Morphology Control in Reaction-Induced Phase-Separated Polymeric Systems

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SYNOPSIS

In this article the morphology control of poly(ethyl acrylate)/poly(methyl methacrylate) (PMMA) semi-interpenetrating polymer networks (IPNs) has been attempted either by changing reaction temperature or by adding the third component at the initial stage of phase separation. The morphological variation was followed via dynamic mechanical behavior and electron microscopy. It was found that raising the polymerization temperature of PMMA or adding linear PMMA to the initial mixture facilitates phase separation during the semi-IPNs formation process. However, the phase separation was further induced by annealing, which indicates that kinetically controlled morphology was not at its equilibrium state. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends have been the subject of numerous investigations due to their technological as well as academic importance. There are many different ways to combine two different polymeric species. Among them, the interpenetrating polymer network (IPN) is a unique type of polymer blend, in which at least one component has a crosslinked structure.[1,2] There are many subclasses of IPNs, depending on their preparation schemes. When either one of the components involved is a linear polymer while the other has a network structure, it is classified as semi-IPN. A typical example in this category is thermoplastic modified thermoset, such as epoxy or unsaturated polyester.

One of the most important features in characterizing or designing polymer blends is their morphology, and the most influential factor is the thermodynamic factor, such as the miscibility between two components.[2–4] In the case of IPNs, since one component is polymerized/crosslinked in the presence of the other component, the phase separation is basically induced by the polymerization reaction; kinetic factors, such

as the rate of polymerization/crosslinking, viscosity variation, and vitrification, become important in determining the final morphology.

This article focuses on a semi-IPN composed of a semicompatible pair of poly(ethyl acrylate) (PEA) and poly(methyl methacrylate) (PMMA). Some data are already available on the blends and IPNs based on this pair. The heat of mixing PEA and PMMA was reported to be nearly zero.[5] A blend of PEA/PMMA (79 : 21 by weight) was reported to exhibit a single broad glass-to-rubber transition region; this behavior was attributed to partial miscibility of the two components.[6] However, when such a blend specimen was annealed at a temperature above the glass transition temperature, T_g, of PMMA, partial phase separation occurred and the specimen became opaque.[7] These results indicate that the PEA/PMMA system is partially miscible or semicompatible and may undergo a lower-critical-solution-temperature (LCST) type of phase separation. Sperling et al. prepared IPNs of PEA/PMMA by a photopolymerization method and observed a broad continuous transition and significant phase separation.[8,9] However, it is expected that phase separation is constrained due to physical interlocking by an added crosslinking agent.
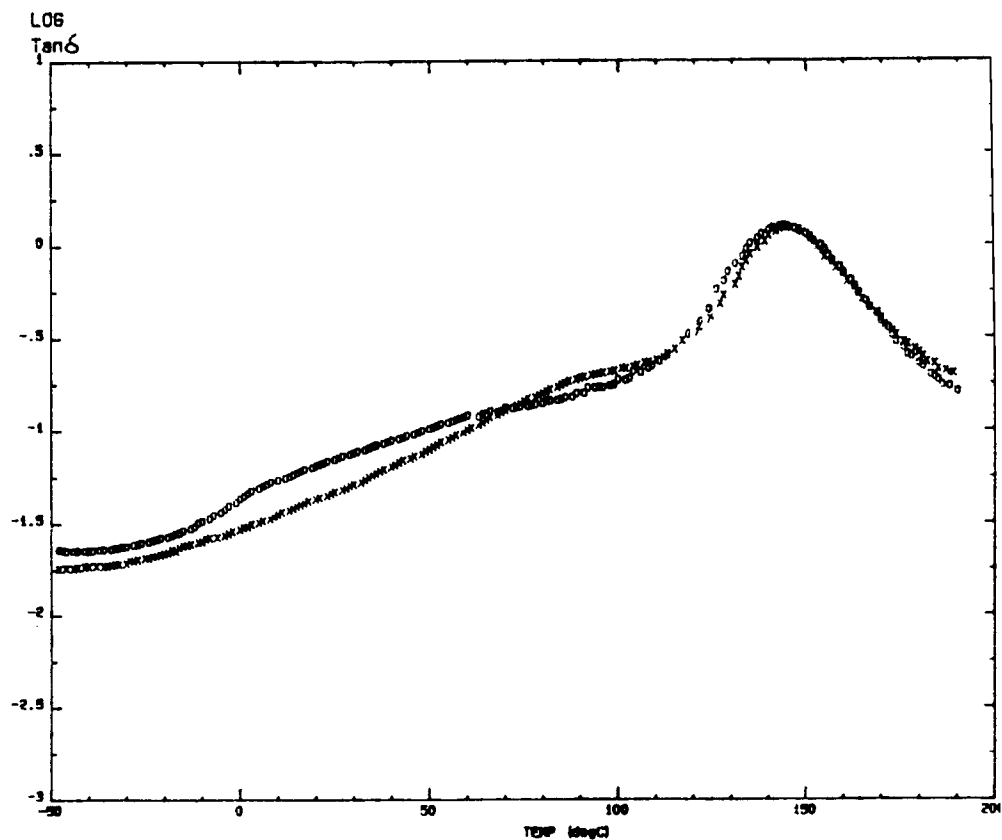
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* To whom correspondence should be addressed.

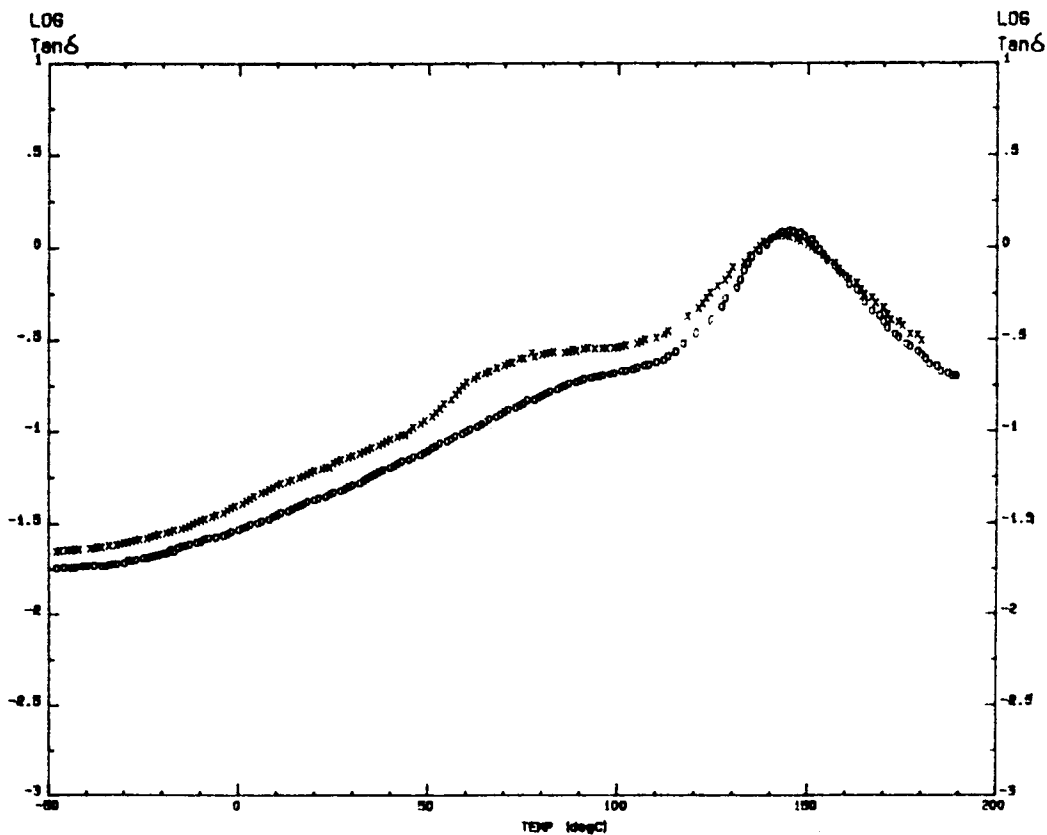**Figure 1** Effect of synthesis temperature in PEA/PMMA semi-IPNs. xxx: PEA/10-MMA/90-1-0°C; ooo: PEA/10-MMA/90-1-40°C.

Figure 2 Comparison of PEA/PMMA semi-IPNs with different PEA contents. xxx: PEA/15-MMA/85-1-0°C; ooo: PEA/10-MMA/90-1-0°C.
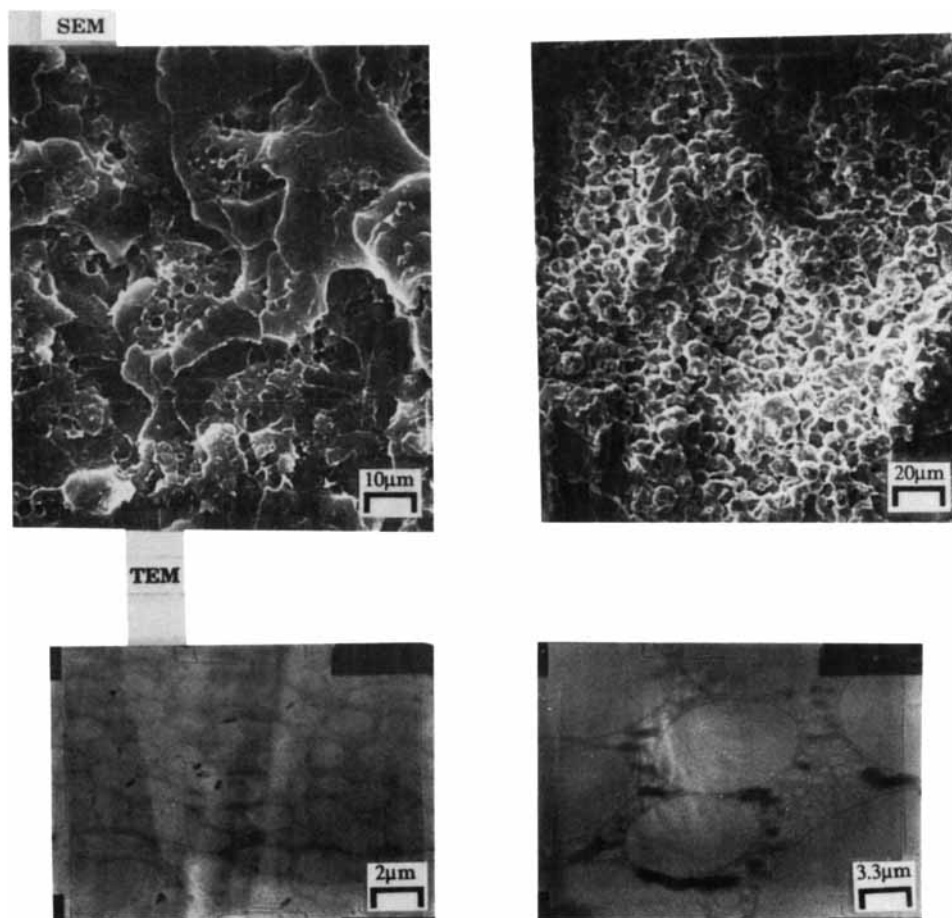
Figure 3 Effect of synthesis temperature on morphology of PEA/PMMA semi-IPNs. Left: PEA/10-MMA/90-1-0°C; right: PEA/10-MMA/90-1-40°C.

In this study the dynamic mechanical behavior and morphological features of semi-IPN composed of linear PEA and crosslinked PMMA were investigated by dynamic mechanical thermal analyzer (DMTA), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The analysis was centered on the effect of polymerizing temperature and the addition of linear PMMA in the early stage of polymerization.

EXPERIMENTAL

The monomers were washed with 5% aqueous NaOH solution to remove the inhibitors and washed repeatedly until no alkalinity appeared. The washed monomers were dried over anhydrous $CaCl_2$ and then distilled under reduced pressure. Benzoin, photoinitiator, and 1,4-butandiol dimethacrylate (BDMA), a crosslinking agent, were used as received.

To provide the necessary contrast for TEM by staining with osmiumtetroxide, less than 1 wt % of butadiene was deliberately added to some of the linear components, PEA and PMMA, in the preparation step.[10] PEA and PMMA were prepared with monomer mixture containing butadiene using azo-bis-isobutylonitrile (AIBN) as an initiator at 70°C.

PEA/PMMA semi-IPNs were prepared by the photopolymerization technique. The linear PEA was dissolved with the mixture of MMA, BDMA (0.1, 1, 2 mole % based on MMA), and benzoin (0.4 wt % based on MMA). The mixture was purged with nitrogen gas and then introduced into a glass mold equipped with an elastomer gasket and spring loaded to follow the shrinkage during the polymerization. The content in the mold was exposed to an ultraviolet (UV) ray for three days in the temperature-controlled environment. Two different temperatures were employed: 0°C and 40°C. Finally, samples were
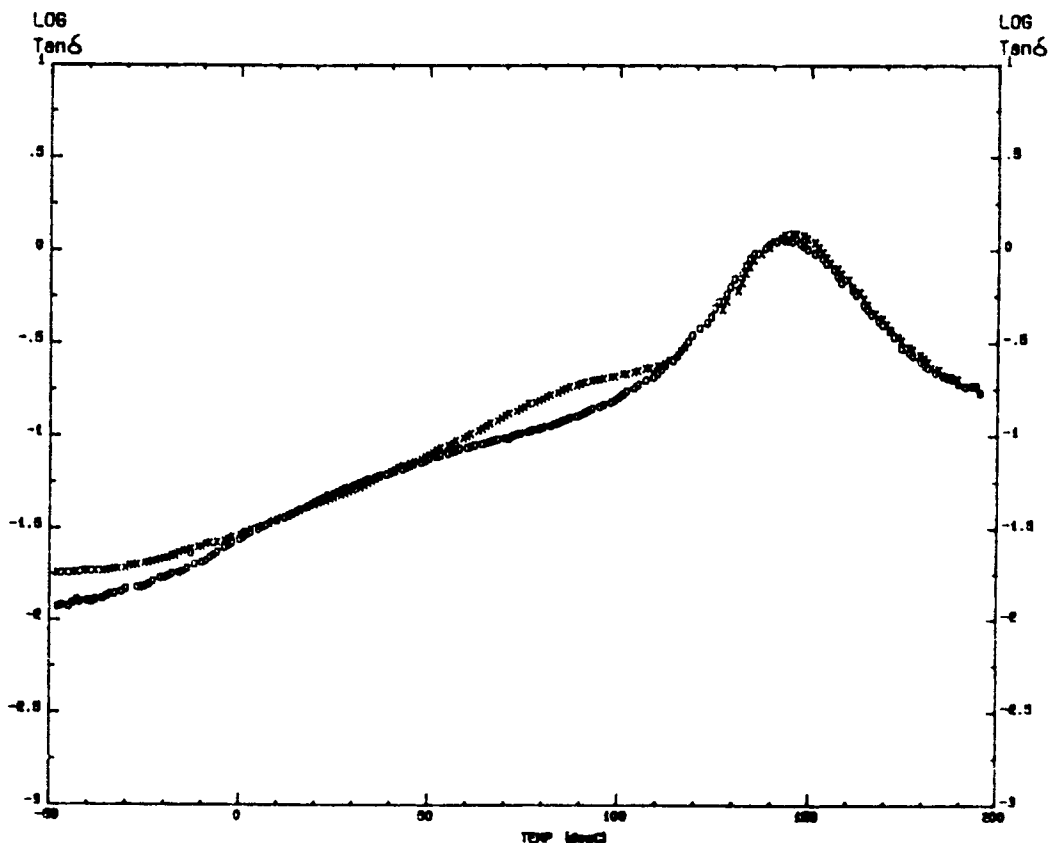
Figure 4 Effect of linear PMMA addition on dynamic mechanical behavior of PEA/
PMMA semi-IPNs. xxx: PEA/10-MMA/90-1-0°C; ooo: PEA/10-PMMA/10-MMA/80-1-
0°C.

carefully dried in a vacuum oven at room tempera-
ture for at least one week and characterized. The
IPN samples containing linear PMMA were pre-
pared by adding the linear PMMA to the initial
mixture and polymerized in the aforementioned
manner.

The samples were coded as follows: the letter
denotes the component (PEA for linear PEA,
PMMA for linear PMMA, MMA for crosslinked
PMMA), and the number immediately following
the letter denotes the weight percent of each com-
ponent. The last two numbers stand for the
mole percent of crosslinking agent added and
the synthesizing temperature, respectively. Some
of the samples were annealed for 10 min at
180°C to examine the stability of morphology ob-
tained.

The dynamic mechanical properties were char-
acterized by the dynamic mechanical thermal ana-
lyzer (DMTA), Polymer Laboratories. Samples
were run at a single cantilever bending mode with
a strain amplitude of 32 μm. Measurements were

carried out from −50 to 180°C with a heating rate
of 2°C/min.

Transmission electron microscopic observations
were performed on thin sections of sample, which
were cut with an ultramicrotome equipped with a
cryogenic cooling unit. The samples were exposed
to osmiumtetroxide vapor at room temperature for
3 days, during which time they darkened. The
stained specimens were at first exposed to air in a
hood for a day, to evaporate the excess OsO_4 depos-
ited on the surface, and then put in a vacuum des-
iccator for 5 days to expel any unreacted OsO_4. The
samples were cut to a thickness of no more than 600
Å and examined with a JEOL TEM 200CX electron
microscope.

Scanning electron microscopy (Hitachi S-570)
was used to examine the fracture surfaces of
specimens. To prepare specimens for the SEM,
the fracture surface was bonded to a specimen
stub and was subsequently coated with a thin
layer of gold. To obtain the controlled fracture
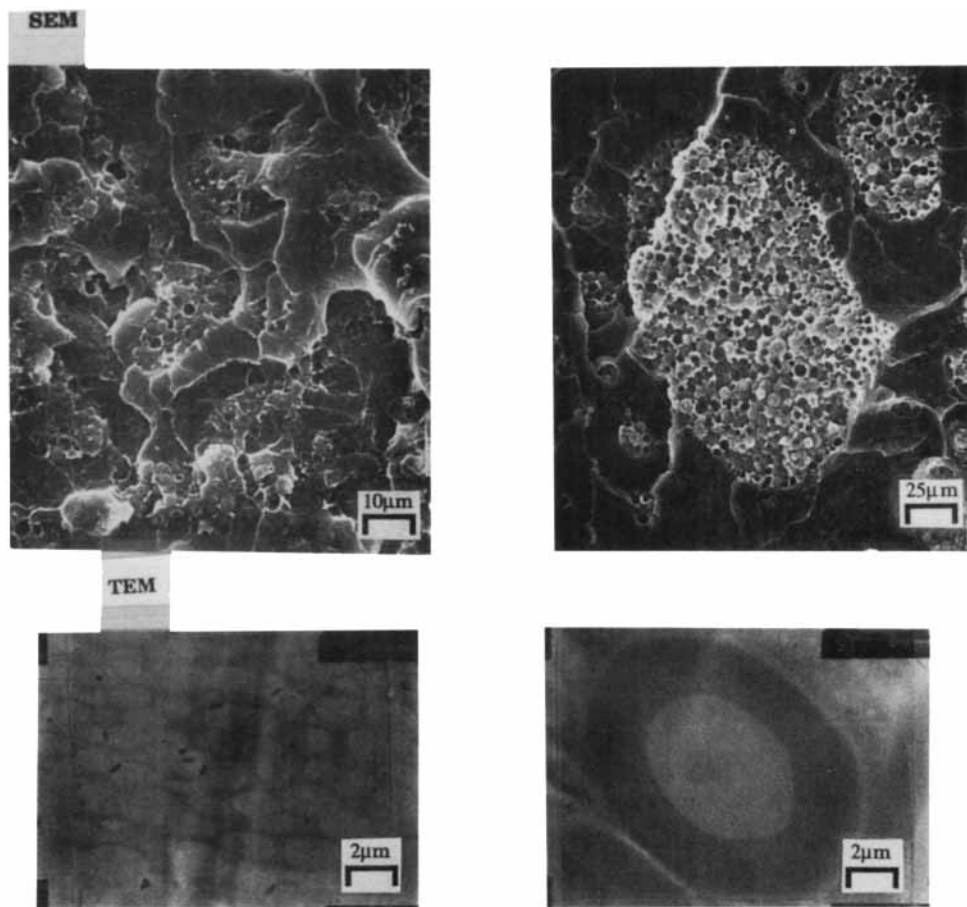surface, all specimens were fractured by the

Figure 5 Effect of linear PMMA addition on morphology of PEA/PMMA semi-IPNs.
Left: PEA/10-MMA/90-1-0°C; right: PEA/10-PMMA/10-MMA/80-1-0°C.

Universal Testing Machine with a fixed strain rate.

RESULTS AND DISCUSSION

Effect of Photopolymerization Temperature

The dynamic mechanical properties of semi-IPNs synthesized under different polymerization temperatures are shown in Figure 1, in which two transition regions are observed. The one at the high temperature corresponds to the crosslinked PMMA, while the one at the low temperature reflects the characteristics of PEA. The shape of the peak representing the PEA-rich phase appears as a broad shoulder and the position of the peak is well above the linear PEA itself (around −20°C), suggesting that considerable phase mixing occurs between PEA and PMMA. The sample prepared at 0°C shows that the peak representing the PEA-rich phase is around 80°C; on the contrary, the corresponding peak is shifted down to around 0°C for the sample prepared at 40°C, indicating the better apparent miscibility in the former sample. To verify that this peak represents the characteristics of PEA, the amount of linear PEA was increased to 15% (Fig. 2). Then the peak became more pronounced while maintaining its shape, confirming that this transition is related to the PEA-rich phase. The cause of such a shift might be viewed in several ways. When the polymerization temperature is lowered, the mobility of polymer chains is reduced due to increased viscosity and the progress of phase separation is hampered by shifting the vitrification point of the system toward a lower conversion. However, since the polymerization/crosslinking rate of MMA is also affected by the temperature sensitivity of photoinitiator, the final morphology of IPNs would be determined by the dynamic balance of those factors. It was pointed out that the degree of phase separation is a function of the reaction rate.[11]
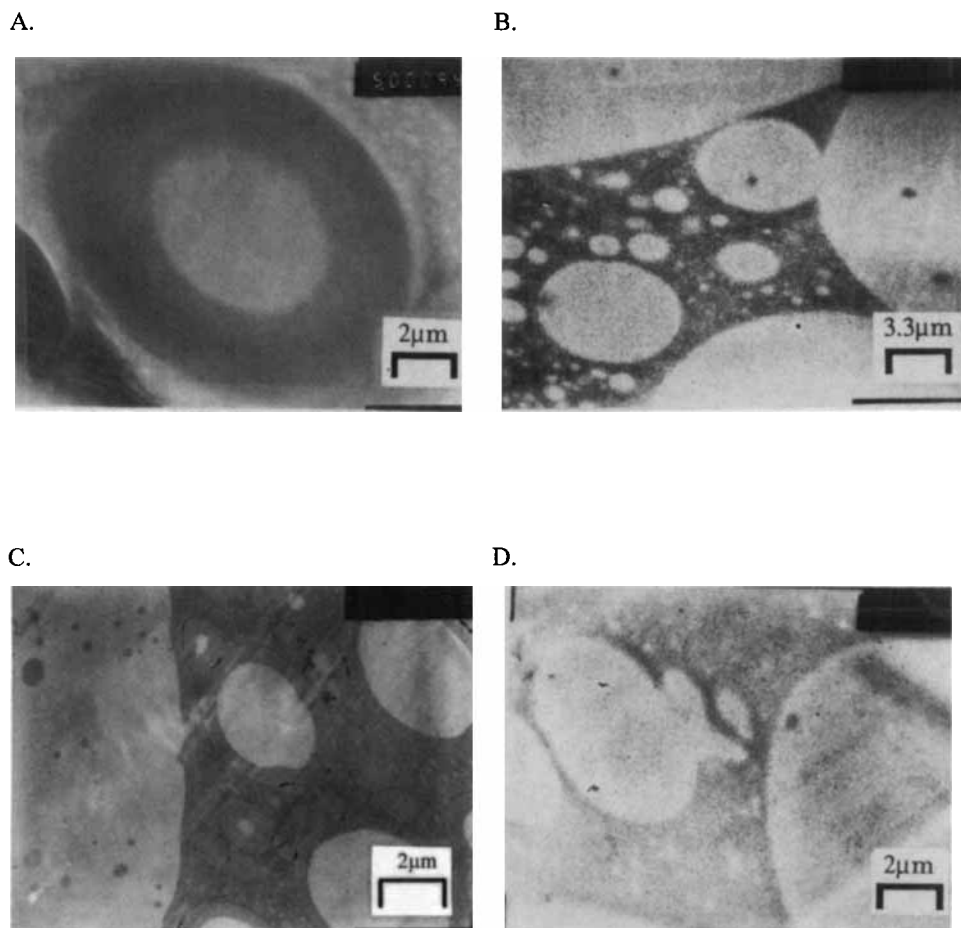
A.

B.

C.

D.

Figure 6 Comparison of morphology with different staining scheme in PEA/10-PMMA/ 10-MMA/80-1-0°C sample. (a) Both linear PEA and linear PMMA stained; (b) unstained; (c) linear PEA stained; (d) linear PMMA stained.

If the degrees of conversion are the same, the time of phase separation is greater for lower reaction temperatures, for which the viscosity of the system is considerably higher. However, the fact that the thermodynamic characteristics of system, such as LCST or UCST, cannot be determined experimentally in this system due to the crosslinked structure of PMMA makes the analysis more complicated.

The apparent decrease of miscibility between components in a 40°C polymerized sample compared to one prepared at 0°C could be also confirmed by comparing the electron micrographs shown in Figure 3. In these photographs, SEM photographs show an aggregated structure composed of small spherical domains. If the aggregate structures are observed by TEM, the white spherical domains mainly composed of PMMA are dispersed in the darkish matrix. Also in the matrix phase, much smaller white domains

are dispersed. When the polymerization temperature is increased from 0 to 40°C, the size of individual spherical domains is almost doubled.

However, the change in morphology cannot be the sole explanation of such a significant shift of transition reflecting PEA characteristics. Considering that there is an early report[6] indicating partial miscibility in the PEA/PMMA pair, the semicompatible nature of the PEA/PMMA pair as well as kinetic factors involved in the sample preparation process seem to play a role in determining the final morphology and dynamic mechanical properties.

Effect of the Third Component Addition

In Figure 4, the effect of adding linear PMMA to the initial mixture of IPN is examined by dynamic mechanical spectroscopy. Both samples are syn-
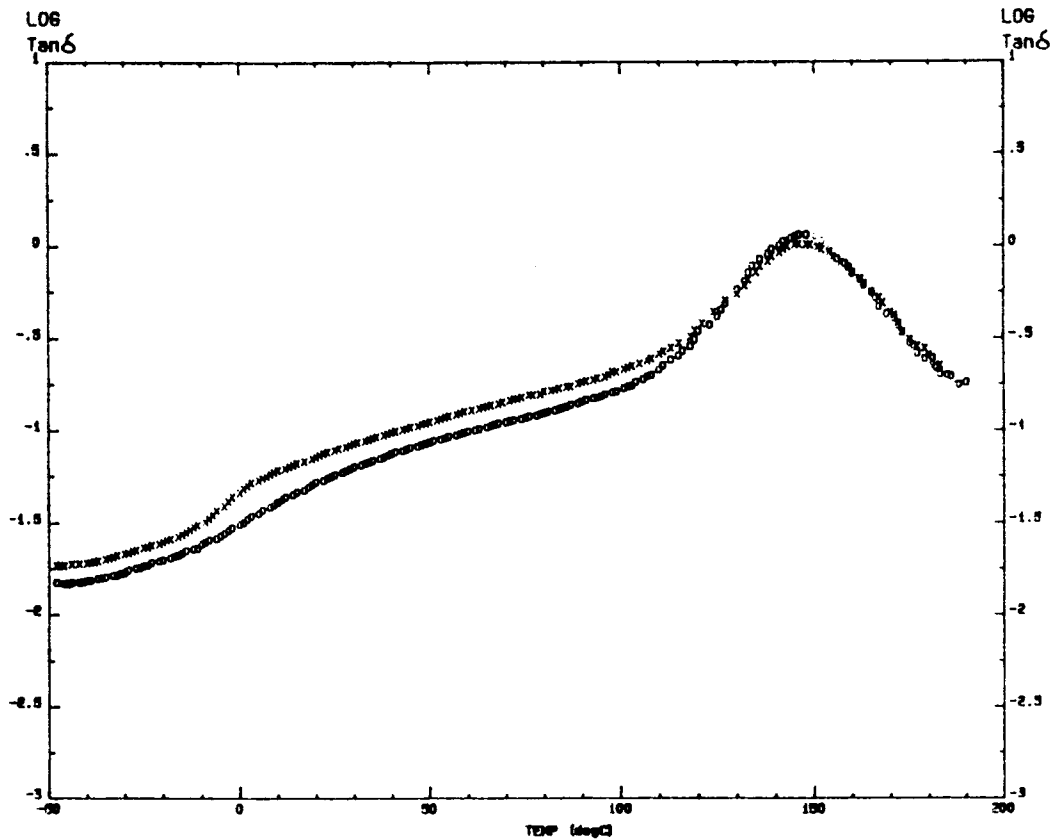
Figure 7 Effect of synthesis temperature on dynamic mechanical behavior of linear PMMA added PEA/PMMA semi-IPNs. xxx: PEA/10-PMMA/10-MMA/80-2-40°C; ooo: PEA/10-PMMA/10-MMA/80-2-0°C.

thesized at the same temperature, 0°C. The sample without linear PMMA shows the peak representing the PEA-rich phase at around 70°C, while the addition of linear PMMA shifts the corresponding peak at least 60 degrees toward a lower temperature. In this case, the kinetic aspects of phase separation cannot be an appropriate explanation because the phase separation may be further constrained due to increased viscosity by addition of linear PMMA to the initial mixture. It is reasonable that the presence of high molecular weight linear PMMA in the early stage of polymerization shifts the onset of the phase separation toward lower conversion.

Figure 5 contrasts the morphological differences between two samples. The addition of linear PMMA turns out to affect the morphology significantly; the spherical domains are more extensively aggregated in the SEM observation and the size of the individual spherical domains becomes larger in the case of adding linear PMMA compared to not adding it in the TEM microphoto-

graphs. The TEM microphotographs reveal interesting features. For example, the linear PMMA added sample shows the darkish shell phase around the spherical domains. In the current sample, since both linear PEA and linear PMMA are stained, the shell may be composed of either linear PEA or linear PMMA. To verify this point, the separate TEM observation was performed on the samples with different staining schemes. In Figure 6, there are four microphotographs. The one at the top is the sample with both linear PEA and linear PMMA stained showing the darkish shell phase. The second from the top is the one without staining. Since the glass transition temperature of the two components is different enough, the morphology could be observed without staining, and there is no shell structure observed. However, if the linear PEA is exclusively stained as in the photograph third from the top, the darkish shell structure appears and the thickness of the shell is different depending on the size of spherical domains. On the other hand, there is no such darkish
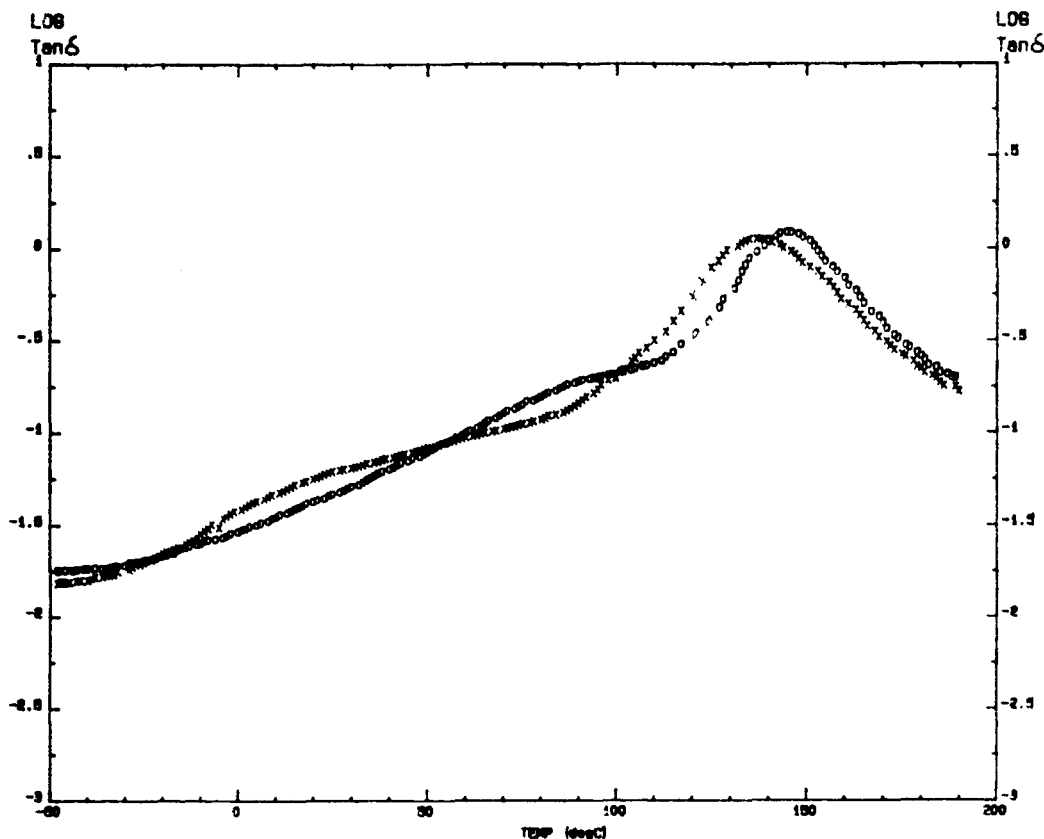
Figure 8 Effect of annealing on dynamic mechanical behavior of PEA/PMMA semi-IPNs. xxx: PEA/10-MMA/90-1-0°C (after annealing); ooo: PEA/10-MMA/90-1-0°C (before annealing).

shell observed if the linear PMMA is exclusively stained, as in the microphotographs at the bottom. Based on these observations, it seems that the spherical domains are the PMMA-rich phase containing a certain amount of PEA in the miscible state, and the darkish shell is the result of understaining due to the high glass transition temperature of the PMMA-rich phase. In addition, there is considerable miscibility between PMMA and PEA.

If the effect of polymerization temperature is evaluated with linear PMMA added to the semi-IPN system, as shown in Figure 7, the change in synthesis temperature does not affect the dynamic mechanical behavior. Therefore, it could be said that the effect of linear PMMA addition at the early stage overrides the change of polymerization temperature.

Effect of Thermal History

It was found incidentally that the second running of DMTA shows considerable difference from the first run, indicating the possibility of the thermal history dependency of the current sample. When the sample, PEA/10-MMA/90-1-0, is annealed for 10 min at 180°C, it is found that the transition of the PEA characteristic observed around 70°C disappears and shifts to a lower temperature in the dynamic mechanical spectra, as shown in Figure 8. When the morphology is compared with SEM and TEM before and after the annealing (Fig. 9), the spherical domains become more aggregated and larger as a result of the annealing, indicating that the kinetically controlled morphology is not at its equilibrium state.

Recently, the phase stability of weakly cross-linked polymer networks has been theoretically investigated,[12] and the effect of crosslinking on the phase boundary of a polymer blend was examined by addition of the contribution of the elastic terms. The prediction that the sequentially formed networks are comparatively less stable than the simultaneous crosslinked ones seems to be borne out by experiments.[2,13]

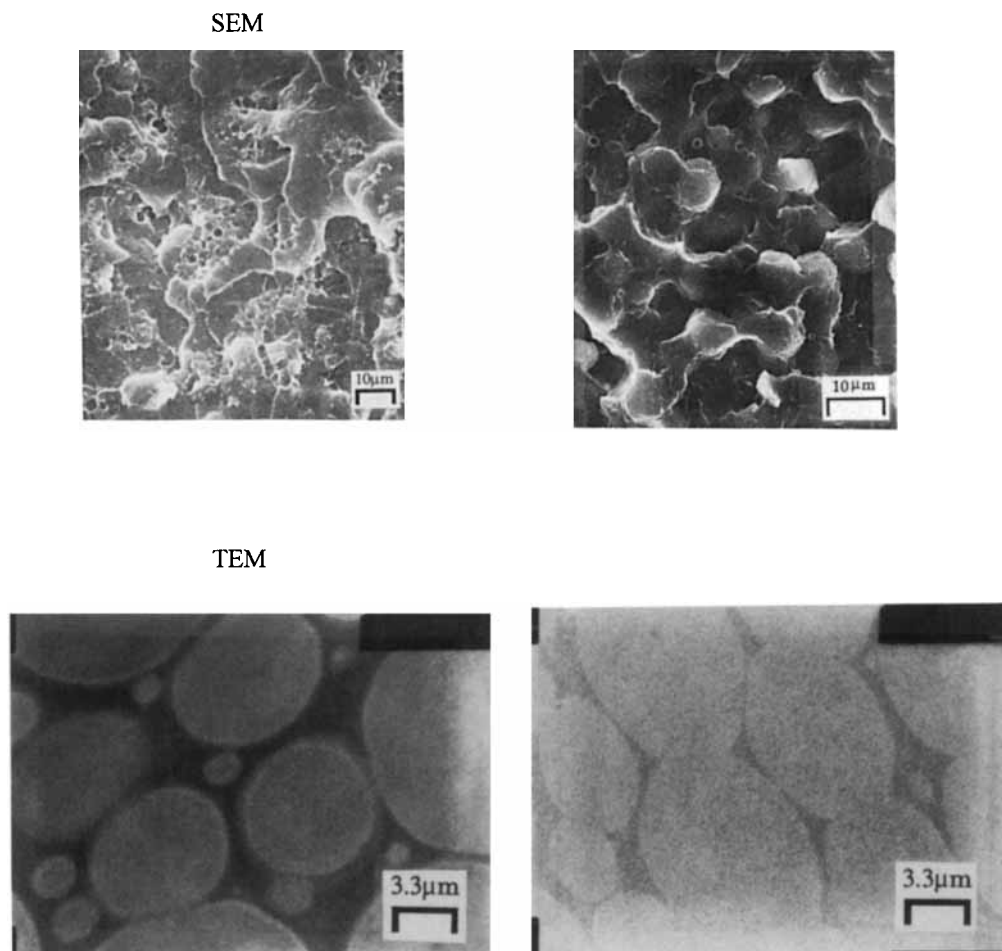SEM

TEM

Figure 9   Effect of annealing on morphology. Left: PEA/10-MMA/90-1-0°C (before annealing); right: PEA/10-MMA/90-1-0°C (after annealing).

CONCLUSIONS

It has been demonstrated that the morphology of the semi-IPNs composed of linear PEA and cross-linked PMMA can be modified by changing various synthetic conditions, based on characterization by DMTA, SEM, and TEM. When the synthesizing temperature is changed from 0°C to 40°C, the relative decrease of the miscibility between components is observed in terms of dynamic mechanical properties and morphology. The addition of linear PMMA to the initial mixture was found to facilitate phase separation during IPN formation by shifting the onset of the phase separation toward lower conversion. However, it was found that the phase separation was further induced by annealing, indicating that kinetically controlled morphology was not at its equilibrium state.

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