Structure development in epoxy resin modified with poly(ether sulphone)

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Structure development during the curing reaction in a ternary mixture of diglycidyl ether of bisphenol A (epoxy), poly(ether sulphone) (PES) and diaminodiphenylmethane (curing agent) was investigated by light scattering, scanning electron microscopy (SEM) and differential scanning calorimetry. In the early stage of curing, the ternary blend was a single-phase mixture. As 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 in light-scattering profile with curing time. SEM observation revealed the formation of a unique two-phase structure: connected globules of epoxy-rich phase arranged regularly (typical periodic distance, 0.5 μm) in a matrix of a PES-rich phase. The unique structure is assumed to be formed under a specific situation: competitive progress of phase separation and of the crosslink reaction. That is, once a loose network is established at the epoxy-rich region in the phase-separated system, further coarsening to a droplet-type structure could be suppressed, eventually resulting in the interconnected globule structure. Compared with neat epoxy resin, the cured ternary resin exhibited higher adhesive strength, in both peel and shear modes. The excellent adhesive property seems to originate from the characteristic connected-globule morphology.

(Keywords: epoxy resin; poly(ether sulphone); light scattering; spinodal decomposition; connected-globule structure; adhesive strength)

INTRODUCTION

Rubber-toughened epoxy resins are prepared by curing epoxy in the presence of liquid rubbers, e.g. carboxyl-terminated butadiene–acrylonitrile liquid rubber[1,2] and amine-terminated butadiene–acrylonitrile liquid rubber[3]. Basically, there are two-phase systems, in which rubber particles are dispersed in an epoxy matrix. Their morphology is similar to that of rubber-toughened thermoplastics, such as ABS (acrylonitrile–butadiene–styrene terpolymer) and HIPS (high-impact polystyrene). In the field of thermoplastics, a new concept has been proposed, i.e. toughening by inclusion of rigid polymer particles in a ductile polymer matrix[4–6]. One can find similar work in the field of thermosetting resins, epoxy resin modified with thermoplastic polymers[7–9]. All of these materials are two-phase systems in which spherical inclusions, a few micrometres or less in size, are dispersed in a matrix.

In contrast, it has been revealed that a co-continuous two-phase structure with unique periodicity is obtained by spinodal decomposition[10,11]. A co-continuous two-phase system consisting of plastic and rubber has been shown to exhibit unique mechanical properties that originate from the co-continuous nature: high initial modulus, large extension and complete strain recovery[12].

The work described here was undertaken in an attempt to obtain a co-continuous two-phase structure in a binary system of rigid thermosetting resin and ductile thermoplastic polymer, and to investigate the structure–property relationship. In order to perform spinodal decomposition, the system has to possess a single-phase region in the phase diagram (temperature vs. composition) and a two-phase region at high temperatures (lower critical solution temperature or *LCST* behaviour) or at low temperatures (upper critical solution temperature or *UCST* behaviour). Recently, Singh and Walsh found *LCST* behaviour in a binary mixture of Phenoxy and poly(ether sulphone) (PES)[13]. Phenoxy is a linear polymer prepared by condensation polymerization of epichlorohydrin and bisphenol A. The chemical structure resembles that of epoxy resin. So, we can expect *LCST*-type phase behaviour in an epoxy/PES system. If it is so, we can also expect spinodal decomposition induced by the increase in molecular weight of epoxy with curing.

First, we examined the phase diagram of an epoxy oligomer/PES system (starting materials). Then, we investigated the structure development during curing by light scattering. The two-phase structure in the cured system was analysed by scanning electron microscopy and differential scanning calorimetry. Adhesive strength, in both peel and shear modes, was measured to ascertain the structure–property relationship. It was hoped that these results would aid in designing high-performance materials by the control of structure development in multicomponent thermosetting resins.

EXPERIMENTAL

The epoxy oligomer, diglycidyl ether of bisphenol A, was supplied by Yuka–Shell Epoxy Co. (Epikote 828; $M_n \simeq 380$). The curing agent was an aromatic amine, 4,4′-diaminodiphenylmethane (DDM). Poly(ether sulphone)

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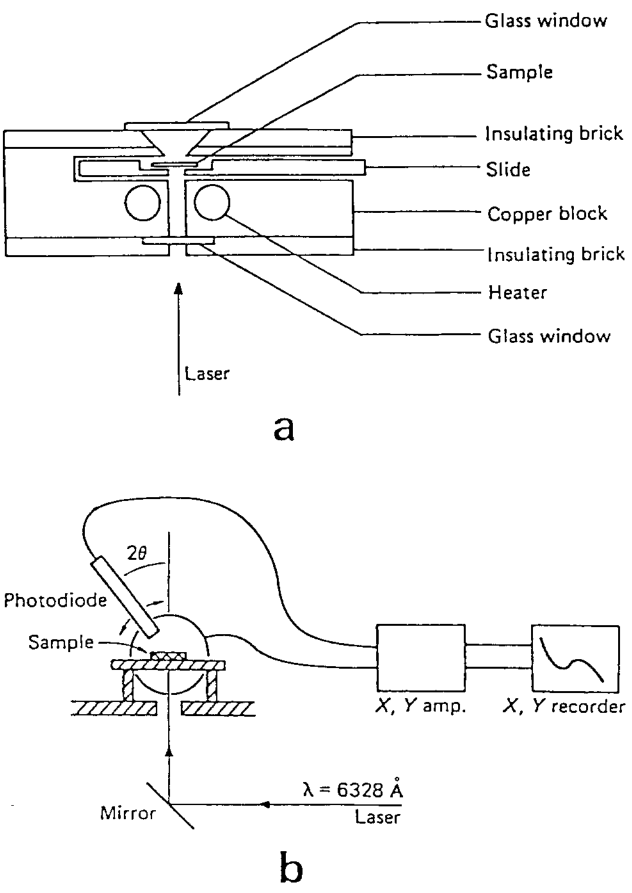

Figure 1 (a) Light-scattering apparatus and (b) hot chamber

(PES) was supplied by Mitsui Toatsu Co.–I.C.I. (Victrex 4100G; $M_n \simeq 17\,700$).

Epoxy oligomer and PES were dissolved at 10 wt% of total polymer in methylene chloride. The solution was cast onto a cover glass (for microscopy). The cast film was further dried under a vacuum of 10^{-4} mmHg for 12 h. The film on the cover glass was inserted in a heating stage, a Linkam TH600 heating–cooling stage. This stage can be programmed to provide a linear rise in temperature at any of 27 different rates. We selected four rates: 5, 3, 2 and 1°C min^{-1}. During the linear temperature rise, we observed the onset of phase separation under the light microscope. Based on this observation, we obtained the phase diagram of the epoxy/PES mixture.

We also prepared solution-cast films of the mixture loaded with DDM in the same way. The ternary mixture (epoxy oligomer/PES/DDM) on the cover glass was placed in a hot chamber kept at a constant temperature and was annealed. The chamber was set horizontally on the light-scattering stage as in *Figure 1*. Radiation from a He–Ne gas laser of 632.8 nm wavelength was applied vertically to the film specimen. The goniometer trace of the scattered light from the film was obtained under a Vv (parallel polarized) optical alignment. Thus, the change in the light scattering profile was recorded at appropriate intervals during isothermal annealing (curing). A light-scattering pattern was also observed by using a photographic technique similar to that of Stein and Rhodes[14].

The glass transition temperature of the cured specimen was measured by d.s.c. (du Pont, model 910).

The cured specimen was fractured in liquid nitrogen. The fractured specimen was immersed in methylene chloride at 24°C for 12 h. Then, the fractured–etched surface was observed under SEM (JEOL T-200).

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

RESULTS AND DISCUSSION

Phase diagram of epoxy/PES mixture

The solution-cast film of the binary mixture of epoxy oligomer and PES was transparent and homogeneous under the light microscope. During the linear temperature rise in the binary mixture, the onset of phase separation was observed under the light microscope when the temperature attained T_s. This temperature T_s varied with heating rate: higher rate yielded higher T_s. Plotting T_s *versus* 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 open circles in *Figure 2a*, indicating the *LCST* (lower critical solution temperature) behaviour. In *Figure 2a*, the glass transition curve is also shown (broken curve). The T_g curve was estimated by the Fox equation, using the d.s.c. data of PES and epoxy oligomer.

On the basis of current understanding of polymer–polymer miscibility, the *LCST* in *Figure 2a* is expected to go down and the two-phase region would prevail in the phase diagram, as the molecular weight of epoxy increases with curing. The T_g of the mixture would be elevated when the molecular weight increases. These situations are schematically demonstrated in *Figure 2b*.

Figure 2b implies that the mixture of composition ϕ is initially a single-phase system at T_{cure}; however, the system will be thrust into a two-phase regime as the curing reaction proceeds. Hence, spinodal decomposition is expected to take place in the curing process.

Structural change by light scattering

An epoxy/PES mixture loaded with DDM, e.g. Epikote 828/PES/DDM = 100/30/26, was a single-phase system at the curing temperature and no appreciable light scattering was detected from the mixture in the early stage of curing. After a certain time lag of ~6 min, a ring pattern of light scattering appeared as shown in *Figure 3*. The ring pattern implies the development of regularly phase-separated structure. It also indicates no preferred

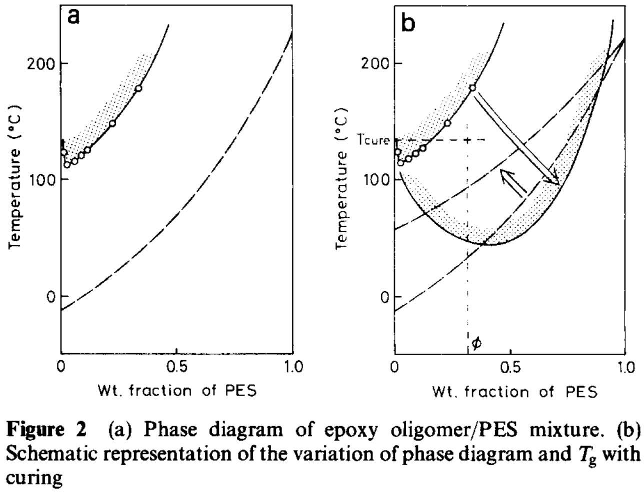

Figure 2 (a) Phase diagram of epoxy oligomer/PES mixture. (b) Schematic representation of the variation of phase diagram and T_g with curing

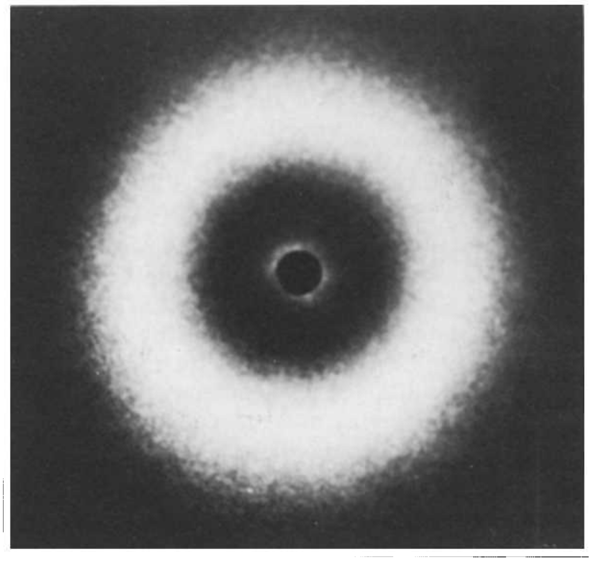

Figure 3 Light-scattering pattern (Vv). The goniometer trace of this ring pattern is shown in *Figure 4* (curve of 600 s)

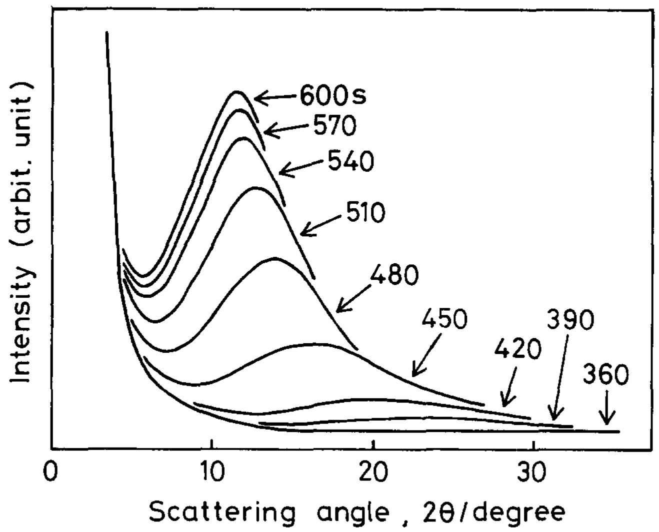

Figure 4 Change in the light-scattering profile with curing: epoxy/PES/DDM = 100/30/26; curing temperature = 140°C

orientation of the structure in the plane parallel to the film surface.

The ring pattern became brighter and its diameter decreased with curing time. This situation is demonstrated in terms of the change in the light-scattering profile given by the goniometer trace of scattered light. A typical example is shown in *Figure 4*. The ring pattern and the characteristic change in scattering profile are the hallmarks of spinodal decomposition.

One can estimate the periodic distance in the phase-separated structure as a Bragg spacing from the peak angle of the scattering profile in *Figure 4*. The variation in the periodic distance with curing time from *Figure 4* is shown by curve d in *Figure 5*. In *Figure 5*, such variations are also shown for another formulation (epoxy/PES/DDM = 100/50/26) and various curing temperatures. All of these curves indicate that the periodic distance increases with time, and eventually levels off, suggesting that further structure development is suppressed by crosslinking or the densification of the PES-rich region by approaching towards the T_g curve as phase separation proceeds (see *Figure 2b*).

Two-phase morphology in cured resin

In *Figure 6* are shown scanning electron micrographs of the cured resins. Compounding formulations and curing conditions are the same as in *Figure 5*.

As described before, these micrographs are obtained by SEM observation of the fractured and etched surfaces. Hence, PES is assumed to be rinsed away and the remaining material is a crosslinked epoxy-rich one. Fine globules of a few micrometres diameter are seen. The size is fairly uniform. Further, particles seem to be connected to each other. The connected-globule structure in our SEM observation implies a two-phase morphology of interconnected spherical domains of epoxy-rich phase dispersed regularly in a matrix of PES, as demonstrated schematically in *Figure 7*. Note here that the periodic distances between the globules in SEM exactly correspond to those obtained by light scattering in *Figure 5*.

The two-phase nature is confirmed by the d.s.c. thermograms in *Figure 8*, indicating two glass transitions. The lower curing temperature results in the lower T_g of the high-T_g (PES-rich) phase. This may be due to incomplete phase separation by approaching the T_g line during the curing reaction.

A plausible scenario for the development of the connected-globule structure may be as follows. After the temperature jump to the curing temperature, the homogeneous mixture starts to phase-separate by spinodal decomposition (as was already discussed in *Figure 2b*), resulting in the development of a co-continuous structure, such as schematically shown in *Figure 9a*. When phase separation proceeds, the periodic distance increases similarly. At the same time, phase connectivity will be interrupted by the increase in interfacial tension, resulting in a dispersed droplet-type

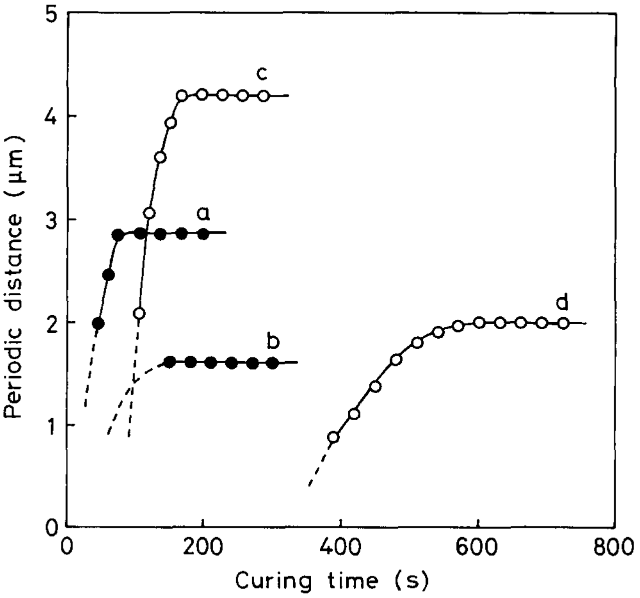

Figure 5 Variation of periodic distance with cure: (●) epoxy/PES/DDM = 100/50/26, curing temperature 200°C (a) and 170°C (b); (○) epoxy/PES/DDM = 100/30/26, curing temperature 170°C (c) and 140°C (d)

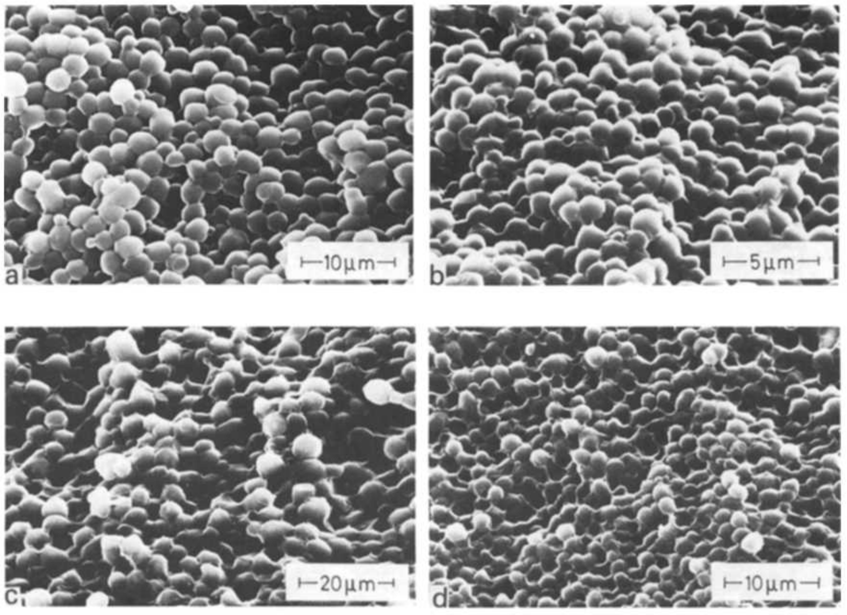

Figure 6 SEM micrographs of cured resins. Compounding formulations and curing temperatures are the same as in *Figure 5*, namely: (a) PES 50 phr, 200°C, 0.5 h; (b) PES 50 phr, 170°C, 3 h; (c) PES 30 phr, 170°C, 3 h; (d) PES 30 phr, 140°C, 3 h

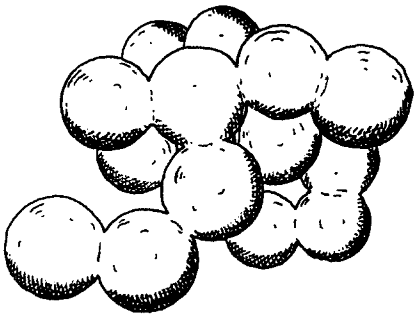

Figure 7 Schematic representation of connected-globule structure

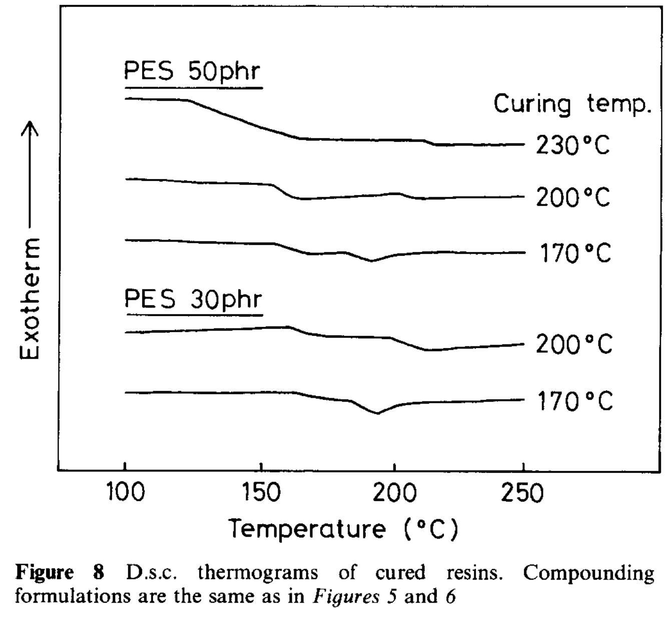

Figure 8 D.s.c. thermograms of cured resins. Compounding formulations are the same as in *Figures 5* and *6*

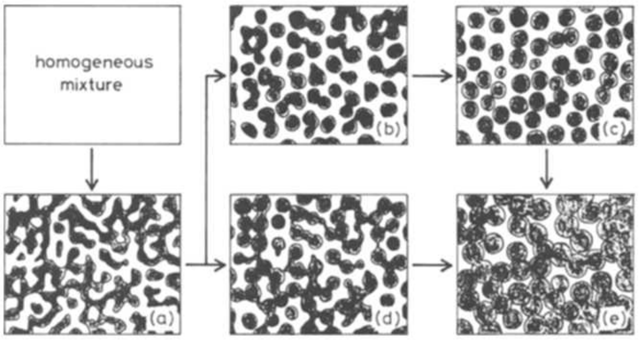

Figure 9 Schematic representation of phase separation scheme, resulting in the connected-globule structure

morphology (*Figure 9b*). However, if a network is already established in the epoxy-rich region, complete interruption cannot be realized (*Figure 9d*) and it eventually results in the connected-globule structure (*Figure 9e*). If, once interruption has taken place, the dispersed droplets grow in size without changing their loci (*Figure 9c*) because they are dispersed in a matrix of PES-rich phase with low mobility (high T_g), then, by futher growth, the droplets finally contact with each other to yield the connected-globule structure (*Figure 9e*).

Anyhow, both routes in *Figure 9* lead to the same final structure of connected globules. However, the periodic distance in the structure would depend on the route: the route through (d) may lead to a short periodic distance, while the route through (b) and (c) may lead to a long one. The former case may be realized when the compounding formulation is PES-rich and/or curing temperature is low (see *Figures 5b* and *5d*).

Multi-step curing

An interesting subject is derived from the above scenario. It is concerned with the control of periodic distance (or domain size). One can expect that, in order to obtain the structure with short periodic distance, coarsening of the phase-separated structure should be suppressed by network formation in the early stage of spinodal decomposition. As discussed before, phase separation competes with the chemical reaction

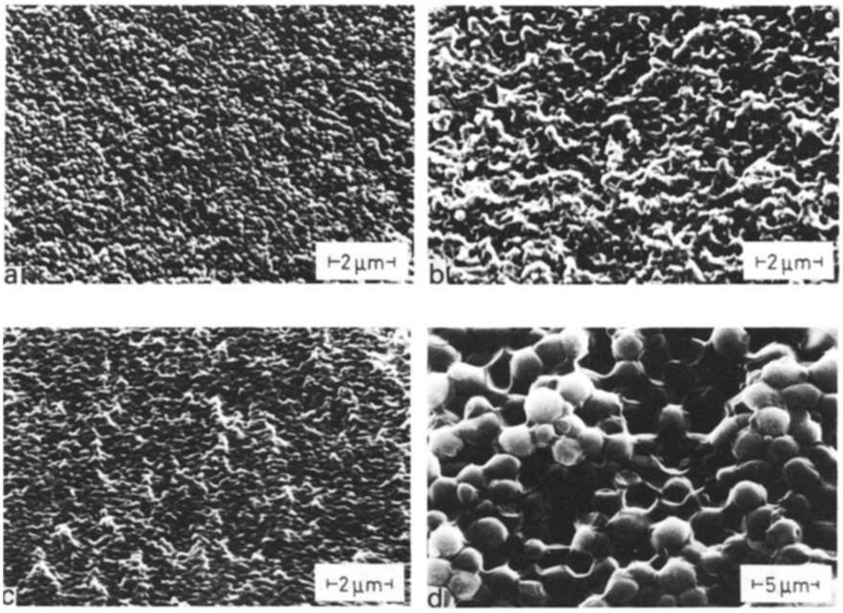

Figure 10 SEM observation of cured resins, by multi-step curing and single-step curing; epoxy/PES/DDM = 100/30/26: (a) 80°C, 6 h; (b) 80°C, 6 h + 150°C, 3 h; (c) 80°C, 6 h + 150°C, 3 h + 230°C, 0.5 h; (d) 150°C, 3 h

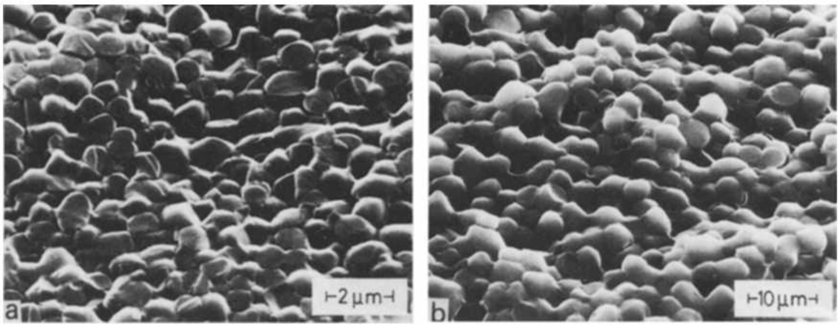

Figure 11 SEM observation of cured resins, prepared by (a) slow heating at 1°C min^{-1} and (b) rapid heating at 5°C min^{-1}; epoxy/PES/DDM = 100/30/26

(molecular weight increase and crosslinking). It is well known that the rate of phase separation at a temperature not far from T_g depends very much on the temperature. It is primarily due to the temperature dependence of chain mobility, such as typically described by the WLF equation[15]. Hence, by lowering the curing temperature towards T_g, the rate of phase separation is expected to be much reduced, while the rate of chemical reaction is not reduced so much, say, of the order of one-half by 10°C reduction.

Figure 10a shows an SEM micrograph of a resin (epoxy/PES/DDM = 100/30/26) cured at low temperature (80°C), showing the two-phase structure with short periodic distance around 0.2 μm. The periodic distance is not affected by a second curing at 150°C and a third curing at 230°C (*Figures 10b* and *10c*). This suggests that the mutual arrangement of globules has been fixed at the first cure at 80°C by network formation in the epoxy-rich globules* (see *Figure 9d*). Note here the dramatic difference in periodic distance between the two-step cure (*Figure 10b*) and the single-step cure (2.3 μm; *Figure 10d*).

Based on the results in *Figure 10*, we undertook another curing programme: a linear rise in temperature, by using the Linkam TH600 heating–cooling stage. By using the slower temperature rise, the specimen experiences a longer time of curing at lower temperatures. Hence, the slow temperature rise is expected to result in a two-phase structure with short periodic distance (or small domain size). This is realized in *Figure 11*. The slower the heating rate, the shorter is the periodic distance. Including other results by various heating rates, the heating rate dependence of periodic distance is shown in *Figure 12*. In this figure, the globule diameters are also plotted by open circles. The globule diameters are slightly larger than the periodic distances for various heating rates, indicating the connectivity in our characteristic two-phase morphology.

Adhesive strength

There have been many efforts to elevate the adhesive strength of epoxy resins, in both peel and shear modes. However, adhesives with high shear strength always have low peel strength, or vice versa. In *Table 1* are shown the peel and shear adhesive strengths of cured resins with and without PES modification. The PES-modified epoxy

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* Conversion after the first step cure at 80°C was estimated to be 85% by a d.s.c. exotherm peak area from 110 to 250°C in the cured specimen. Conversion after the second cure was estimated to be more than 98%

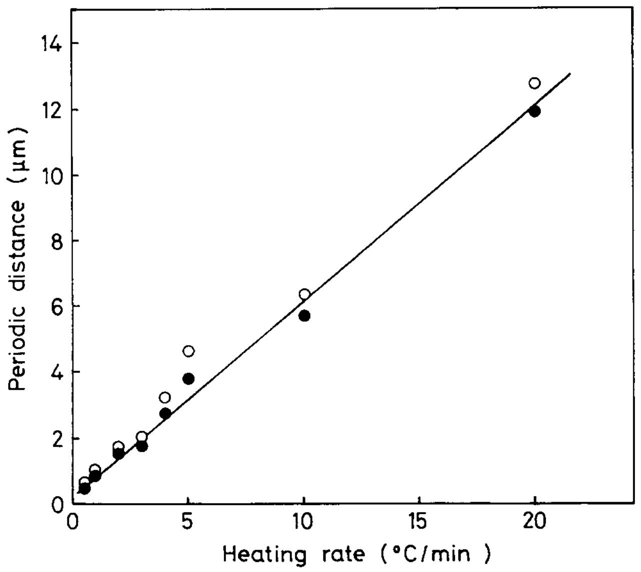

Figure 12 Variation of globule structure with heating rate: (●) periodic distance, (○) globule diameter; epoxy/PES/DDM = 100/30/26

resin with connected-globule structure exhibits higher strength, not only in peel but also in shear mode, than the unmodified resin.

We believe that this excellent adhesive property originates from the characteristic connected-globule structure in which both epoxy-rich and PES-rich phases are continuous.

CONCLUDING REMARKS

We have found the development of characteristic connected-globule morphology in PES-modified epoxy resin. The chemical reaction during curing is very complicated. It may involve chain extension, branching and crosslinking. The T_g of epoxy increases with curing. The reaction induces phase separation. That is, the complex chemical reaction causes a change in the physical state of the mixture. Chemical complexity is superimposed on physical complexity. This may be hard to understand and discuss in detail. However, if we pay attention only to the competitive situation of chemical and physical processes, we are able to control the morphological development. We believe that this is an important aspect for the design of high-performance materials in multicomponent thermosetting resins.

Table 1 Adhesive strength

	T-peel strength (kg inch^{-1})[a]	Shear strength (kg cm^{-2})[b]
	ASTM D1002	ASTM D1876
Unmodified resin[c]	0.35	225
PES-modified resin[d]	1.36	260

[a] Adherent, aluminium; cross-head speed = 300 mm min^{-1}
[b] Adherent, steel; cross-head speed = 2 mm min^{-1}
[c] Epoxy/DDM = 100/26; cured at 80°C for 6 h and 150°C for 3 h
[d] Epoxy/PES/DDM = 100/30/26; cured at 80°C for 6 h and 150°C for 3 h

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