

Entanglement Fluctuation during Phase Separation in Polymer Blends

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SYNOPSIS

For perhaps the first time, the dynamics of liquid-liquid phase separation was studied by time-resolved mechanical spectrometry in order to establish the relationship between blends' properties and the phase structures during spinodal decomposition (SD). The selected system was chlorinated polyethylene (CPE)/ethylene-vinyl acetate copolymer (EVA). It was found that in the early and intermediate stage of SD, the storage modulus (G') and the loss modulus (G'') increase with time after the initiation of the isothermal phase separation; in the later stage, G' and G'' decrease as phase separation proceeds. An entanglement fluctuation model was presented to manifest this phenomenon; it was found that the rheological behavior agrees well with the expectations of the model in the early stage. For the later stage, the reduction of G' and G'' can be attributed to the increment of phase-domain size. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The relationship between polymer blends' properties and their structures has been widely investigated in the past few years, but it is still somewhat obscure. One of the main difficulties is that it is not easy to obtain the property and structure parameters simultaneously.

The properties of the blends depend mainly on the component proportion; much research has focused on this issue.^{1,2} After the proper component proportion has been found, a new problem lies ahead of us. At a particular component proportion, how can we obtain higher properties? That is, how to improve the blends' properties as much as possible by changing the blends' phase structures. Although much attention has been paid to this aspect, people solve this problem empirically or by means of a large number of experiments, and it is not often effective. The reason is that lack of knowledge of the quantitative relationship between the property and the structure hampers the process.

If a system's structure varies spontaneously at one special condition, and the structure parameters are easy to obtain, then one can measure the property parameters as the structure varies. It seems easy to obtain the relationship between the structure and the property in this way. Such a system is of blends possessing lower critical solution temperature (LCST) or upper critical solution temperature (UCST) phase diagrams, when, if the blend's temperature rises or lowers, the system undergoes a phase-separation process. There are two kinds of phase-separation mechanisms: nucleation growth (NG) and spinodal decomposition (SD). At $T_b < T < T_s$ (T_b , the cloud point; T_s , the spinodal point), phase separation takes place according to the NG mechanism, whereas at $T > T_s$, it should occur according to the SD mechanism. The initial stage of SD can be adequately described by the linear theory of Cahn³; in the later stage, the phase structure is similar at different phase-separation times.^{4,5} Thus, if the property parameters are measured during phase separation, and the structure's variation follows one certain law, the relationship between the structure and the property can be established easily. Only if the relationship is established can people hope to obtain the properties of polymer alloys at

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will by controlling the phase structure in them. The rheological studies on the phase separation in polymer blends in this work try to solve, preliminarily, this issue.

Rheological properties are of crucial importance in the characterization and modeling of the flow behavior of polymers.⁶ Yet, with a few exceptions, rheological investigations of polymer blends have dealt with immiscible systems.^{7,8} For miscible blends, systems such as polystyrene (PS)/poly(phenyl oxide) (PPO)⁹ and poly(acrylonitrile-*co*-styrene)/poly(styrene-*co*-maleic anhydride) blends¹⁰ have been studied. For systems exhibiting phase-separation behavior, complete rheological studies have been done by Aji et al.¹¹ They investigated the changes of rheological properties in the vicinity of the temperature of phase separation T_s . They found that the Cole-Cole plot appeared to be a sensitive tool in the study of the miscibility and phase separation of polymer blends. However, to our knowledge, rheological studies on the kinetics of phase separation have not been conducted yet.

Considering those just mentioned, we selected one system made of chlorinated polyethylene (CPE)/ethylene-vinyl acetate copolymer (EVA); it has been studied in detail by the small-angle light-scattering technique.¹² The storage modulus (G') and the loss modulus (G'') were measured as the SD proceeds. To interpret the dynamic rheological behavior during SD, an entanglement fluctuation model was presented; it describes the rheological behavior in the early and intermediate stages of SD quite well. For the later stage, considering the increment of phase-domain size, the rheological behavior is also clear.

EXPERIMENTAL

CPE and EVA used here are commercial products of Aldrich Co. Cl and VA content are 47.1 and 40% by weight, respectively. The number-average molecular weight is 58,400 for CPE and 27,400 for EVA. Blending to different compositions was made from THF solutions of 3% total polymers by weight at room temperature. The polymer solutions were left in an air current until the major part of the solvent was evaporated. The resulting films were then placed under vacuum at 60°C for at least 2 weeks to remove the residual solvent in the sample. The films obtained in this way were transparent, showing a homogeneous state. The resulting films were then molded at a temperature just above the glass transition temperature to form a disc with a diameter

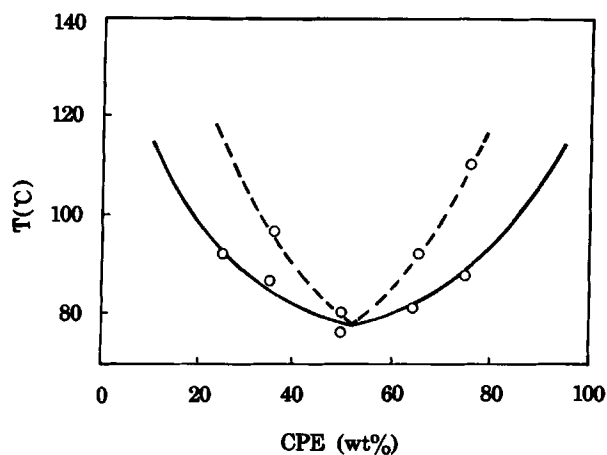


Figure 1 Phase diagram of CPE/EVA blend determined by SALS technique.

of 25 mm and thickness of 1.5 mm. The samples were now ready for rheological measurements.

Cloud and spinodal points were measured with a small-angle light-scattering technique; the methods, described in detail, will be presented elsewhere.¹² Figure 1 is the phase diagram of CPE/EVA blends; it exhibits three types of states as a function of temperature, manifesting the system with a low critical solution temperature.

Rheological measurements were carried out in the linear viscoelastic region by dynamic oscillation using parallel plates in a time-resolved Rheometrics Mechanical Spectrometer 605 as the SD proceeds. Time-sweeps were performed with a constant frequency of 3.8 rad/s at given temperatures. The gap between the plates was 1 mm for all experiments.

DESCRIPTION OF THE MODEL

In the homogeneous state, one component of the blend can dissolve in another component to form a "solid solution," and the polymers can be taken as ideal chains where the Flory theorem holds. We may visualize the polymer chain as a succession of units or "blobs" of size ξ ; inside one blob, the chain does not interact with other chains. Thus, the solution is essentially a closely packed system of blobs: The network made of polymer chains' entanglement is essentially constructed by the interpenetrating "blobs." Hence, the total number of the topological entanglement points per unit volume is¹³

$$N_e = \rho / M_e = p_{11}\phi_1^2 + p_{22}\phi_2^2 + 2p_{12}\phi_1\phi_2 \quad (1)$$

where ρ is the density of the blend; M_e , the average entanglement molecular weight of the blend; p_{ij} , the contact probability of entanglement between two chains of species i and j ($i, j = 1, 2$); and ϕ_k , the volume fraction of one component ($k = 1, 2$). Then, the number of entanglement points along one chain in the homogeneous blend is

$$n_{e0} = p_{11}(N_{01}/N_0)^2 + p_{22}(N_{02}/N_0)^2 + 2p_{12}(N_{01}/N_0)(N_{02}/N_0) \quad (2)$$

where N_{01} and N_{02} are the total number of chains of polymer 1 and polymer 2, respectively, and $N_0 = N_{01} + N_{02}$.

Now, let us consider a local inhomogeneous system. Assume that C_{0j} is the average concentration of polymer j ($j = 1, 2$) and that ΔC_j is the concentration fluctuation of polymer j after the initiation of the phase separation. Taking a cell of unit volume, then the number of chains for polymers 1 and 2 is $C_{01} + \Delta C_1$ and $C_{02} + \Delta C_2$, respectively. It is reasonable to assume that the volume of the cell keeps constant as the concentration fluctuations take place; thus, $\Delta C_2 = -(\rho_2/\rho_1)\Delta C_1$, where ρ_1 and ρ_2 are the density of pure polymers 1 and 2, respectively. Therefore, the total number of polymer chains in the cell is $C_{01} + C_{02} + \Delta C_1 + \Delta C_2$. Because of $C_{01} + C_{02} \gg \Delta C_1 + \Delta C_2$, we can take the total number of polymer chains in the cell as a constant. Thus, if there is local inhomogeneity, the number of entanglement points along one chain is

$$\begin{aligned} n_e &= p_{11}[(C_{01} + \Delta C_1)/n_0]^2 \\ &+ p_{22}[(C_{02} + \Delta C_2)/n_0]^2 \\ &+ 2p_{12}[(C_{01} + \Delta C_1)/n_0][(C_{02} + \Delta C_2)/n_0] \\ &= n_{e0} + \Delta n_e \end{aligned} \quad (3)$$

where $n_{e0} = p_{11}(C_{01}/n_0)^2 + p_{22}(C_{02}/n_0)^2 + 2p_{12}(C_{01}/n_0)(C_{02}/n_0)$ is the number of entanglement points per chain in the homogeneous state. Δn_e is the entanglement fluctuation caused by the concentration fluctuations and is defined as

$$\begin{aligned} \Delta n_e &= (P_{11} + P_{22}a^2 - 2aP_{12})(\Delta C_1/n_0)^2 \\ &+ 2[(P_{11}r_1 - P_{22}ar_2) \\ &+ P_{12}(r_2 - ar_1)](\Delta C_1/n_0) \end{aligned} \quad (4)$$

where $a = \rho_2/\rho_1$, $r_1 = C_{01}/n_0$, and $r_2 = C_{02}/n_0$. If $A = P_{11} + P_{22}a^2 - 2P_{12}a$, $B = (P_{11}r_1 - P_{22}ar_2) + P_{12}(r_2 - ar_1)$, and $y = \Delta C_1/n_0$; thus,

$$\Delta n_e = Ay^2 + 2By \quad (5)$$

There may be three cases for variation of Δn_e with concentration, as shown in Figure 2.

According to Wu,¹³ $p_{11} = \rho_1/M_{e1}$, $p_{22} = \rho_2/M_{e2}$, and $p_{12} = (\rho_1\rho_2)^{1/2}/M_{e12}$. M_{e1} and M_{e2} are the entanglement molecular weights of pure components 1 and 2, respectively, and M_{e12} is that of a hypothetical pure component of density $(\rho_1\rho_2)^{1/2}$ having the entanglement probability between the two dissimilar chains in the blend. Thus, if $A > 0$, $M_{e12} > (M_{e1}M_{e2})^{1/2}$. One can then see that M_{e12} is a very important parameter that determines the entanglement fluctuation during phase separation.

In the early stage of SD, the concentration fluctuation follows⁴:

$$\begin{aligned} C(r) - C(0) &= \sum_{\text{exp}} [R(q)t] [A(q)\cos(qr) + B(q)\sin(qr)] \\ R(q) &= D_c q^2 [-(\partial^2 f/\partial C^2) - 2kq^2] \end{aligned} \quad (6)$$

where $q = 2\pi/\Lambda$ is the wavenumber of the spatial composition fluctuations and Λ is the corresponding wavelength. Figure 3 is the schematic representation of spatial concentration fluctuation of one compo-

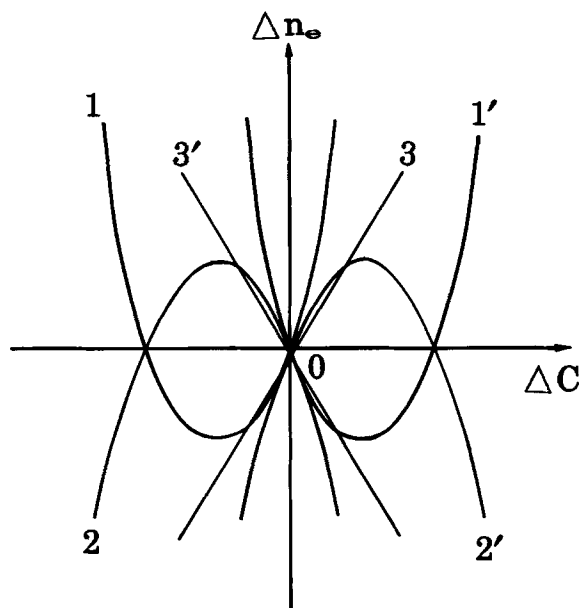


Figure 2 Sketch of the number of entanglement points per chain as a function of the concentration fluctuations during phase separation according to Eq. (5). Curve 1 ($A > 0, B > 0$); curve 1' ($A > 0, B < 0$); curve 2 ($A < 0, B > 0$); curve 2' ($A < 0, B < 0$); curve 3 ($A = 0, B > 0$); curve 3' ($A = 0, B < 0$).

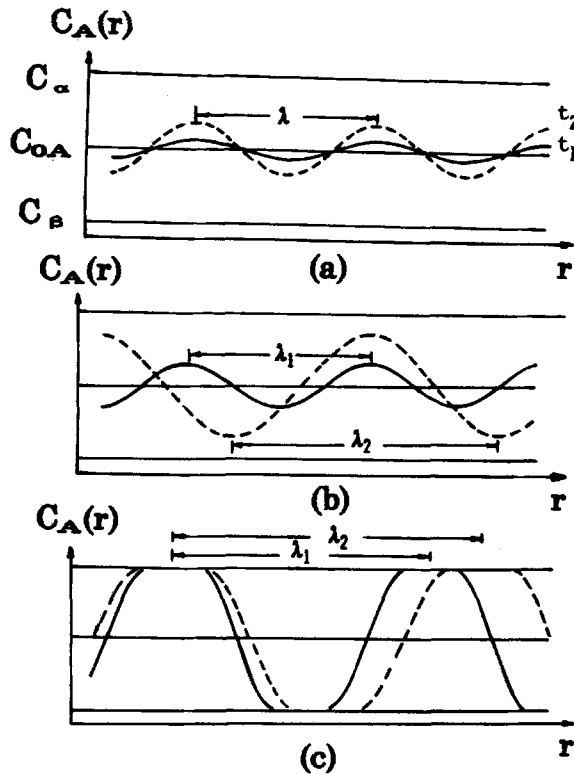


Figure 3 Schematic representation of concentration fluctuations of one component [$C_A(r)$] in critical composition during phase separation: (a) early stage SD; (b) intermediate stage SD; (c) late stage SD. Time evolution of the fluctuation within each stage is shown by solid (t_1) and broken (t_2) lines ($t_1 < t_2$). C_α and C_β are the equilibrium concentrations of one component A in the coexisting two liquid phases. λ is the correlation length.

ment [$\phi_1(r)$] in the critical mixture at three different stages of unmixing. In the early stage of SD, $|\Delta C|$ increases with time, but the correlation length keeps constant; in the intermediate stage, both $|\Delta C|$ and the correlation length increase with time; and in the later stage, $|\Delta C|$ reaches its equilibrium value while the correlation length still increases with time. If $\Delta C(t, 1)$ is the concentration fluctuation at time t in one unit of time, then $\Delta C(t_1, 1) < \Delta C(t_2, 1)$ when $t_1 < t_2$ in the early stage of SD. According to Eq. (6), it approaches zero at the later stage of SD. If $\Delta n_e(t, 1)$ is the number increment of entanglement points at time t in one unit of time, from Eq. (5):

$$\Delta n_e(t, 1) = A\Delta C(t, 1)[\Delta C(t+1) + \Delta C(t)] + 2B\Delta C(t, 1) \quad (7)$$

According to the variation of $\Delta C(t, 1)$ with t , one can obtain an idea of the variation of $\Delta n_e(t, 1)$ with

t . Although in the intermediate stage the concentration fluctuations are not clear, due to the fluctuations increasing exponentially in the early stage and approaching zero at the later stage, the tendency of variation for $\Delta C(t, 1)$ and $\Delta n_e(t, 1)$ should be clear and definite. The variation of $\Delta C(t, 1)$ and $\Delta n_e(t, 1)$ are schematically shown in Figure 4; the value of $\Delta n_e(t, 1)$ indicates the acceleration of the variation for n_e . As shown later, the details of the variation do not affect our discussion of the rheological behavior during phase separation.

For a melt of long polymer chains, the entanglements between chains make the polymer behave like a "rubber" network in a span of time ($t < \tau_t$); τ_t is the terminal relaxation time. It has been found that the elastic modulus is related to ν_0 (Ref. 14):

$$E \approx T/(\xi^3\nu_0) \quad (8)$$

where T is the absolute temperature; ξ , the size of the "blob"; and ν_0 , the average interval between en-

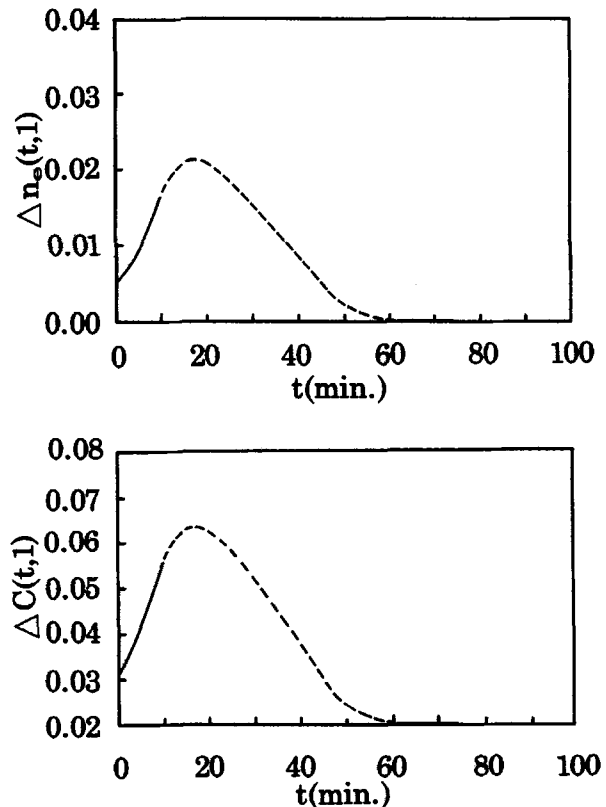


Figure 4 Schematic representation of the sketch of $\Delta C(t, 1)$ and $\Delta n_e(t, 1)$ as a function of time t . The solid line is calculated according to Eqs. (6) and (7); the dotted line is supposed to characterize the intermediate stage behavior of $\Delta C(t, 1)$ and $\Delta n_e(t, 1)$.

tanglement points along one chain. It can be also written as

$$E \approx Tn_e/\xi^3 \quad (9)$$

For the Newtonian fluid, $E \approx 3G$, where G is the steady shear modulus that can be related to the dynamic moduli G' and G'' in the frame of the Maxwell model by

$$\begin{aligned} E = 3G &= (1 + \omega^2\tau^2)G'/(\omega^2\tau^2) \\ &= (1 + \omega^2\tau^2)G''/(\omega\tau) \quad (10) \end{aligned}$$

where ω and τ are the frequency and terminal time, respectively. For the non-Newtonian fluid, the relationship between the elastic modulus and the shear modulus is still an open question. Since the ω used in this experiment is constant and relatively low, although the blends investigated here are non-Newtonian fluids, we suppose that the blends are very close to the Newtonian fluid. Thus, Eq. (10) can hold in this case.

Finally, the property parameters are related to the number of entanglement points. Submitting Eq. (3) to Eq. (9) and Eq. (10), the effects of entanglement fluctuation on the elastic modulus E and dynamic moduli G' and G'' during phase separation is clear at a glance. The schematic representations of the variation of E during phase separation are shown in Figure 5.

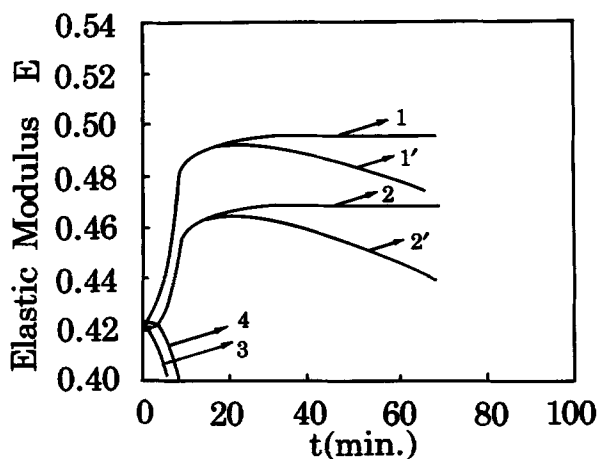


Figure 5 Sketch of elastic modulus as a function of time t during phase separation according to Eq. (9). Curve 1 ($A > 0, B > 0$); curve 2 ($A > 0, B < 0$); curve 3 ($A < 0, B < 0$); curve 4 ($A < 0, B > 0$); curve 1' ($A > 0, B > 0$; domain size effect considered); curve 2' ($A > 0, B < 0$; domain size effect considered).

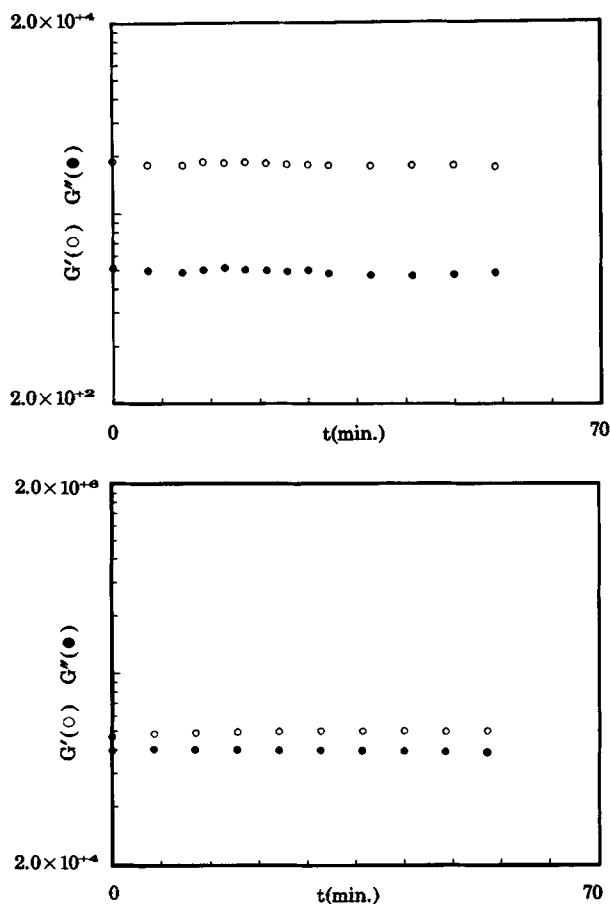


Figure 6 Time-sweeps of G' and G'' for pure CPE and EVA at 143°C : (○) G' ; (●) G'' .

COMPARISON TO EXPERIMENTAL RESULTS

Figure 6 shows the time-sweeps of pure component CPE and EVA at 143°C with a constant frequency 3.8 rad/s. It was found that there were not any changes for the storage modulus (G') and the loss modulus (G'') in the time of measurements. Thus, there are not any changes (including chemical and physical changes in the chain) that affect the rheological properties at 143°C for the two pure components. Figure 7 shows time-sweeps of G' and G'' for the miscible blend PS/PVME (80/20, wt %) at 160°C below the cloud-point temperature¹⁵; it is shown that both G' and G'' remain constant in the experimental time. The result shows that the rheological properties of the blend are steady in the homogeneous region. On the other hand, Figure 8 shows the rheological behavior for the blend CPE/EVA (52/48, wt %) at 143°C in the spinodal region according to Figure 1; G' and G'' clearly vary with

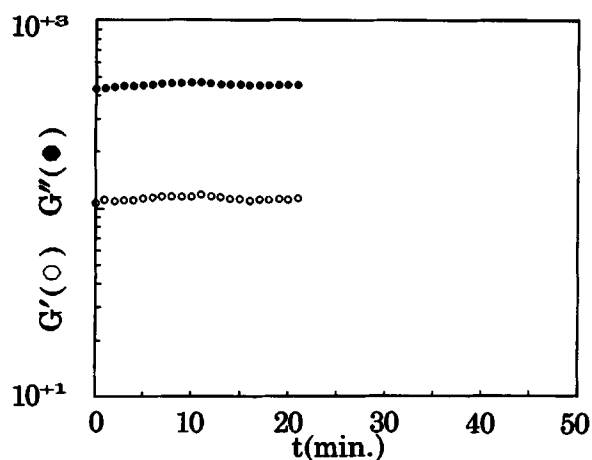


Figure 7 Time-sweeps of G' and G'' for blend PS/PVME (80/20, wt %) at 160°C in the homogeneous state: (○) G' ; (●) G'' .

time. Thus, the variation of G' and G'' with time can only be attributed to the change of phase structures during SD.

As shown in Figure 8, in the 15 and 24 min after the initiation of phase separation, G' and G'' increase with time and reach their maximum values, respectively. Then, G' and G'' decrease slightly with time. The time when they reach their maximum is different, and the rate of increasing or decreasing for G' and G'' is also different.

According to the results of the small-angle light-scattering studies on the blend CPE/EVA (52/48, wt %),¹² the early and intermediate stage last about 12 min when unmixing at 143°C. Since G' obtains its maximum at $t = 15$ (min) after the initiation of the phase separation, it is clear that the time $t = 15$ (min) is close to the time $t = 12$ (min) when the

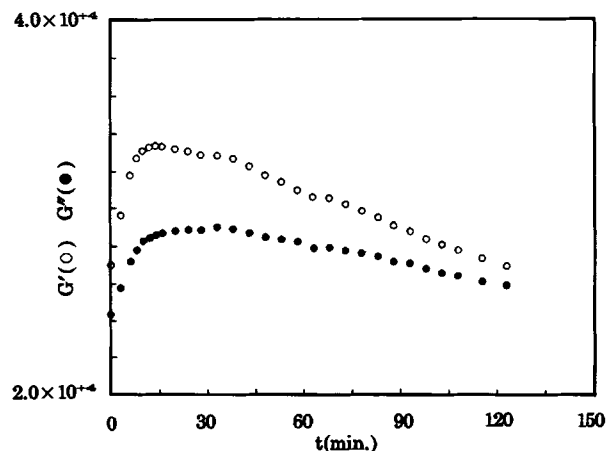


Figure 8 Time-sweeps of G' and G'' for blend CPE/EVA (52/48, wt %) at 143°C: (○) G' ; (●) G'' .

concentration fluctuation approaches its equilibrium value. This demonstrates that the concentration fluctuation results in the increment of G' , as expected by our model.

It appears that the experimental data do not completely agree with what the model describes. As shown in Figure 5, it is obvious that curves 3 and 4 do not describe the experimental facts; the experimental data increase more quickly in the early stage compared with the expectations of curves 1 and 2. Nevertheless, after we take into account some of the factors, the model describes the rheological behavior quite well.

First, the time-sweeps of G' are delayed about 1 or 2 min after the initiation of phase separation. It is difficult to overcome this delay due to the shortcomings of the instrument itself. Therefore, some information about the initial stage of SD is lost. However, we pursued the recovery of the lost information by conducting the measurement as soon as the sample was put in, while the unmixing temperature T is kept near T_s . To our pleasant surprise, G' at time $t = 0$ is larger than that at $t = 0.5$ and $t = 1$ min, as shown in Figure 9, just as curve 2 in Figure 5 expects. On account of using the same spectrometer, the time-sweeps for the same blend do not show this phenomenon, shown in Figure 7. Thus, it cannot be ascribed to the error of the instrument. Detailed results of this system will be presented elsewhere.¹⁵ In contrast to the CPE/EVA blend, the results show that the coefficient B for the PS/PVME blend is negative.

Second, as shown by the model, when the system enters a later stage of SD, the concentration fluctuations approach its equilibrium value. Hence, the number of the entanglement points reaches a max-

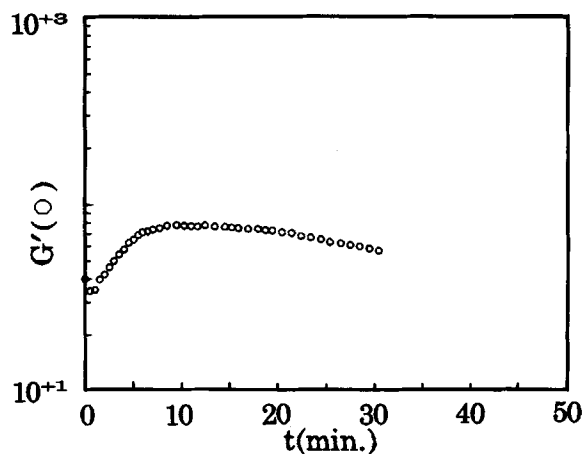


Figure 9 Time-sweeps of G' for blend PS/PVME (80/20, wt %) at 190°C.

imum and keeps constant. Thus, the G' and G'' should keep constant, too. However, for the later stage, the phase domain size increases with time.³ According to Vollenberg and Heikens,¹⁶ when keeping the filler volume fraction constant, as the diameter of the filler increases, the elastic modulus of the system decreases. The results convincingly explain the reduction of G' and G'' of the CPE/EVA blend in the later stage of SD. Although in the intermediate stage the phase domain size increases with time, it seems that the increment of domain size only slows the increment of G' and G'' . For the early stage of SD, the domain size keeps constant; it has no effect on the rheological behavior.

After taking into account these observations, it is obvious that the entanglement fluctuation model describes the rheological behavior during phase separation quite well, as shown by curves 1' and 2' in Figure 5. The variation tendency shown by the experimental data agrees well with the expectation of curve 1' in Figure 5, implying that in the CPE/EVA blends $M_{e12} > (M_{e1}M_{e2})^{1/2}$.

It should be noted that the concentration fluctuations in the intermediate stage are not explicit and that there is no quantitative relationship between the domain size and the elastic modulus. We cannot isolate the contribution of concentration fluctuations to E from that of domain size increment. Experimentally, as the unmixing temperature T is close to T_s , the early stage of SD lasts for a long time. Thus, the rheological properties are functions of concentration fluctuations since the domain size remains constant in the early stage. However, since the separation process is relatively slow when T is near T_s , it takes a long time for the concentration fluctuation to approach its equilibrium value, and G' varies very slowly as time passes. However, if the unmixing temperature is high compared with T_s , the initial stage finishes in a few minutes. Then, we only obtain the information about G' in the intermediate and later stages, where two kinds of competitive effects exist, and they are difficult to separate. Hence, the experimental method remains to be improved.

One problem may also be presented: Why do the G' and G'' reach their maxima at different times? At the point of $t = 15$ min, now that the number of entanglement points approaches its equilibrium value, it seems reasonable for G' to reach its maximum at this point. It appears that G'' should also reach its maximum at this time. Actually, G' and G'' reflect the different motions of chains. G' depends upon the density of the entanglement points and has no relationship with the chain length; on the

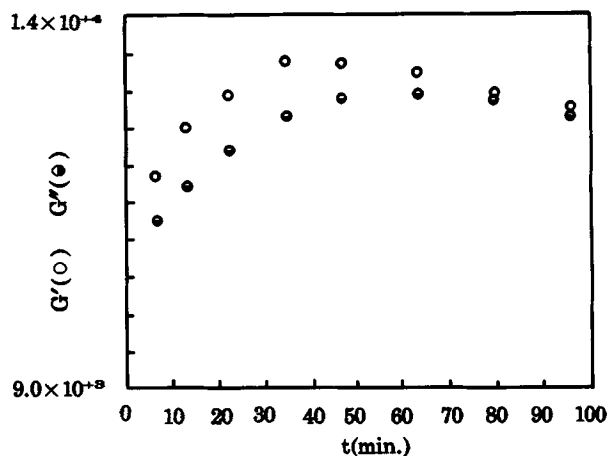


Figure 10 Time-sweeps of G' and G'' for blend CPE/EVA (52/48, wt %) at 130°C: (○) G' ; (●) G'' .

other hand, G'' is sensitive to the chain length. According to the Doi-Edwards model,¹⁷ there are two kinds of relaxations for chains in the entanglement network:

1. Contraction of chains from the deformed network, which does not change the topological structures of the network. The relaxation time is relatively short and $t \propto M^2$, where M is the molecular weight.
2. Reptation of the primitive chains from the old "tubes" to form new "tubes," which changes the topological structures. The relaxation time is long and $t \propto M^3$.

Obviously, the first relaxation provides the system with elasticity, and the later characterizes the flow property. Thus, G' responds to the increment of n_e more rapidly compared with G'' . When n_e reaches its equilibrium value, G' reaches its maximum first; later, it is the turn for G'' to reach its maximum.

Figure 10 shows the time-sweeps of G' and G'' for CPE/EVA (52/48, wt %) at 130°C with a constant frequency 3.8 rad/s. G' and G'' vary in the same way as at 143°C: G' and G'' reach their maxima at 30 and 60 min after the initiation of phase separation, respectively. It has been found that the phase separation proceeded to the later stage at 26 min.¹² Obviously, this is another example whose rheological behavior can be described quite well by our model.

CONCLUSION

Perhaps for the first time, rheological studies have been conducted on the phase separation of polymer blends; the results show that the concentration fluctuation

tuations result in entanglement fluctuation during phase separation. The changes in G' and G'' in the early and intermediate stages can be explained convincingly by the entanglement fluctuation model presented. In the later stage, the concentration fluctuation approaches its equilibrium value, while the phase domain size increases with time, which reduces the G' and G'' slightly with time. The different response delays to the increment of n_e for G' and G'' can be reasonably attributed to the different relaxations of polymer chains.

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