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Phase behaviour and phase separation in polymer blends of poly(methyl methacrylate) with poly(vinyl acetate)

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Summary

Phase behaviour and phase separation in a binary polymer blends of poly(methyl methacryate)(PMMA)with poly(vinyl acetate) (PVAc) was invistigated by cloud method and light scattering. A lower critical solution temperature(LCST)type phase diagram was found.The mixture system of PMMA/PVAc is miscible.Kinetic study on demixing at the two-phase region above the LCST was carried out by light scattering.

Introduction

Generally,the miscible mixtures tend to phase separation at elevated temperatures. The LCST behaviour is typical for miscible polymer blends.Some miscible polymers also exhibit phase separation at low temperature(1).In this brief report,we present the miscibility and phase separation of PMMA with PVAc blends.

Experimental

PMMA(Mw=1.98x10^5,Mw/Mn=2.5)and PVAc(Mw=2.6x10^6,Mw/Mn=3.2) were commercial.Blends were prepared by solution casting a common solvent.The polymers in various proportions were dissolved to a total of 3 wt% in chloroform.Solution was cast onto a cover glass for microscopy and light scattering.Solvent was allowed to evaporate slowly at 30°C.The blends were dried under vacum at 80°C for 72h.

The blend film on the cover glass was on a hot plane and

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*To whom correspondence should be addressed was annealed with a rate 5°C/min.When the film became opaque, we judged that the blend was in the two-phase region in the phase diagram.

Isothermal experiments were carried out in a hot chamber set in a light scattering photometer.The intensity of the scattered light of spinodal decomposition was given.

Results and Discussion

All of the solution cast films of PMMA /PVAc blends with different composition were optically clear.Even after annealing for 24h at 110°C,they were transparent and no indication of phase separation was seen under an optical microscope. These results imply that PMMA is miscible with PVAC at any composition.

Figure 1 is the phase diagram of PMMA with PVAc blends. Solid cure is binodal line and open point is spinodal one , respectively.The spinodal point was determined dynamically by using time-resolved light scattering technique(2).It has the critical composition of PMMA ϕ_c and critical temperature T_c as given by

$$\phi_c = 0.55$$
$$T_c = 146^\circ C$$

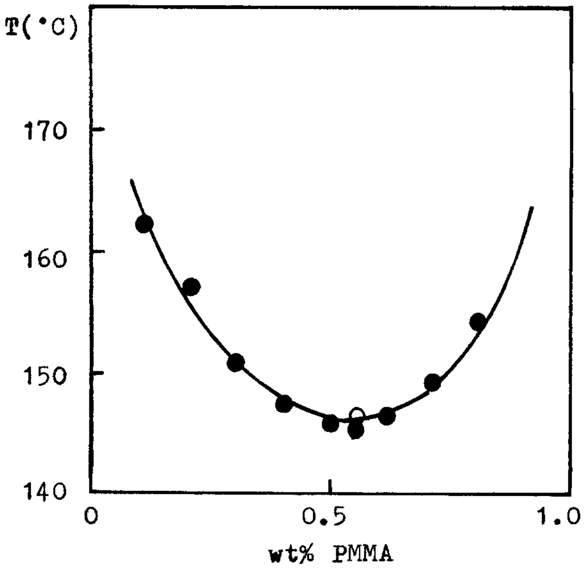

Fig.1.Phase diagram of PMMA with PVAc blends.

Figure 2 shows the change of light scattering profile with time after the temperature jump-up from the single phase region(30°C) to the two-phase region(180.6°C).The scattering peak is due to the periodic structure developed by demixing.

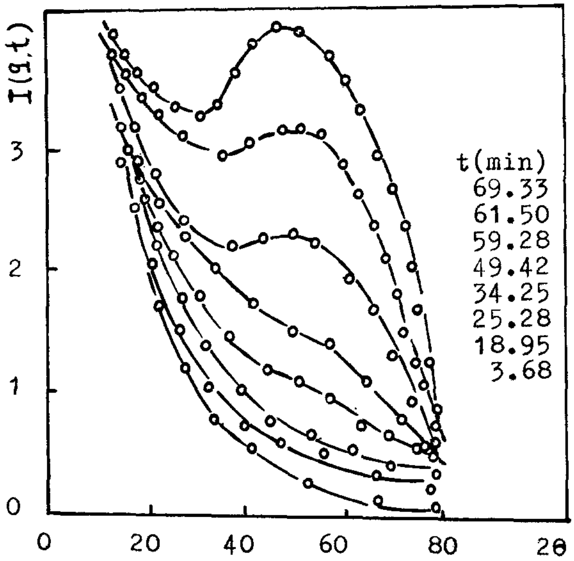

Fig.2.Change of light intensity profiles of PMMA/PVAc(55/45) with time at various scattering angles at 180°C.

The relative intensity distribution at various times were plotted as a function of the scattering angle 2θ.The peak position shifts to smaller angles with annealing time t. The increases of scattered intensity with time is believed to be a consequence of phase separation to a spinodal decomposition mechanism.

The linearized Cahn's theory for spinodal decomposition(3) predicts that the scattered intensity I(q,t) as a function of wave vector q and time t is described in terms of a growth rate R(q) as

$$I(q,t) = I(q,0)\exp(2R(q)t) \quad \ldots\ldots\ldots\ldots(1)$$

$$R(q) = -Mq^2(d^2f/d\phi^2 + 2Kq^2) \quad \ldots\ldots\ldots\ldots(2)$$

Where M is the mobility,i.e.,the Onsager coefficient,f the free energy density,and ϕ the concentration in volume fraction and K the coefficient of gradient term.Figure 3 shows the plots of lnI(q,t) vs.time t at fixed wave vector q.It reveals that in the early stage of phase separation the evolution time of scattered light intensity I(q,t)is of an exponential growth.This result is compared with Cahn's theory.

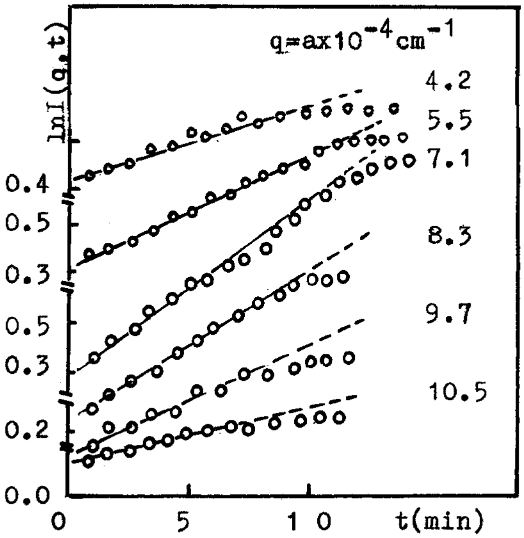

Fig.3.Change of scattered intensity at various q with time at 180.6°C.

Cahn's theory predicted that there exist a maximum R(qm) for the growth rate R(q) which characterizes the growth behaviour.It implies that the growth rate R(q) increases with q at small q range and decreases at large q range, and there exists a maximum R(qm) at qm.In order to approach the problem the experiments were done with extending wave vector q range. The results were shown in Figure 4.The maximum R(qm) was

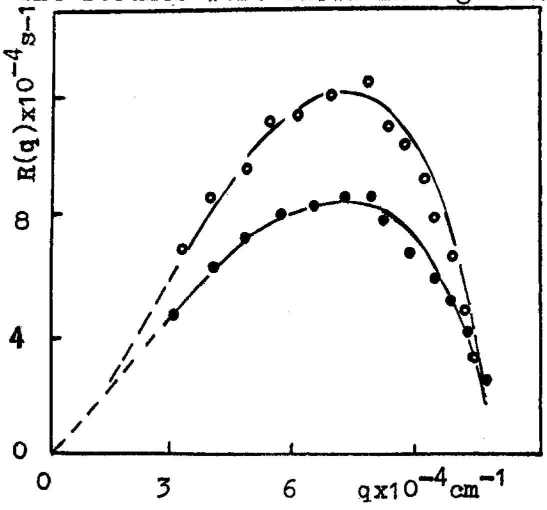

Fig.4.Variation of R(q) with q at different temperatures(● 174.5°C,o 180.6°C).

obtained with light scattering.

Figure 5 shows plot of $R(q)/q^2$ vs. q^2 based on Cahn's theory. A fairly good linear relationship was experimentally obtained, but some deviation are seen in small q range. Except for in the small q range, the early stage of spinodal decomposition for the mixture under investigation can be described by the linear spinodal decomposition theory well. From the plots one can estimate the apparent diffusion coefficient D_{app} from the intercept of $R(q)/q^2$ at q=0, as following

$$D_{app} \sim 10^{-13} cm^2 s^{-1}$$

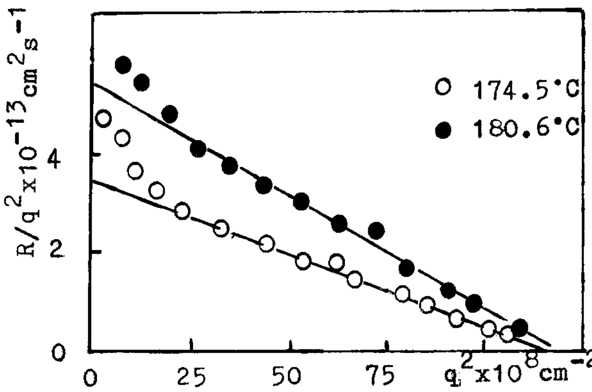

Fig.5. $R(q)/q^2$ vs. q^2 for different temperatures.

The shape of the scattering function $S(q,t)$ ($S(q,t) \sim I(q,t)$) has been analyzed in accordance with the recent scaling law of Furukawa(4). The self-similarity in the microdomain structure in the late stage demands the scaling law for the structure function $S(q,t)$

$$S(q,t)=qm^{-d}\tilde{S}(q/qm) \quad \text{..............(3)}$$

where $\tilde{S}(X)$ is a universal function independent of t. Furukawa (4) proposed the following formula for $\tilde{S}(X)$:

$$\tilde{S}(X)=(1+y/2)X^2/(y/2+X^{2+y}) \quad \text{...........(4)}$$

For the critical composition, y=2d and off-critical composition y=1+d with d being the dimensionality of growth.The shape of the scattered intensity is predicted as $S(q<qm)\sim q^2$ and $S(q>qm) \sim q^{-y}$.For 3-dimensional growth,y is equal to 6 for the critical composition and 4 for off-critical mixtures.Figure 6 shows the log-log polts of scattered intensity versus q for the 45 wt% PVAc mixture.The value of y is approximately 6 ($q > qm$) . Suggesting that the spinodal decomposition process of 45 wt% PVAc is reminiscent of the behaviour of critical mixtures.

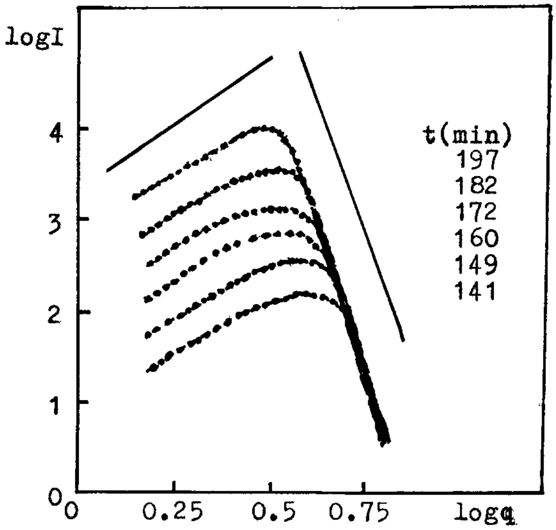

Fig.6.Scaling test with Furukawa theory.

Figure 7 shows the scaled structure factor $\tilde{S}(X)$ determined for the unmixing of critical mixture at 180.6°C for various unmixing time t.The time region where $\tilde{S}(X)$ depends on time is shown in Figure 7(a) and the scaled region where $\tilde{S}(X)$ is independent of time is shown in Figure 7(b).The result predicts that the scaled structure factor can be constructed and the dynamical scaling is found to exist in the late stage of the spinodal decomposition and compare with Furukawa's theory(4). In Figure 7 the theoretical scaled structure factor is shown by the solid line.The scaling law of structure function given by Eq.(3) with d=3 is satisfied for the critical concentration at the late stage of the spinodal decomposition.Hashimoto(5) has also obtained the similar result studing demixing process in a binary polymer blends of PS/PVME.

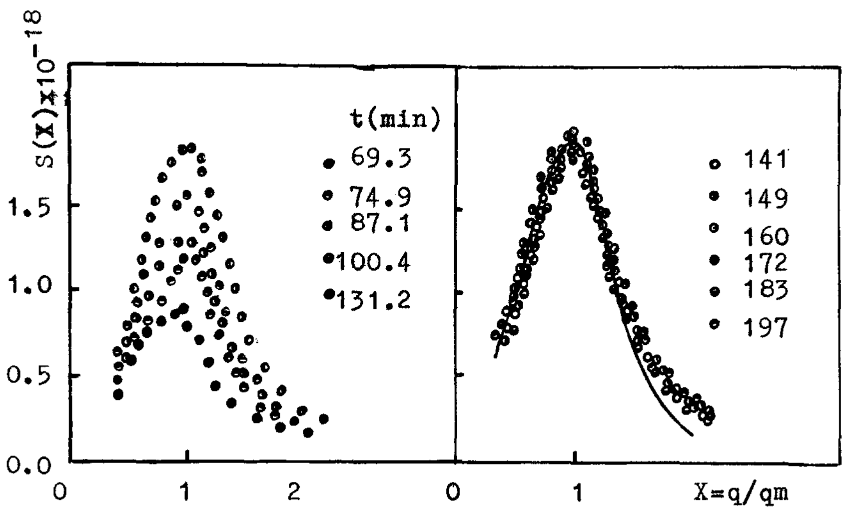

Fig.7.Variation of $\tilde{S}(X)$ determined with unmixing time t for critical mixture at 180.6°C.

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