceivable because, first, nucleation growth is well recognized to be a very slow process and it may be skipped (i.e. nothing happens at the metastable region) and, second, nucleation occurs accidentally and the subsequent growth results in an irregular domain structure (it never results in the regular structure that gives a light scattering peak).

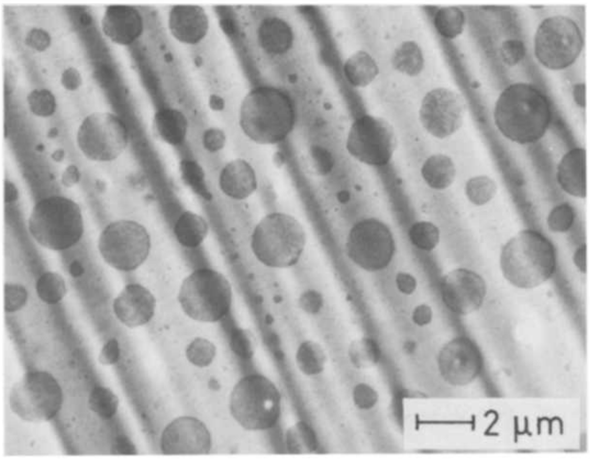

Figure 10 TEM of cured resin (epoxy/pre-reacted CTBN/piperidine = 100/20/5); cured at 90°C for 12 h

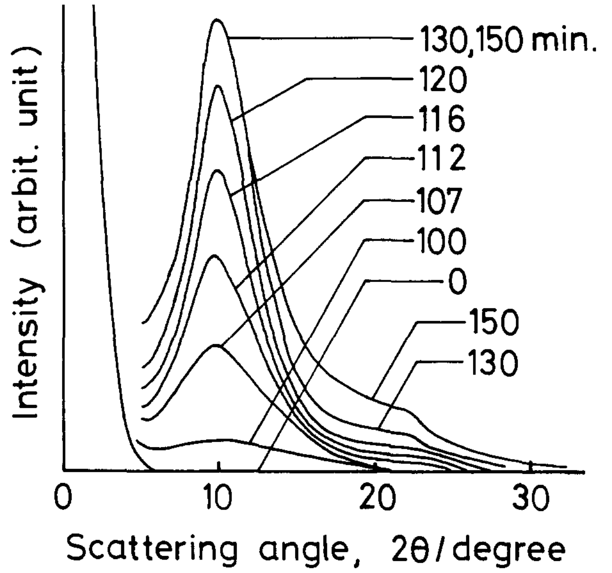

Figure 11 Change of light scattering profile with curing. Compounding formula and curing temperature are the same as in *Figure 10*

Figure 11 shows the light scattering profiles at various stages of curing. The scattering profile of the fully cured resin has two peaks. The small-angle peak can be assigned to the interdomain spacing between the large domains. The wide angle peak can be assigned to the overall spacing, including small domains. During the curing, the small angle peak appears after a certain time lag and the wide angle peak appears at a fairly late stage. Both peak angles are almost constant during the curing process.

The time variation of peak intensity $I(\theta_m)$ is plotted and compared with the change of TBA modulus in *Figure 12*. The intensity of the small angle peak levels off at the gel point (indicated by arrow), while the wide angle peak starts to increase just before the gel point and levels off soon after the gel point.

These results may imply that the regular arrangement of the large domains is accomplished in a similar way to *Figure 1d* and the phase decomposition of matrix phase then takes place under an extremely deep quench* to yield the small domains between the large domains.

Structure – property relationships

So far, we have shown that curing of a mixture of epoxy and liquid rubber results in three types of two-phase structure: uniform spherical domain structure[4], bimodal spherical domain structure (*Figure 10*), and co-continuous structure (*Figure 5a*), depending on the curing conditions. Among these two-phase structures, the most interesting is the last, especially in relation to the properties or performance of cured materials.

In *Figure 13*, the stress–strain behaviour of the cured resin with co-continuous (interconnected globule) structure is compared with that with spherical domain structure. The former has lower initial modulus and slightly larger elongation at break than the latter. The dramatic difference is in the yielding phenomenon: the former does not exhibit a yield point. This may originate from the co-continuous nature.

As shown in *Figure 14*, the cured resin with co-continuous structure exhibits excellent vibrational damping efficiency, better than neat resin and the modified resin with spherical domain structure. We believe that this also originates from the co-continuous nature.

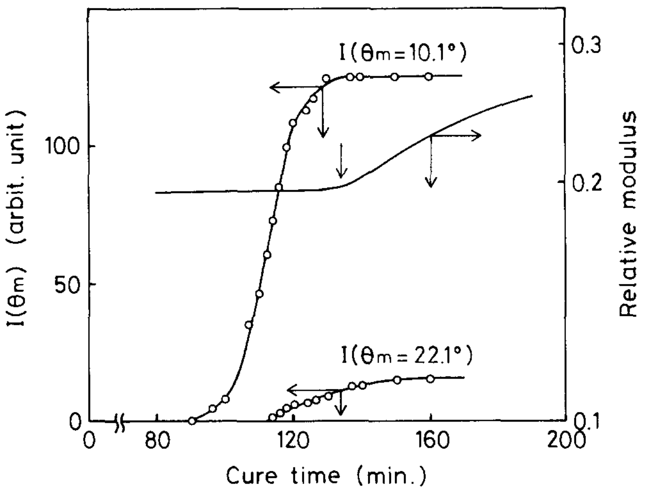

Figure 12 Time variation of TBA modulus and scattered light intensities at small and wide angles. Compounding formula and curing temperature are the same as in *Figure 10*

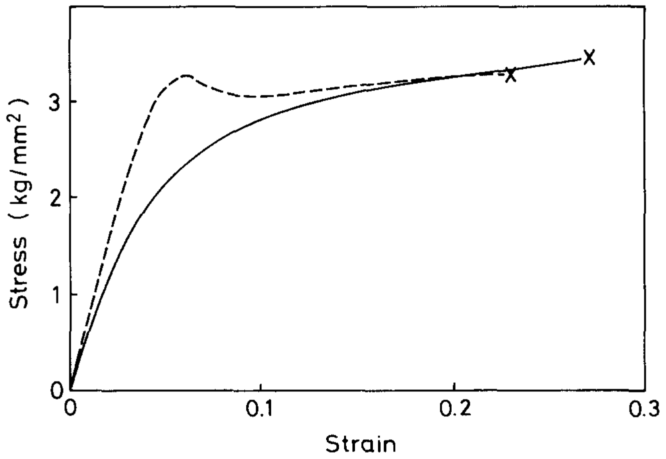

Figure 13 Stress–strain curves of cured resins (epoxy/ATBN/Versamid = 100/45/50) with co-continuous structure (——) and spherical domain structure (- - -). The former was cured at room temperature for 10 h and post-cured for 1 h. The latter was cured at 100°C for 1 h

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* At this stage, near the gel point, the UCST is expected to be very far above the cure temperature. Hence the thermodynamic quench depth, in terms of the temperature difference between UCST and cure temperature, should be extremely large.

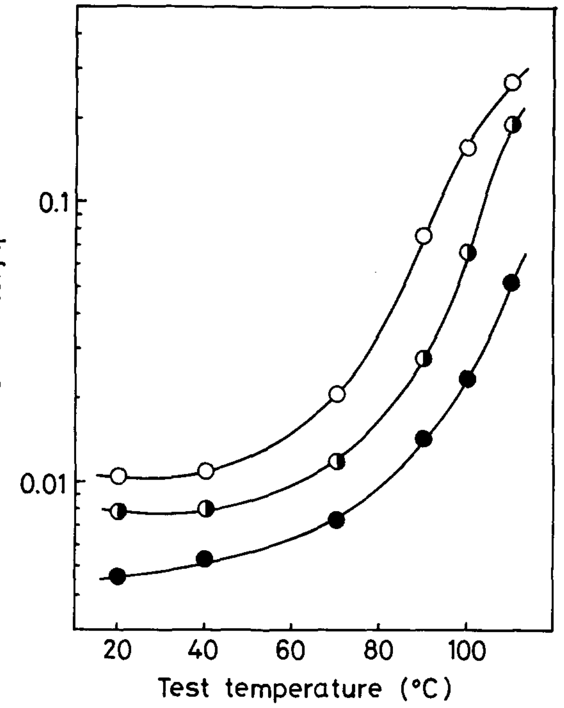

Figure 14 Vibration damping efficiency (loss factor η) determined by the resonance frequency method for epoxy/ATBN/Versamid = 100/45 (0)/50. ○, ATBN-modified resin with co-continuous structure; cured at 24°C for 10 h and post-cured at 100°C for 1 h. ◑, ATBN-modified resin with spherical domain structure; cured at 100°C for 1 h. ●, neat resin; cured at 100°C for 1 h

The cured resin with co-continuous strength also exhibited a high T-peel strength of 2.6 kg cm^{-1}, while the strength of the neat resin was 1.2 kg cm^{-1}. On the other hand, the shear strength of the former resin was slightly lower (214 kg cm^{-2}) than the latter (233 kg cm^{-2}). However, the former exhibited cohesive failure, while the latter exhibited interface failure.

CONCLUSION

High temperature cure of a mixture of epoxy with liquid nitrile rubber resulted in the development of monodisperse spherical domain structure (*Figure 2*). Faster cure yielded smaller domains (*Figure 3*). High temperature cure using a curing agent with extremely low reactivity yielded a bimodal distribution of spherical domains (*Figures 10* and *11*). Low temperature cure resulted in the development of co-continuous two-phase structure (*Figures 5a* and *8*). The morphological variation in the cured resins has been successfully interpreted in terms of a phase separation scheme based on spinodal decomposition, which is induced by the molecular weight increase of epoxy in the curing process. This implies that one can control the two-phase morphology by paying attention to the competition progress of phase separation and cure reaction. We believe that this is an important aspect for the design of high performance materials in multi-component thermosetting resins. As an example, vibrational damping material was demonstrated.

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