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Thermodynamically reversible and irreversible control on morphology of multiphase systems

Part II *Morphology control by spinodal decomposition and nucleation and growth*

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Morphology and properties of polymer alloys can be controlled by thermodynamically reversible (structure freeze-in) or irreversible (structure lock-in) processes via simultaneously manipulating miscibility, mechanisms of phase separation, glass transition (structural relaxation), and cure kinetics of polymer systems. Using phase diagrams consisting of binodal and spinodal curves, the morphology of epoxy/carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) systems can be controlled by the mechanism of nucleation and growth or by spinodal decomposition. We have found that the particle size of the rubber reinforcement in epoxies is affected by the mechanisms of phase separation. Phase separation by nucleation and growth gives larger rubber particles than the corresponding phase separation by spinodal decomposition. This contrast in the morphology development is the consequence of controlling phase separation through chemorheological behaviour. Modification of the phase separation kinetics in epoxy/CTBN systems was extremely effective at altering both morphology and properties of these alloys. This technique offers a means to shift the glass transition temperature of the rubber-rich phase while leaving the glass transition temperature of the epoxy-rich phase intact. Such control over morphology is the key to ultimately controlling material properties.

1. Introduction

Recently, the technology of polymer blends and alloys has gained a world-wide recognition as a cost-effective means of solving design problems and meeting changing specifications. Alloys and blends are revolutionizing the materials suppliers' ability to offer an eclectic balance, or combination, of properties in response to specific customer requests. The new sophisticated materials management now integrates material, design, and processing into a materials system approach. Fusing together engineering and the science of chemistry and physics produces a new approach to the understanding and development of materials.

This new approach is based upon the recognition of the full complexity of microstructure and the fact that properties depend upon structure. The relationships between structure and properties, and between properties and performance, become the touchstone of modern materials developments. Such a structural approach to material developments and applications, of necessity, placed major emphasis on the fabrication and processing of materials to control structure and properties. There grew the clear recognition that properties and performance were the consequences of the full thermo-mechanical and compositional history of materials. As our understanding of the materials science and technology grew, it stimulated a competition among materials, and a competition between processings, and consequently materials and processing technologies became an equally dominant factor.

Improving scientific understanding of alloying and blending mechanisms is the key for exploding utilization of polymers and composites. Polymer blends and polymer alloys are often used synonymously; however, thermodynamically speaking, there is a distinction between these two terms. Polymer alloys are conditionally miscible thermodynamically. This means that the components of the alloy are homogeneous (single phase) under at least one specific set of thermodynamic conditions. Alloys, as such, provide the opportunity to change morphology and properties through variations in thermal history. Polymer blends, however, do not form single-phase systems under material processing and application conditions. Their properties are largely dependent on mechanical dispersion and are usually tied to the arithmetic average of the values of the components. Polymer alloys can be synergistic polymer systems. As such, their properties can exceed a simple arithmetic averaging value (additive rule) of multicomponent systems.

Integration of polymer alloying technology considers: (1) phase diagrams composed binodal and spinodal curves, (2) enhancing miscibility, (3) phase separation via nucleation and growth, spinodal decomposition, and Ostwald ripening process,

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(4) structural relaxation (glass transition) and/or cure reaction, and (5) composite mechanics and mechanical spectrum. The initial state for processing alloy systems starts from a homogeneous state of a single-phase condition. Then the morphology of end-products can be either single phase or multiphase depending upon the kinetics of phase separation and structural relaxation (or cure reaction). On the other hand, integration of polymer blending technology, pays attention to: (1) rendering compatible the agents, interficial tension, interdiffusion, and adhesion, (2) co-vulcanization, (3) dynamic vulcanization, and (4) rheology and morphology in multiphase fluid systems. The system is in a multiphase state during material processing, and the morphology or domain structure is controlled via rheology and chemorheology of multiphase fluids in Banbury mixers, extruders or other processing equipment. In this report, we will discuss polymer alloying technology, while the blending technology will be discussed elsewhere.

Because of the unique behaviour, such as morphology development and mechanisms of phase separation, in polymer alloys, there are many diversified applications for using polymer alloys. These applications include membranes, damping materials, structural adhesives, electronic packaging and high-performance engineering materials, controlled release of bioactive materials [1, 2], self-regulating heat insulating or retaining materials, light switches and optical information storage materials [3, 4]. Previously we discussed the phase diagram and mechanisms of phase separation in rubber–epoxy alloy systems [5]. In this study, we will demonstrate how to manipulate the mechanisms of phase separation in the rubber–epoxy alloy system to achieve specific morphologies and properties. In the subsequent reports, we will discuss the correlation between morphology and mechanical strength, and using polymer alloying technology to tailor rigid and flexible composite matrices and damping materials.

2. Phase diagrams and phase separation of alloy systems

The details of phase diagrams and phase separation in polymer alloy systems have been discussed in the previous report [5]. For a system containing a simple miscibility gap of high consolute temperature (UCST system), at a constant temperature above the consolute temperature, T_c (sometimes called critical temperature), the Helmholz free energy, G, must curve upward everywhere. As the temperature drops below T_c, the Helmholz free energy at a given temperature, T_0, will vary with composition, c, as depicted by the top curve of Fig. 1. The points of common tangency to this curve (f and g, Fig. 1) define the composition of two coexisting phases at T_0 (binodal points). If the composition lies between the compositions a and b, the lowest free energy is a two-phase mixture with one phase having composition a and the other b.

In addition, there are two inflection points at which $(\partial^2 G/\partial^2 c)$ vanishes. These two points occur at d and e and are called the spinodal points for the temperature T_0, lying somewhere between a and b. Between these two spinodal points, $(\partial^2 G/\partial^2 c)$ is negative, and the mixture is said to be in an unstable state, because any infinitesimal composition fluctuation will cause a decrease in the free energy and hence phase separation. The metastable region exists between the spinodal and the binodal curve (phase boundary). If the single phase is cooled from above the phase boundary into this region, it would be metastable and would only decompose into the two phases if the second phase can nucleate. Any attempt by the system to separate into regions differing only slightly in composition will raise the system free energy. If, however, the single phase is brought within the unstable region (between points d and e) the system can continuously lower its free energy by continuous compositional change until it reaches a two-phase state at a and b.

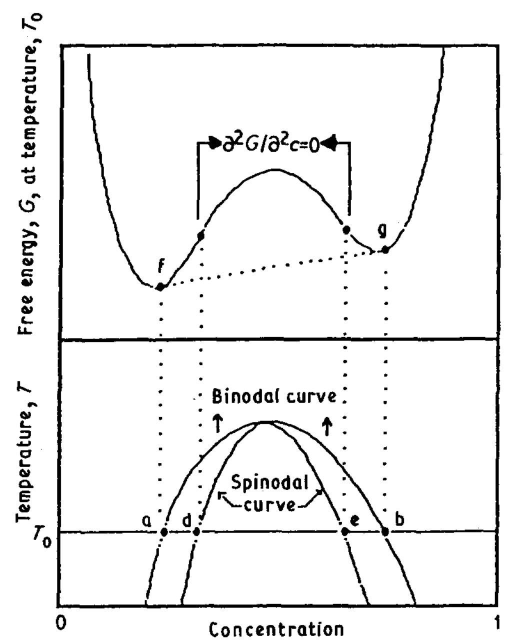

Figure 1 Phase diagram of binodal and spinodal curve.

The mechanisms of phase separation in the two regions, metastable and unstable, are radically different. In the unstable region, the mixture is unstable to infinitesimal fluctuations. There is no thermodynamic barrier to phase transformation, and thus, separation should occur by a continuous and spontaneous process. Because the mixture is initially uniform in composition, this spontaneous process must occur by a diffusional flux against the concentration gradient, that is, by uphill diffusion with a negative diffusion coefficient. There is no sharp interfacial boundary between the phases in the initial stage of this type of phase separation. This process is called spinodal decomposition (SD).

On the other hand, in the metastable region, because the mixture is stable to all infinitesimal composition fluctuations, a finite fluctuation is required for a phase transformation. The new phase starts from small nuclei which then proceed to grow and extend. The molecules that feed the new phase follow ordinary transport phenomena by downhill diffusion with a positive diffusion coefficient. This process is called nucleation and growth (NG).

In the metastable region, two basic stages of phase development may be distinguished. The first is the nucleation and growth stage during which concentration fluctuations produce nuclei of the new phase which grow from the super-saturated matrix. The second stage is the coalescence process (Ostwald ripening stage). During this coarsening stage, the total surface of the dispersed phase is reduced. Fluctuation effects play a negligible part in this stage. In this stage, the average diameter, D, of the particles are seen to obey a kinetic law of the Lifshitz–Slyozov–Wagner asymptotic law [6–8].

Spinodal decomposition is one of the few phase transformations in which the kinetic theory has been well studied [9–17]. The reason for this is that the entire decomposition process can be treated as a purely diffusional problem and, further, many of the characteristics of decomposition, especially morphology, can be described by an approximate solution to the diffusion equation. Since Cahn and co-worker [12, 13] demonstrated that glasses may undergo spinodal decomposition, there has been wide spread tendency to assume that the kinetic mechanisms for all those demixing processes which lead to textures displaying some degree of connectivity must be spinodal decomposition. This extreme view, however, cannot be justified, because other mechanisms, for example (as has been suggested by Haller [18]) nucleation and growth followed by coalescence, may also lead to similar formations. Conclusions reached from a mere inspection of an electron micrograph are certainly insufficient and may be grossly misleading. Only a detailed analysis of thermodynamics in the miscibility gap (or phase diagram) and the initial kinetic process can show whether, in a given case, we are indeed dealing with spinodal decomposition.

According to the theory of spinodal decomposition [9, 12]. The amplification factor, $R(\beta)$, of the concentration fluctuations can be given by

$$R(\beta) = -M(\partial^2 g/\partial^2 c)\beta^2 - 2M\kappa\beta^4 \qquad (1)$$

where M is the molecular mobility, g is the free energy density of the homogeneous material having composition c, κ is the gradient energy coefficient and is positive, and β is the wave number.

Equation 1 tells us that any sinusoidal component present initially in the composition profile of a specimen will grow or shrink exponentially according to whether $R(\beta)$, the amplification factor, is positive or negative. Outside the spinodal region, $(\partial^2 g/\partial^2 c) > 0$; consequently $R(\beta)$ is negative for all values of β and any existing fluctuation will diminish with time. Therefore, the system should homogenize. For this reason, a continuous and spontaneous process of concentration decomposition resulting in the formation of a periodic or quasi-periodic texture can only occur in the unstable region where $(\partial^2 g/\partial^2 c)$ is negative.

In the spinodal region, the critical value wave number, β_c, is given by the value

$$\beta_c^2 = -1/2\kappa(\partial^2 g/\partial^2 c) \qquad (2)$$

β_c corresponds exactly to a wavelength where all the contributions to the free energy cancel each other out, and forms the boundary between positive and negative $R(\beta)$. A wavelength with $\beta < \beta_c$ will grow and $\beta > \beta_c$ will shrink.

The interdiffusion coefficient, D, is defined by the expression

$$D = M(\partial^2 g/\partial^2 c) \qquad (3)$$

Then Equation 1 can be rewritten as

$$R(\beta) = -D\beta^2(1 - \beta^2/\beta_c^2) \qquad (4)$$

M is always positive, D is negative within the spinodal, which corresponds to an uphill diffusion. From Equation 4 it is seen that the maximum of $R(\beta)$ occurs for a wave number $\beta_m = \beta_c/2^{1/2}$. The spatial components of wavelength $\lambda_m = 2\pi/\beta_m$ is called the spinodal wavelength of the system. Because $R(\beta)$ has a steep maximum and because it occurs in an exponential, it is convenient to ignore the growth of all wavelengths but those near the fastest growing ones. This principle of selective amplification is a good first approximation.

It should be mentioned here, that the unique morphology created by the initial stage of its spinodal decomposition consists of an interface between two coexisting phases which is diffuse and its thickness increases with decreasing ΔT ($\Delta T = T - T_s$) and becomes infinite at the spinodal temperature, T_s. T_s is the temperature at the spinodal curve. The periodic domain structure, λ_m, varies with the heat-treatment temperature, T, and is described by

$$1/\lambda_m^2 = q(T - T_s) \qquad (5)$$

where q is a constant depending on the system.

In the second stage of the spinodal decomposition, the domain structure becomes large and the rate of growth of the composition fluctuation amplitude is slowed down. This period corresponds to a coarsening of the texture. This process is an Ostwald ripening process where differences in solute concentration due to various particle sizes set up concentration gradients which tend to resorb smaller particles and make the large ones grow at their expense. We have discussed this type of coarsening mechanism in the section on nucleation and growth.

3. Discussion

Drake and McCarthy [19] found that the incorporation of low levels of a liquid carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) to a normally brittle epoxy resin significantly improved the crack resistance and impact strength without a reduction in other thermal and mechanical properties. This enhancement in crack resistance and impact strength is brought about by the formation during cure of a predominately rubbery second phase. The size of the particles making up this second phase is usually between 0.1 and 5 μm [20]. These modified thermoset resins have found wide application in structural film adhesives for metal–metal bonding in aircraft, in paste adhesives for automotive and industrial application, in electronic encapsulation, in epoxy solvent and powder coating, and in advanced aircraft and aerospace composites. However, in most epoxy applications, the final properties are strongly dependent on the morphology generated during cure of these systems. The morphology is determined by a large number of variables, such as the miscibility of the epoxy and rubber prior to cure, the cure agent, the time and temperature of cure. In some cases, optimum toughness is provided with a multi-modal distribution of particle sizes.

Siebert and Riew [21] first described the chemistry of rubber particle formation in an admixed model involving CTBN, a liquid diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Epon 828), and a piperidine catalyst. They proposed that the composition of the rubber particles in the dispersed phase critically depended upon the *in situ* formation of the epoxy–CTBN–epoxy adduct, which is then further chain-extended and cross-linked with additional epoxy resin. This progression provides a chemical bond between the dispersed rubber phase and the matrix resin and occurs with piperidine, a selective catalyst. Most other cure agents, however, favour either the epoxy–epoxy reaction or an epoxy–amine reaction, and the carboxyl–epoxy reaction is suppressed. Rowe *et al.* [22] demonstrated a maximum in fracture energy in this system when the bound acrylonitrile (AN) content of the CTBN was between 12% and 18%. They also showed a general decrease in average particle size from 3 μm at 12% bound AN to 0.2 μm at 25% bound AN.

Manzione *et al.* [23, 24] studied the morphology of an Epon 828/CTBN system and used piperidine as curative. They used three different types of CTBN rubbers – CTBN (X13), CTBN (X8) and CTBN (X15), which contain 26%, 16% and 10% acrylonitrile, respectively. They used 10 p.h.r. CTBN rubber and 5 p.h.r. piperidine in the formulations, and cured the samples at three different temperatures (90, 120 and 150 °C). They found all samples were phase separated except the Epon 828/CTBN (X13) compound which was cured at 150 °C. This finding is of interest, although the miscibility and the phase diagrams of Epon 828/CTBN systems with or without cure agents were not investigated in their study.

A selective cure agent may enhance the carboxyl–epoxy reaction and increase the interface mixing between the epoxy and the CTBN as discussed by Siebert and Riew [21]; however, we believe that good mechanical properties can also be achieved by controlling phase morphology through phase separation mechanisms of nucleation and growth, spinodal decomposition, or Ostwald ripening processes. As mentioned before, in the initial stage of spinodal decomposition a gradual mixing interface develops instead of a sharp interface boundary. We believe we can control the sizes of the rubber particles by properly manipulating the kinetic processes of phase separation. Therefore, we are more concerned with the mechanism of phase separation (spinodal versus nucleation and growth) than with specific types of chemical reactions promoted by selective cure agents. Our approach to the development of morphology of epoxy–CTBN systems is therefore different from the previous studies [20–24]. We will begin by constructing miscibility gaps (binodal and spinodal curves) of uncured epoxy–CTBN systems. Then we will study the effects of cure agents on the miscibility gaps of these systems. Finally, the morphology of these systems will be manipulated through the kinetic processes of the cure reactions and subsequent phase separation.

3.1. Experimental procedure

The epoxy resin used in this study is a low molecular weight liquid diglycidyl ether of bisphenol-A (DGEBA), Epon 828. The rubber modifiers employed are low molecular weight copolymers of butadiene and acrylonitrile having carboxy end groups (trade name Hycar (CTBN)). Three different rubber systems of varying acrylonitrile content were used in this study. Chemical and physical properties and nomenclature of the rubbers are presented in Table I. Mixtures of the rubber-modified epoxy without curatives were prepared for miscibility studies using laser light scattering. The CTBN rubber content in the mixtures was varied from 2–40 p.h.r. (part per hundred of epoxy resin). Samples for light scattering were prepared by hand mixing Epon 828 with CTBN (X8) at 80 °C under a dry nitrogen environment and then degasing.

Samples for mechanical spectra (MS) and scanning electron microscopy (SEM) measurements were prepared from degased mixtures of Epon 828/CTBN (X8) or Epon 828/CTBN (X13) containing curative. Curatives used were Versamid 140 (polyamide) or Jeffamine D230 (difunctional polyoxypropyleneamine). Mixing was accomplished at 50 °C under a dry nitrogen environment and then degassing. The ingredients for modifying kinetics of cure or phase separation (pre-gel of rubber-rich phase) were also added at this stage. Test specimens were prepared by

TABLE I Physical properties of CTBN

	Hycar polymers		
	CTBN (1300X13)	CTBN (1300X8)	CTBN (1300X31)
Acrylonitrile content (%)	26	18	10
Molecular weight, M_n	3200	3600	3800
Viscosity (CP) 27 °C	570000	135000	60000
Specific gravity	0.96	0.948	0.924
Solubility parameter	9.14	8.77	8.45
Functionality	1.8	1.8	1.9

pouring the degased mixture into a vertical Teflon mould and curing at 120 °C for 4 h under a dry nitrogen environment. Mechanical spectra were measured on a rheometric mechanical spectrometer (RMS). Fractured samples with exposed fresh surfaces were used for SEM measurements.

3.2. Results

The construction of a phase diagram consisting of binodal and spinodal curves of an epoxy/CTBN by Rayleigh–Brillouin laser light scattering has been discussed previously [5]. The miscibility gap (or upper consolute temperature) of the epoxy/CTBN (X13) system (26% AN content in the CTBN) is far below room temperature. The miscibility gap of the epoxy/CTBN (X31) (10% AN content in the CTBN) is above 150 °C. Only the phase diagram of Epon/CTBN (X8) was studied and replotted from [5] as shown in Fig. 2.

As has been discussed, there are two different methods for controlling morphology of multiphase systems, depending on whether cure reactions occur during material processing. In the absence of cure, the morphology can be controlled by a temperature-jump (or vaporizing the solvent) from an equilibrium and single phase state (stable region) into a metastable, an unstable, or even another stable region. Then the formation of morphological structure will occur according to the mechanisms of phase separation as discussed above. When cure reactions predominate, the control of morphology requires the programming of cure conditions in which the system begins with a homogeneous single phase before cure reactions begin. The morphology of the system can be controlled in a homogeneously single phase or in a heterogeneously separated phase by locking-in the morphological structure via cross-linking reactions during various stages of phase separation. Once cure reactions start, the molecular weight of the polymer system increases, the immiscibility zone is expanded and phase separation can occur. By properly manipulating the kinetics of cure and phase separation, desirable material properties can be obtained.

As mentioned earlier and shown in Fig. 2, the upper critical temperature is about 65 °C for Epon/CTBN (X8), and is far below room temperature for Epon/CTBN (X13). However, during cure, the critical temperature (or phase separation temperature) of these two systems will increase. Phase separation can occur even for samples that are cured at a temperature higher than the critical temperature. In this study, our purpose is to demonstrate the concept of controlling morphology via kinetics of phase separation and chemorheology regardless of curative type. The concept of lock-in morphology control is to manipulate the kinetics of phase separation by use of chemorheology during cure reactions. Two curatives were selected in this study. Versamid has a high viscosity and short gel time. This curative is believed to provide chemorheological behaviour which will reduce the kinetic rate of phase separation by allowing morphology lock-in at the initial stage of phase separation. On the other hand, Jeffamine D230 promotes a rapid kinetic rate of phase separation.

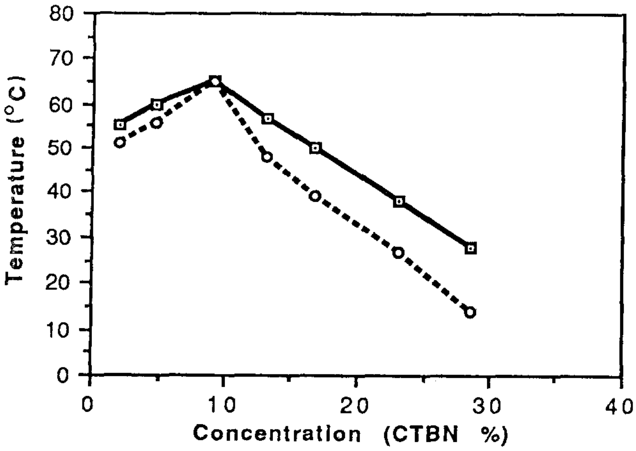

Figure 2 Phase diagram of epoxy/CTBN (X8): (——) binodal curve, (—○—) spinodal curve.

Figs 3–5 illustrate the mechanical spectra of Epon/CTBN (X8). The data were measured from − 80 to 120 °C at a frequency of 10 rad s^{-1} and 0.3% strain. Fig. 3 represents a sample of Epon/CTBN (X8)/Jeffamine D230 having weight ratios of 100:40:32, respectively. Figs 4 and 5 describe Epon/CTBN (X8)/Versamid samples having weight ratios of 100:40:50 and 100:10:50, respectively. All three samples were cured at 120 °C for 4 h. The glass transition temperatures for both the rubber-rich and epoxy-rich phases, and dynamic mechanical properties at room temperature (22 °C) are listed in Table II. As shown in Fig. 3 and Table II, the glass transition temperature, T_g (which is defined as the temperature at the peak value of tan δ), of the rubber-rich phase is − 51 °C (RT_g = − 51 °C), and the T_g of the epoxy-rich phase is 81 °C (ET_g = 81 °C). In this sample, the damping peak (tan δ) of the rubber phase is very pronounced and ET_g was little affected by the content of CTBN rubber. These results show that there was extensive phase separation in this sample. As shown in Table II, the tan δ value for this sample is small and is close to the value obtained with neat epoxy (no CTBN content). In fact, while the storage shear modulus for neat epoxy is somewhat higher than the sample described above, the corresponding value of T_g is identical (ET_g = 81 °C).

The data for the Versamid cured samples are shown in Figs 4 and 5 and are also listed in Table II. Cure conditions used for these samples were the same as those used for the sample cured with Jeffamine. Both samples have an identical RT_g (− 51 °C), but different values of ET_g which are lower than that of the neat epoxy. For neat epoxies, tan δ is small and almost identical for both curatives. However, when there is an intermixing between the rubber phase and epoxy phase, tan δ increases and ET_g decreases as shown in the Versamid-cured samples represented in Figs 4 and 5. If full phase separation occurs, as shown in the Jeffamine-cured sample (Fig. 3), then both values of tan δ and ET_g will be close to that of neat epoxy.

Fig. 6 shows micrographs obtained from scanning electron microscopy (SEM) measurements at × 10 000. Two different CTBN rubbers and curatives

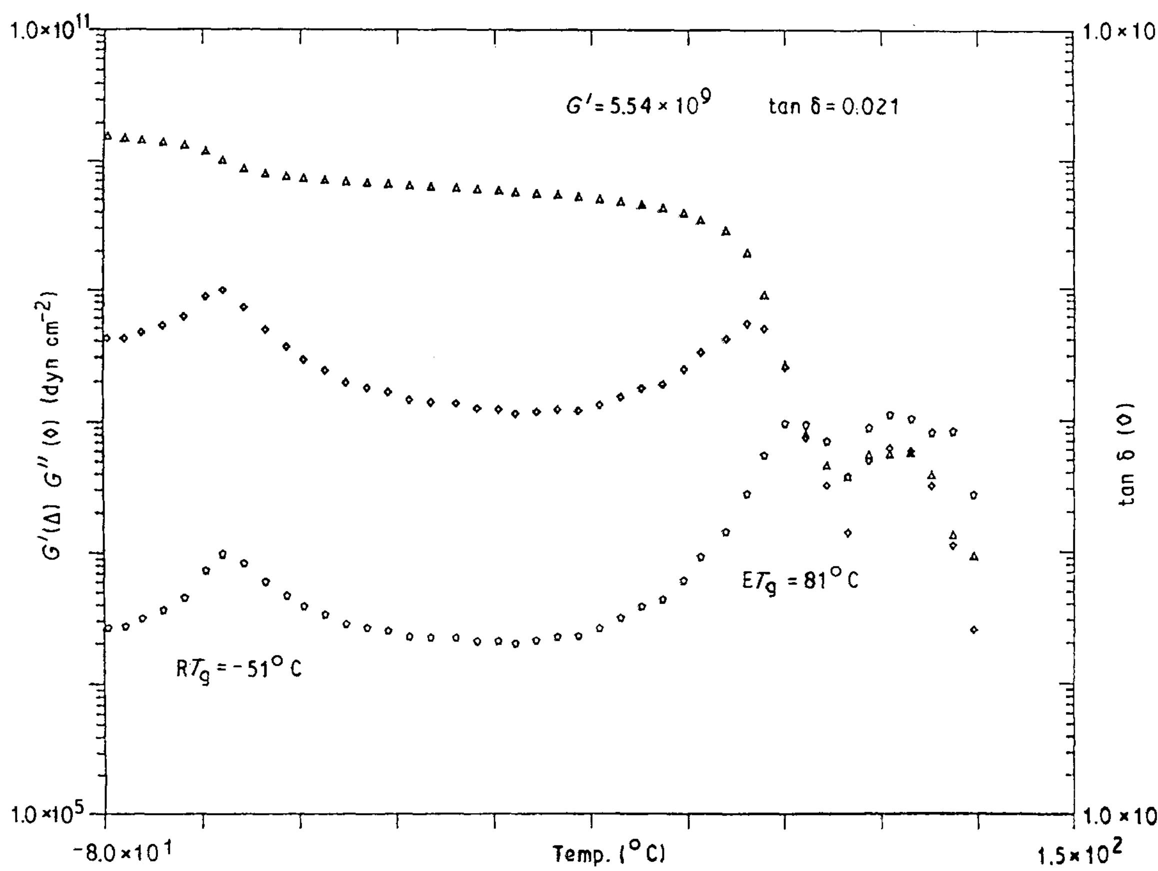

Figure 3 Mechanical spectrum of Epon/CTBN (X8)/Jeffamine (100:40:32).

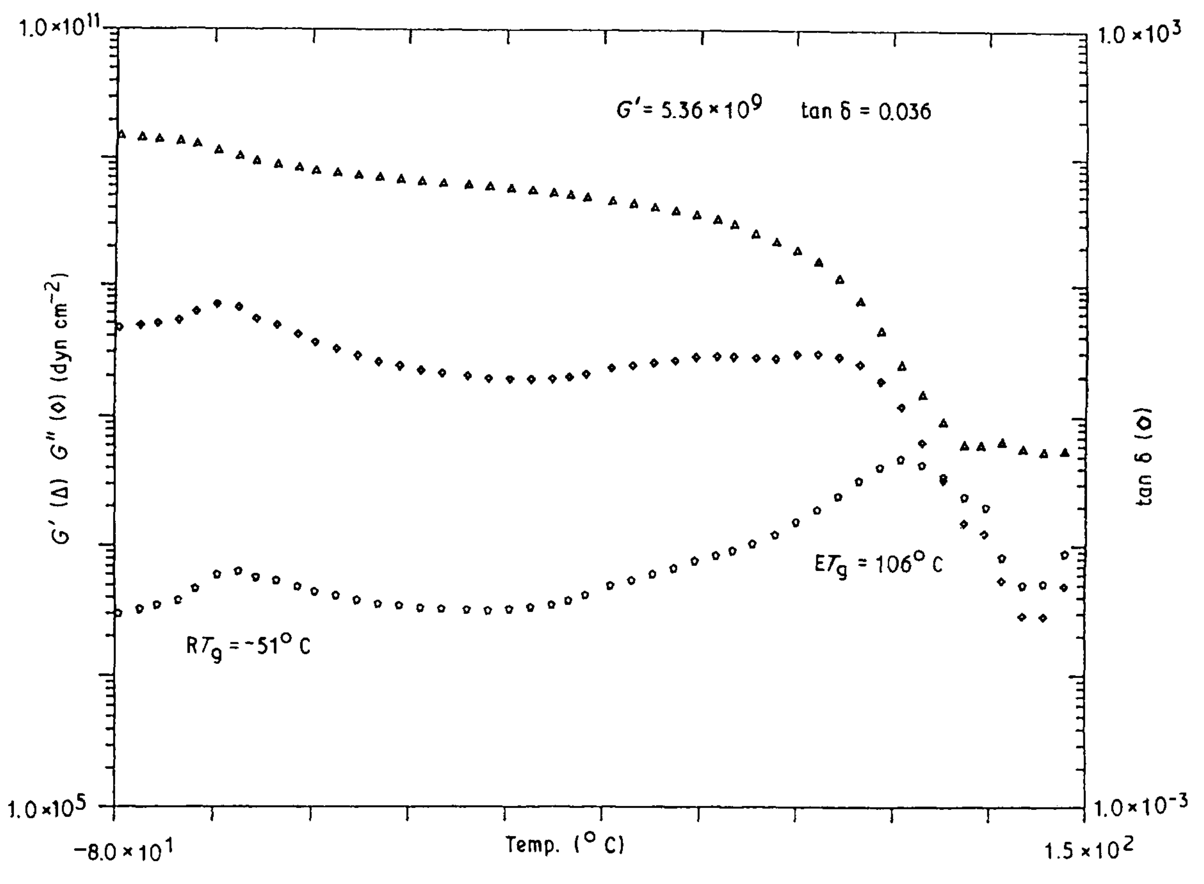

Figure 4 Mechanical spectrum of Epon/CTBN (X8)/Versamid (100:40:50).

(Jeffamine and Versamid) were used in the samples. All samples contained 40 p.h.r. rubber. RT_g, ET_g, and dynamic mechanical properties at room temperature (22 °C) are listed in Table II. As shown in Fig. 6, the size of the rubber particles varies with the particular CTBN chosen. With Jeffamine as a curative, the average particle size of rubber for the Epon/CTBN (X8) system is 2 μm, but only 0.5 μm for the Epon/CTBN

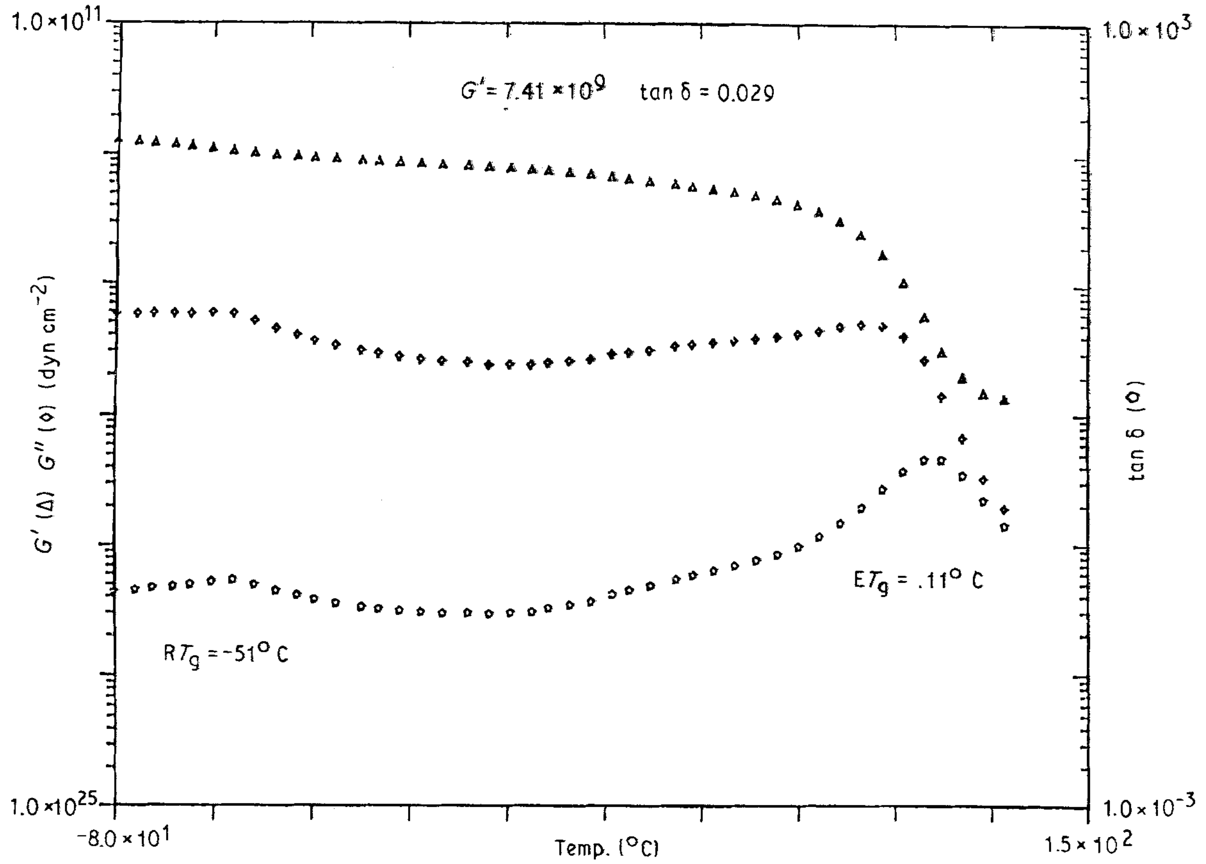

Figure 5 Mechanical spectrum of Epon/CTBN (X8)/Versamid (100:10:50).

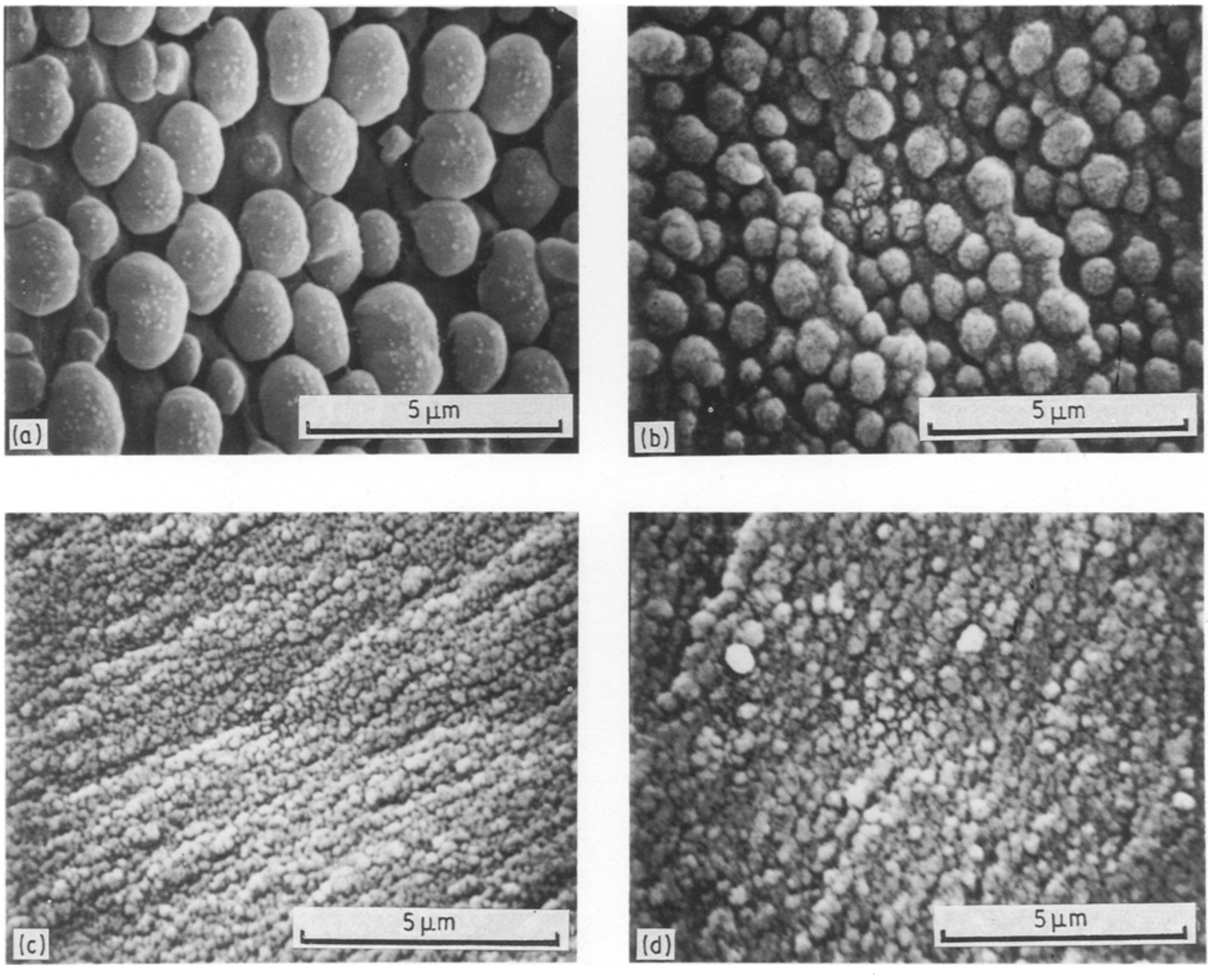

Figure 6 Morphology of epoxy/CTBN. (a) Epon/CTBN (X8)/Jeffamine (100:40:32). (b) Epon/CTBN (X13)/Jeffamine (100:0:32), (c) Epon/CTBN (X8)/Versamid (100:40:50), (d) Epon/CTBN (X13)/Versamid (100:40:50).

TABLE II Properties of epoxy systems

Epoxy system	RT_g (°C)	ET_g (°C)	tan δ	G' (10^8 Pa)
Epon/Jeffamine (100:32)	None	81	0.024	11.3
Epon/CTBN (X8)/Jeffamine (100:40:32)	− 51	81	0.021	5.54
Epon/CTBN (X13)/Jeffamine (100:40:32)	− 32	81	0.034	6.11
Epon/Versamid (100:50)	None	121	0.023	8.29
Epon/CTBN (X8)/Versamid (100:10:50)	− 51	111	0.029	7.41
Epon/CTBN (X8)/Versamid (100:40:50)	− 51	106	0.036	5.36
Epon/CTBN (X13)/Versamid (100:40:50)	− 32	101	0.045	5.02

(X13) system. Both samples are optically opaque. The morphology clearly shows a droplet structure with a sharp boundary interface between the rubber and epoxy phases. This result indicates that the mechanism of phase separation for developing these morphological structures is due to nucleation and growth. The reason for this is that, during cure, the molecular weight of the polymer system is increased and, consequently, the immiscibility gap increases. Eventually, the immiscibility gap of the polymer system is raised above the cure temperature. This causes the polymer system to change from a single-phase equilibrium state to a metastable state and, therefore, phase separation is initiated by nucleation and growth. Because the immiscibility gap of Epon/CTBN (X8) is higher than that for Epon/CTBN (X13), we would expect that phase separation in Epon/CTBN (X8) would occur earlier than that in Epon/CTBN (X13) under similar cure conditions. Thus, the particle size of the rubber phase in Epon/CTBN (X8) should be larger than that in Epon/CTBN (X13). This in fact is shown in Fig. 6.

When Versamid was used to replace Jeffamine as curative, the morphological structure was drastically different. The chemorheological behaviour of Versamid in rubber-modified epoxy systems tends to retard the kinetics of phase separation. Nevertheless, the immiscibility gap is raised during cure, in a manner similar to the Jeffamine-cured samples. Eventually, the polymer system changes from a single-phase equilibrium state to a metastable state. Initially phase separation occurs by nucleation and growth, but the retarded kinetics results in another change from the metastable state to an unstable state as molecular weight continues to increase during cure. As pointed out earlier, the kinetics of phase separation when governed by spinodal decomposition are very fast. Phase separation occurs continuously and spontaneously. Thus we found with the Versamid curative, the morphological behaviour of the samples were dominated by spinodal decomposition, as shown in Fig. 6.

Recalling Equation 5, during the initial stages of spinodal decomposition, the particle size of the rubber particle is inversely proportional to the square root of the difference between the cure temperature, T, and spinodal temperature, T_s (i.e. $(T - T_s)^{-0.5}$). The spinodal curve (T_s) of Epon/CTBN (X8) is higher than that of Epon/CTBN (X13), and cure reactions will elevate the spinodal curves above the cure temperature. Once this occurs, the value of $(T - T_s)$ for Epon/CTBN (X8) is greater than that of $(T - T_s)$ for Epon/CTBN (X13). Consequently, the particle size of the rubber phase in

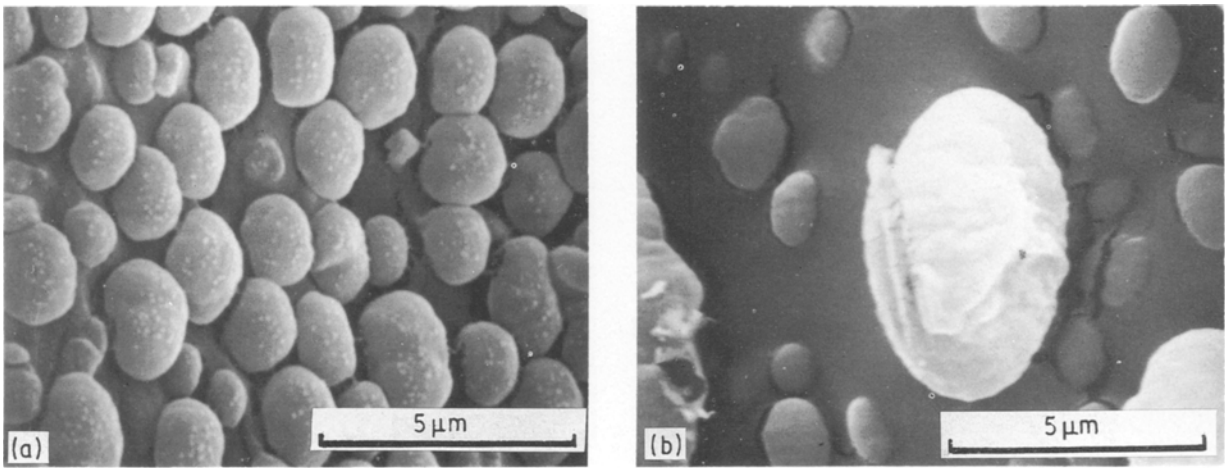

Figure 7 Morphology versus cure history of epoxy/CTBN (X8)/Jeffamine (100:40:32). (a) Control, (b) cured at 90 °C for 6 h.

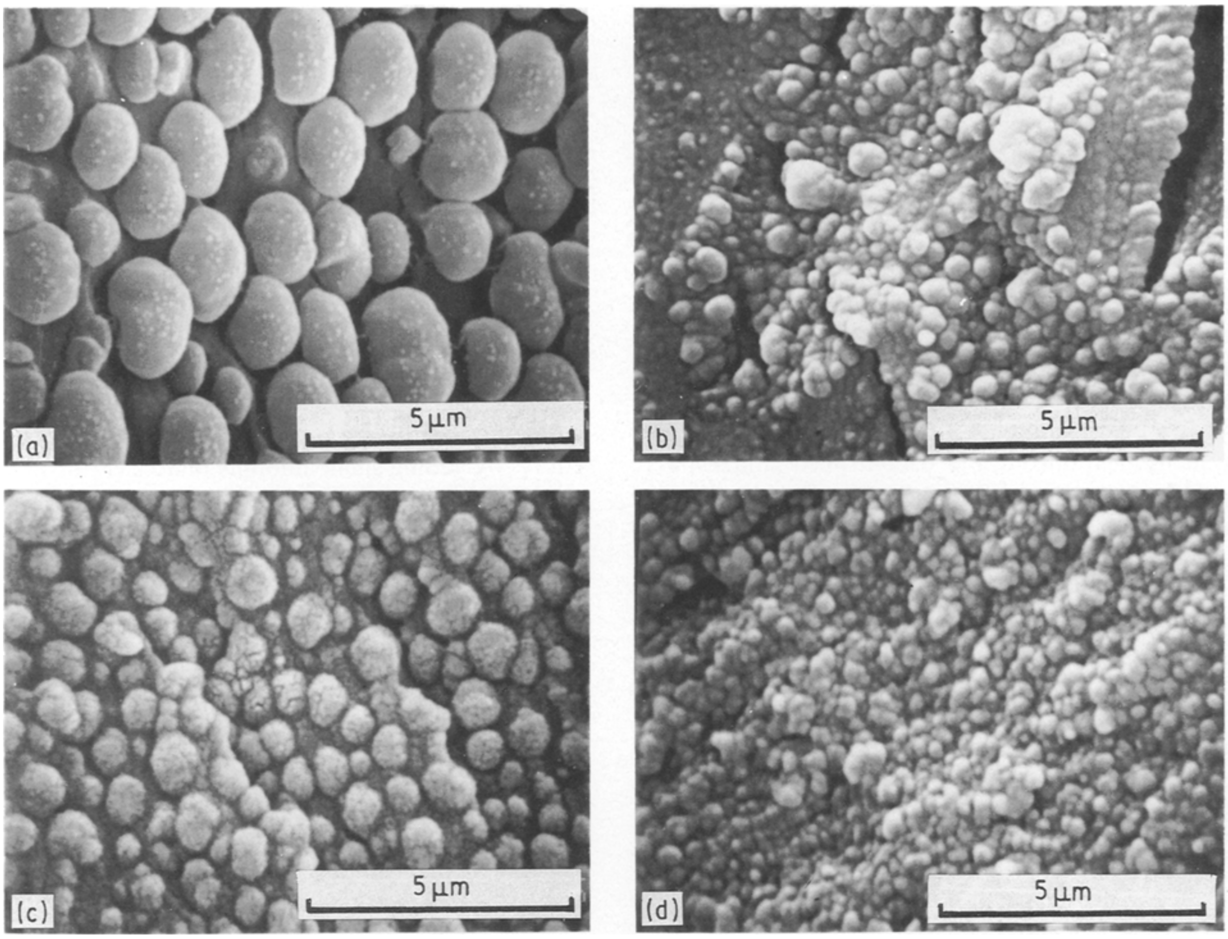

Figure 8 Morphology versus cure kinetics modification of (a, b) epoxy/CTBN (X8)/Jeffamine (100:40:32) and (c, d) epoxy/CTBN (X13)/Jeffamine (100:40:32), SEM × 10 000. (a, c) Control, (b, d) with Ancamine 2071 added.

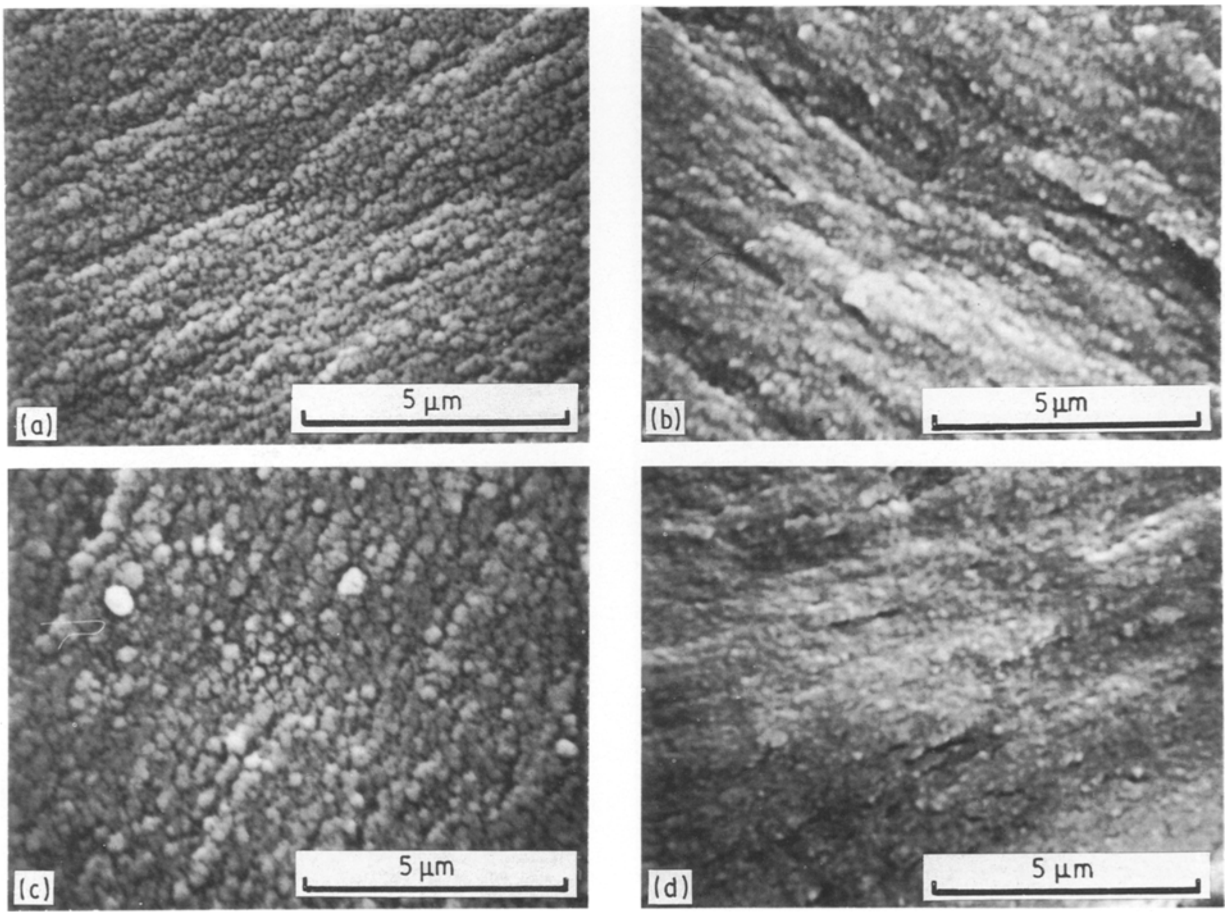

Figure 9 As Fig. 8, for Versamid (100:40:50).

Epon/CTBN (X8) should be smaller than that of Epon/CTBN (X13). This is illustrated in Fig. 6. With Versamid as a curative, the average particle sizes of rubber for Epon/CTBN (X8) and Epon/CTBN (X13) are 0.2 and 0.3 μm, respectively. These particle sizes are smaller than the wavelength of visible light and the samples are nearly transparent.

We know that the morphology and properties of polymer alloys for thermosetting materials depend upon the kinetics of phase separation and cure. If we can manipulate the kinetic rates of phase separation and/or cure during material processing, we would be able to control the morphology and properties of the materials. In doing so, the four different polymer systems mentioned in Fig. 6 (controlled samples) were used for further modifications of the kinetics of phase separation and cure in order to manipulate the morphology and properties. Two of the simplest methods for modifying cure kinetics include changing cure temperature and adding cure accelerators. We tried both methods for modification of cure kinetics. Modification of cure kinetics by changing cure temperature was found to be the least effective method for morphology and properties control in rubber-modified epoxy systems. Three different cure histories, 90, 120, and 150 °C for 6, 4, and 3 h, respectively, were used for these four polymer systems. The results showed that the mechanical spectra for each polymer system were virtually unaffected by the changes of cure histories. The morphologies of each polymer system also showed little variation with changes in cure histories. The Epon/CTBN (X8) system cured with Jeffamine at 90 °C was the sole exception. The morphology of the Epon/CTBN (X8)/Jeffamine system cured at 90 °C showed a bimodal distribution of rubber particle sizes. 2 μm size particles appeared at all three cure temperatures, but 5 μm size particles appeared only at a cure temperature of 90 °C. The morphologies of Jeffamine cured at 90 and 120 °C (controlled samples) for the Epon/CTBN (X8) are shown in Fig. 7.

The seemingly easy method for modifying cure kinetics is by adding small amounts of accelerator to the polymer systems. In this case, 10 p.h.r. Ancamine 2071 (aliphatic polyamine) was added to all four polymer systems to check the changes in morphology and properties. Again we found that the mechanical spectra of these polymer systems were virtually unaffected by this cure kinetic modification. However, the particle sizes of all four polymer systems were reduced compared with those of the unmodified cure systems. The cure history used for this cure kinetic modification was at 120 °C for 4 h cure. The morphologies of these samples along with the controlled samples were shown in Figs 8 and 9.

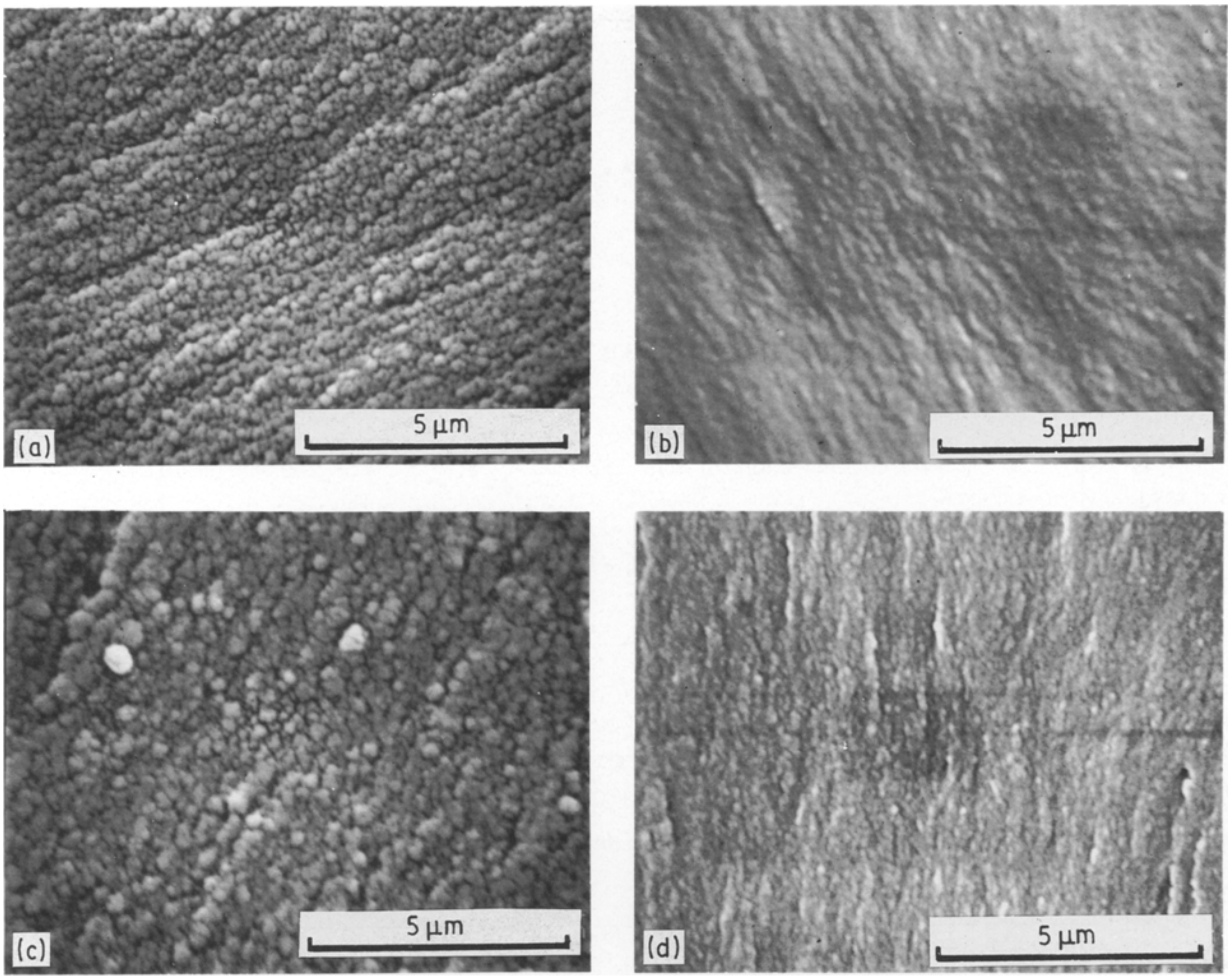

Figure 10 Morphology versus phase separation kinetics modification of (a, b) epoxy/CTBN (X8)/Jeffamine (100:40:32) and (c, d) epoxy/CTBN (X13)/Jeffamine (100:40:32), (a, c) Control, (b, d) with phase separation kinetics modification.

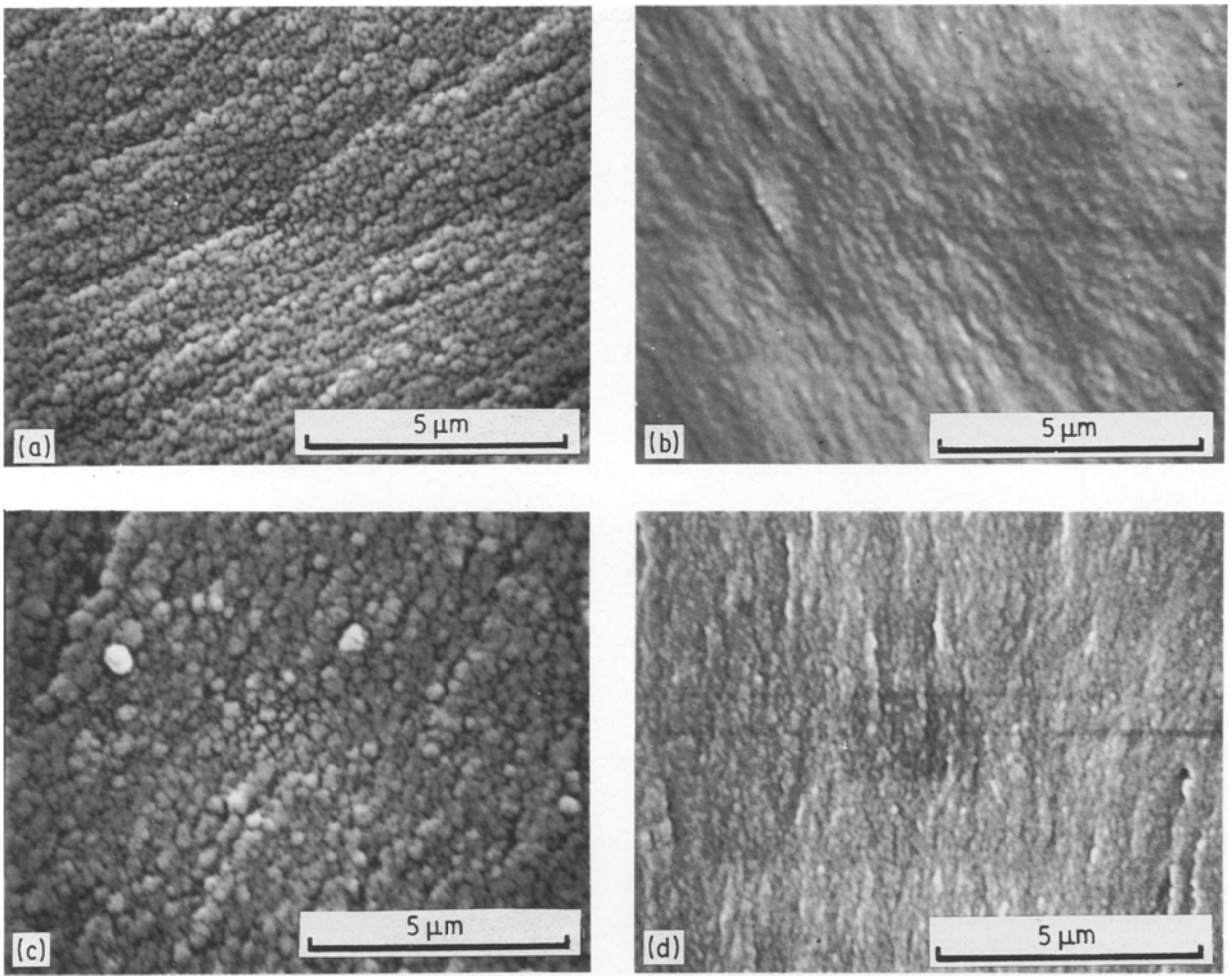

Figure 11 As Fig. 10, for Versamid (100:40:50).

The modification of phase separation kinetics was found to be the most effective method for morphology and properties manipulation in rubber-modified epoxy systems. We were able to reduce the kinetic rate of phase separation via pre-gelation of the rubber phase which increased the interdiffusion coefficient. This modification was achieved by incorporating an organic peroxide, such as 1,1-*bis*-(*t*-butylperoxy)-3,3,5-trimethy-cyclohexane (Lupersol 231–3 p.h.r.), in the rubber phase. The morphologies of the four polymer systems with phase separation kinetics modification along with the controlled samples are shown in Figs 10 and 11. This method leads to a drastic change in morphology having either a good intermixing boundary (Fig. 10) or a homogeneous single-phase morphology (Fig. 11). This method also leads to more effective control of the properties of these materials as demonstrated in the mechanical spectra shown in Figs 12–15. In Figs 12 and 13, the glass transition of temperature of the rubber-rich phase was shifted upwards by about 30 °C for both the Epon/CTBN (X8) and the Epon/CTBN (X13) with Jeffamine cure compared with the corresponding alloys having no peroxide. When Versamid was used as a curative, the glass transition of temperature of the rubber-rich phase for both the Epon/CTBN (X8) and the Epon/CTBN (X13) system disappeared and became a single phase morphology as shown in Figs 14 and 15. The glass transition temperature of the epoxy-rich phase for these four polymer systems was little affected by this modification. The glass transition temperatures for the rubber-rich phase and the epoxy-rich phase for these four samples with modification of phase separation are listed in Table III along with the data of the control samples. These results are of interest and practical importance, because a key for using rubber–epoxy systems in high-performance material applications is the ability to alter the glass transition temperature of the rubber-rich phase without depressing the glass transition temperature of the epoxy-rich phase. These experiments prove we can effect such changes. It is believed that the mechanical strength can be drastically improved by having an intermixing boundary morphology and a graduated modulus between the two phases which should enhance interfacial bonding and reduce stress concentrations. This remains to be verified experimentally.

4. Conclusions

We have demonstrated that polymer alloying technology is an effective method for tailoring the morphology and properties of materials. The key for successful

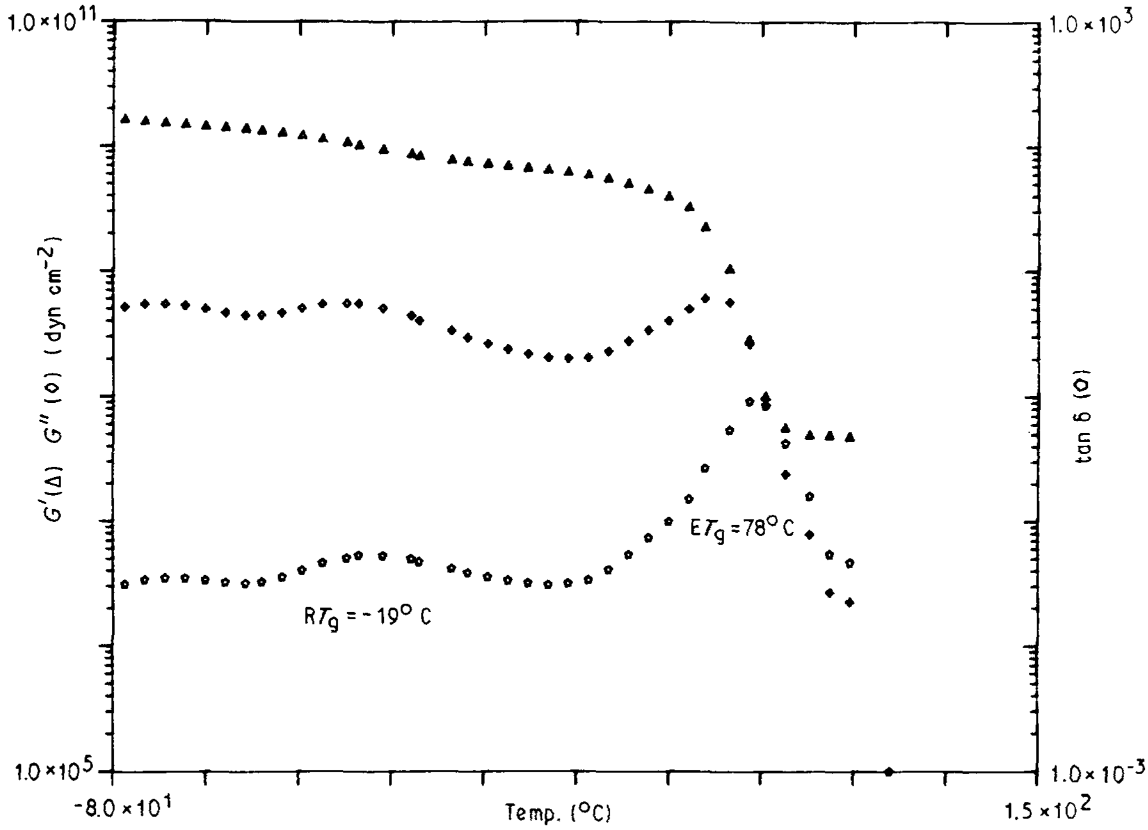

Figure 12 Mechanical spectrum of Epon/CTBN (X8)/Jeffamine (100:40:32) with phase separation kinetics modification.

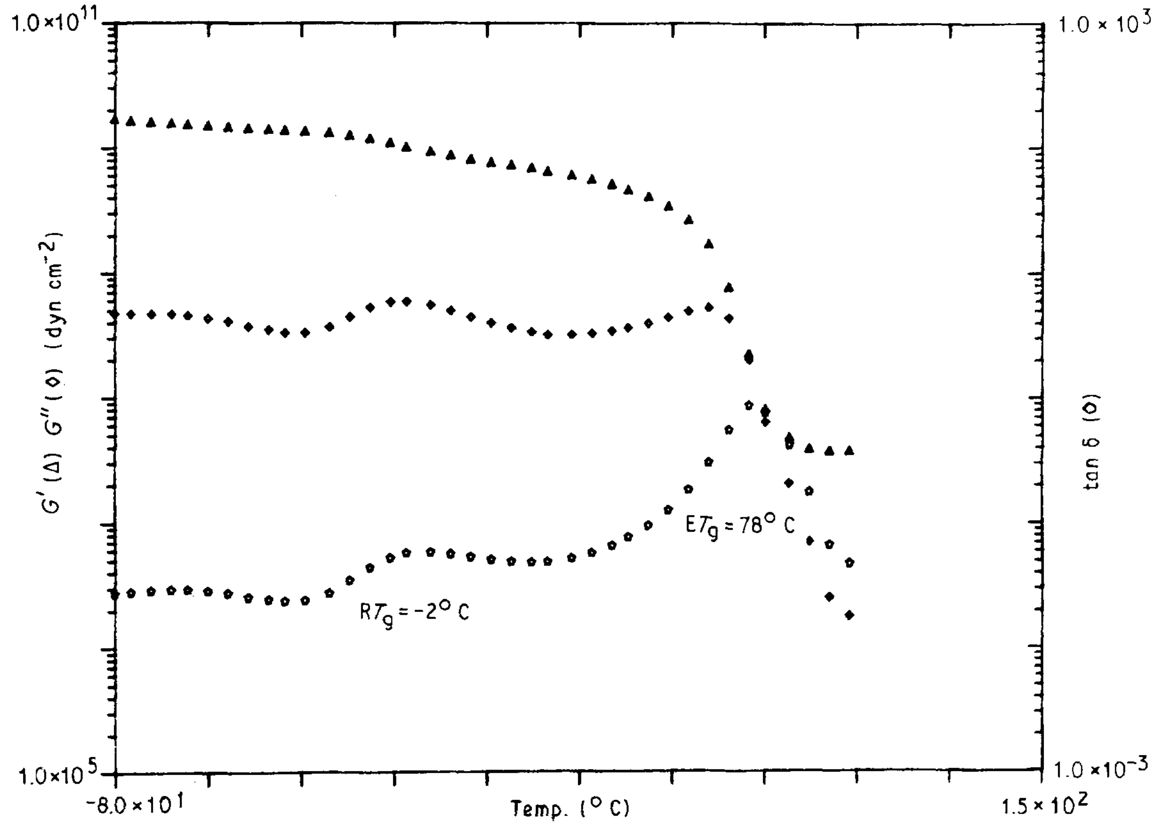

Figure 13 As Fig. 12, for Epon/CTBN (X13)/Jeffamine (100:40:32).

use of such technology is the understanding of phase diagrams consisting of binodal and spinodal curves. The kinetic processes of phase separation which include such phenomena as nucleation and growth, spinodal decomposition, and Ostwald ripening process are important aspects in morphological control.

Particle size of the rubber reinforcement phase in epoxies is affected by the mechanism of phase separation. Nucleation and growth gives larger rubber particles than spinodal decomposition. This same particle size is also affected by the acrylonitrile content of the CTBN. A higher acrylonitrile content gives a smaller

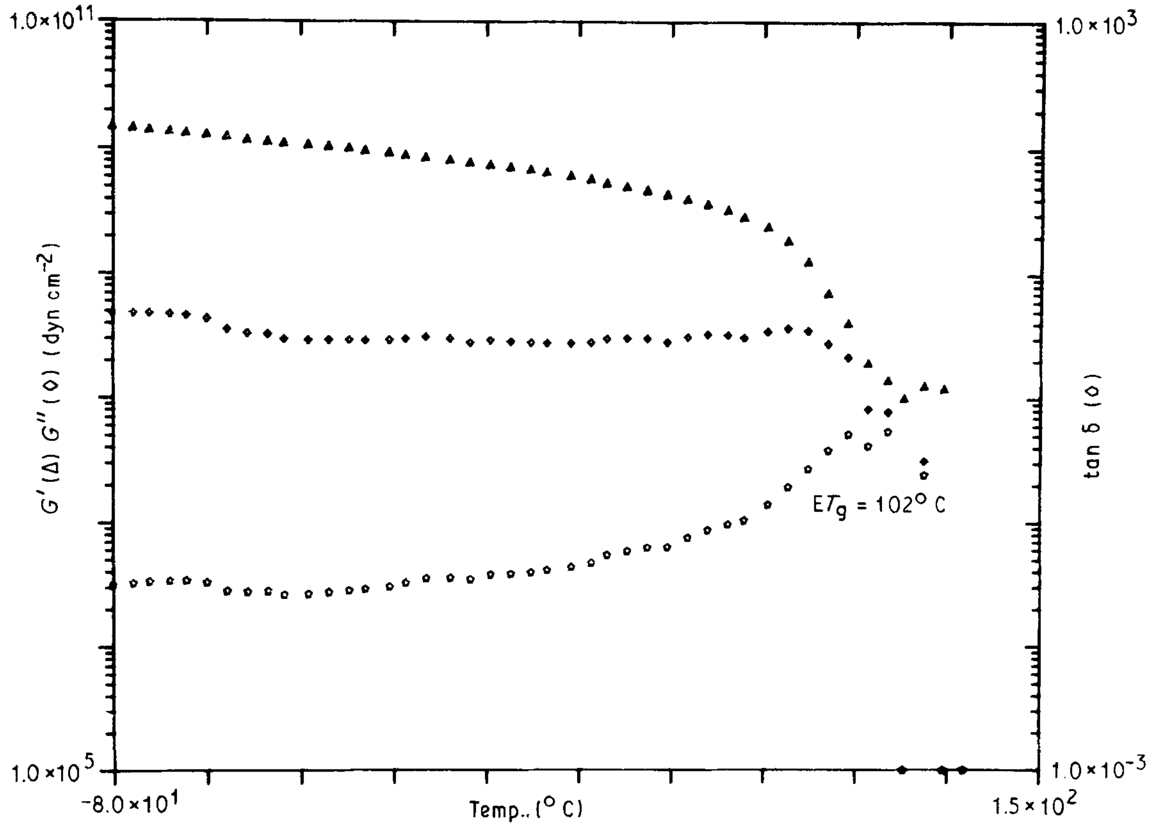

Figure 14 As Fig. 12, for Epon/CTBN (X8) Versamid (100:40:50).

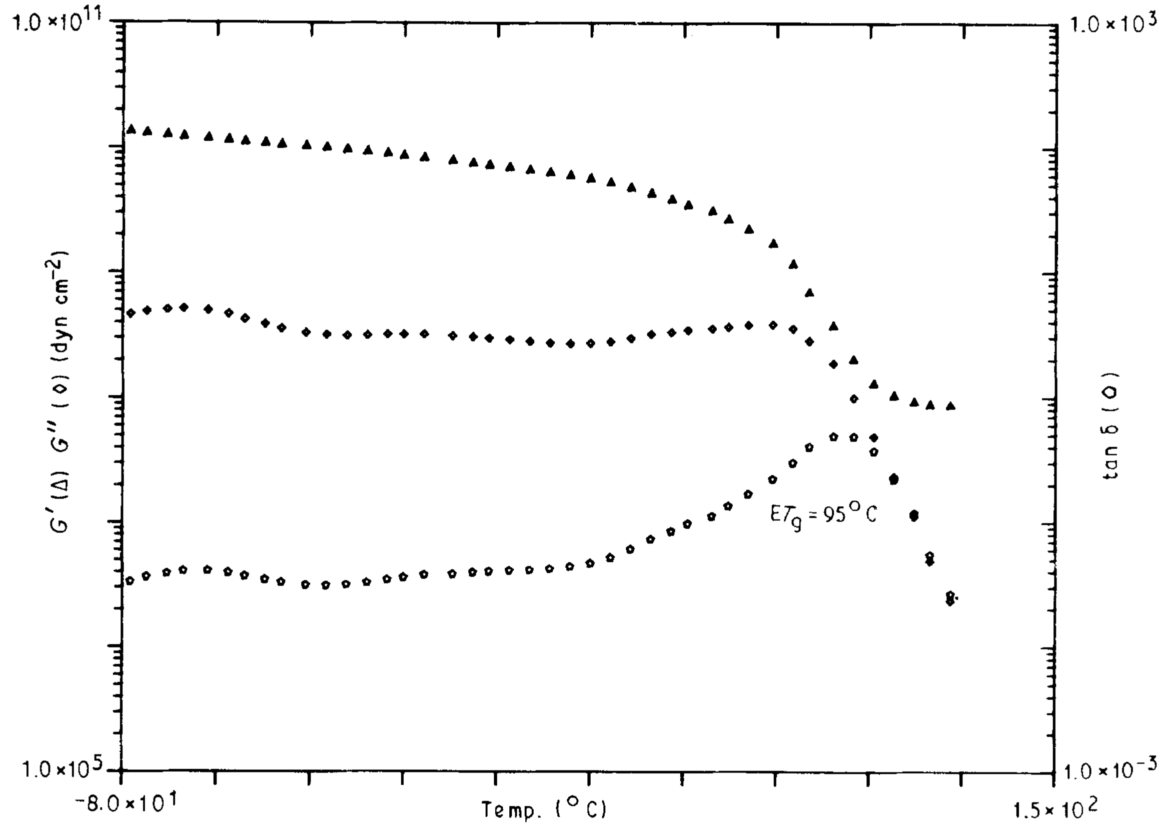

Figure 15 As Fig. 12, for Epon/CTBN (X13)/Versamid (100:40:50).

particle-size rubber when the mechanism of phase separation is dominated by the nucleation and growth, but a contrary result occurs by the mechanism of spinodal decomposition.

Modification of the cure kinetics by changing cure temperature has little effect on either morphology or properties of epoxy/CTBN alloys. Modification of cure kinetics by addition of accelerator does change the morphology of these epoxy systems but has little effect on the mechanical spectrum.

Modification of the phase-separation kinetics by pre-gelling the rubbery phase in epoxy/CTBN

TABLE III Properties of epoxy systems

Epoxy system	RT_g (°C)	ET_g (°C)
Epon/CTBN (X8)/Jeffamine (100:40:32)	− 51	81
Epon/CTBN (X8)/Jeffamine (100:40:32) (with PS[a] modification)	− 19	78
Epon/CTBN (X13)/Jeffamine (100:40:32)	− 32	81
Epon/CTBN (X13)/Jeffamine (100:40:32) (with PS modification)	− 2	78
Epon/CTBN (X8)/Versamid (100:40:50)	− 51	106
Epon/CTBN (X8)/Versamid (100:40:50) (with PS modification)	None	102
Epon/CTBN (X13)/Versamid (100:40:50)	− 32	101
Epon/CTBN (X13)/Versamid (100:40:50) (with PS modification)	None	96

[a] PS: phase separation.

systems was extremely effective at altering both morphology and properties of these alloys. This technique offers a means to shift the glass transition temperature of the rubber-rich phase while leaving the glass transition temperature of the epoxy-rich phase intact. We believe this ability will lead to the design of epoxy/rubber alloys for high-performance applications such as flexible matrices for composites, improved rigid matrices for composites, structural adhesives, and special high-damping materials.

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