

UNMIXING KINETICS AND ITS MORPHOLOGY OF POLY (ETHYLENE OXIDE) WITH POLYETHERSULPHONES BLENDS

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ABSTRACT

Unmixing kinetics in a binary polymer mixture of polyethersulphones with poly (ethylene oxide) by spinodal decomposition has been investigated with time-resolved light scattering and microscope methods. The results showed that time evolution of scattered light intensity is of an exponential growth. The maximum growth rate $R(q_m)$ of phase separation has been obtained. The experimental data did not satisfy the condition that the plot of $R(q)/q^2$ vs q^2 should be linear. For unmixing system annealing at 30 °C for three hours, its morphology manifested dish structure. The experimental data of the Bragg spacing D_m can be correlated with a straight line which expresses the power-law relation, $D_m = b\tau^c$.

INTRODUCTION

The kinetics of the phase separation in a polymer blends quenched into the miscibility gap is the subject of many theoretical and experimental investigations^[1]. The study of unmixing processing is important from a practical view for designing the structure and properties of the polymer materials.

Generally phase separation of polymer mixtures can usually be classified into two types: liquid-liquid phase separation where the concentration is the order parameter, and solid-solid phase accompanying by the crystallization. In the field of phase separation, the liquid-liquid phase separation by spinodal decomposition was studied mostly.

Concerning theoretical studies, an attempt was first made by van Artsen^[2] to apply the linearized Cahn-Hilliard theory for the spinodal decomposition^[3] to polymer solution. The theory predicted that as a function of wave vector q and time t the scattered light intensity $I(q, t)$ is described in terms of a growth rate $R(q)$ as follows,

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

$$R(q) = -Mq^2(\partial^2 f / \partial \Phi^2) + 2Kq^4 \quad (2)$$

where M is the mobility, f the free energy density, and Φ the concentration in volume fraction and K the coefficient of gradient term.

In most of the studies, light scattering techniques were used and the data analysed by Cahn-Hilliard theory in the early stage. However almost no experimental data can satisfy the condition that the growth rate $R(q)$ as a function of wave vector q shows a maximum and the plot $R(q)/q^2$ vs. q^2 should be linear. To our knowledge the results obtained by Nose^[4] show the best agreement with the Cahn-Hilliard theory but still the q_m -value obtained by the plot of $R(q)/q^2$ vs. q^2 seems not quite reasonable.

The miscibility of polyethersulphones (PES) with poly (ethylene oxide) (PEO) was first reported by Walsh^[5] who observed features which suggested lower critical solution temperature behaviour (LUST). In this paper we have obtained phase boundaries of

PEO/PES of different molecular weights using microscopic method. The unmixing behaviour by the spinodal decomposition was observed at several temperatures. The morphology of the samples annealing at 30 °C for unmixing system was reported.

EXPERIMENTAL

The polyethersulphone was kindly supplied by Jilin University. It has a quoted reduced viscosity of 0.39 dl/g as a 1% solution in DMF at 27 °C. PEO was produced by Beijing Chemical Factory with quoted molecular weights of 6000, 20000 and 200,000, respectively. PES and PEO samples were dried before use.

A series of PEO/PES was prepared by dissolving in DMF at room temperature to form 5 wt% solution. Blends were prepared by evaporation of solvent from the mixed solution on a cover glass at 60 °C in a vacuum oven for microscope and light scattering observation.

The laser light scattering apparatus used in the study records the changes of the scattered intensity with time during phase separation coupled with a temperature-jump procedure. A plane-polarized laser beam (He-Ne laser of 2 mw, and $\lambda = 632.8$ nm) was used as an incident source. Temperature was controlled with an accuracy of ± 0.2 °C. The scattered intensity was recorded by mechanical mapping recorder.

The cloud points were determined using an optical microscope fitted with a hot stage. Observations were made at a heating rate of 4K/min.

RESULTS AND DISCUSSION

The cloud point curves are shown in Figure 1. With the increase in molecular weight of PEO in the sample decreases correspondingly the cloud point temperature. The minimum of the cloud point on the curves appears close to a 70:30 = PEO:PES ratio. The result was different from Walsh's report⁹.

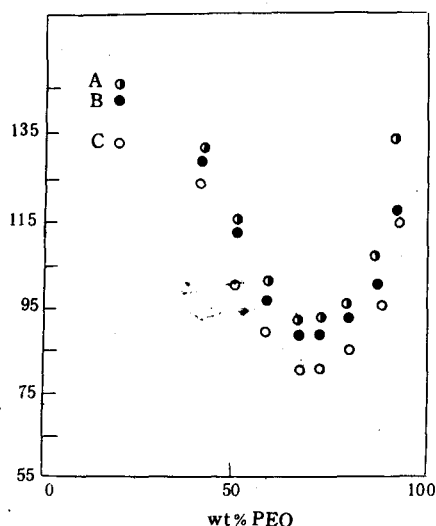


Fig 1 The cloud point curves against composition for PES blends with PEO of molecular weights (A) 6000, (B) 20000, (C) 200000

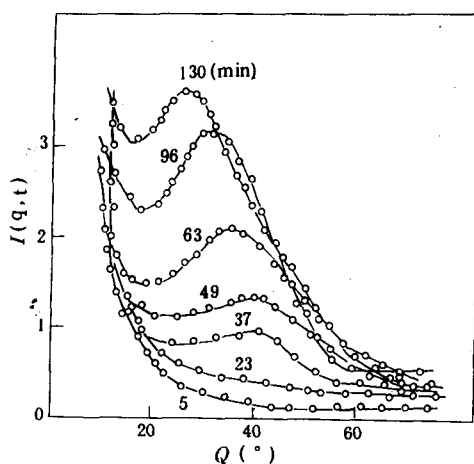


Fig 2 Time-evolution of light scattering profiles during isothermal phase separation at 97 °C for 70:30 PEO/PES blend

The dynamics of the phase separation process was investigated by using the time-resolved light scattering technique. Typical changes of the scattered intensity at various q 's with time for 30 wt% of PES mixture quenched from 20 °C to 97 °C (PEO: 20000) was shown in Figure 2. When the blend undergoes phase separation a clear scattering maximum develops at a particular angle. As phase separation proceeds further the scattering maximum shifts to lower scattering angle corresponding to phase growth. Meanwhile the scattered intensity increases dramatically with demixing time. Time increase of scattered light intensity with time is believed to be a consequence of phase separation according to a spinodal decomposition mechanism.

As the unmixing progresses with the time, the scattered intensity level increases, and the scattering maximum appears at the scattering vector q about $8.0 \times 10^{-3} \text{ nm}^{-1}$ some 35 min after homogenization. Figure 3 shows the scattered intensity change with time at various scattering vectors, where the relatively intensity is plotted in logarithmic scale. It is clearly seen that the scattered intensity exponentially increases with time t in the early stage of the spinodal decomposition. The isothermal unmixing process suggests that the phase separation process in the early stage may be described in the context of the linearized theory of the spinodal decomposition.

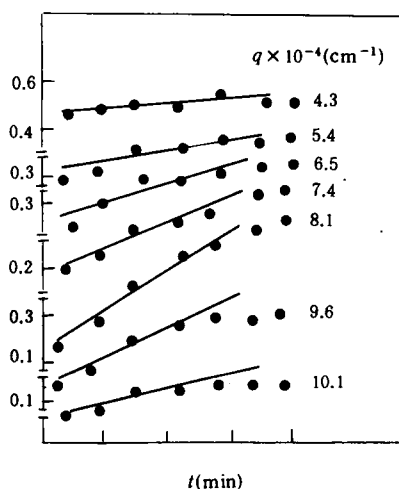


Fig. 3 Changes of scattered intensity at various q 's with time at 97 °C for 70:30 = PEO:PES blend

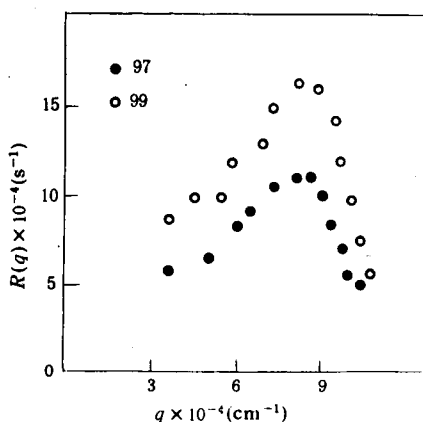


Fig. 4 Variation of $R(q)$ with q at different temperatures (○ 97 °C, ● 99 °C)

Cahn-Hilliard theory predicts that there exists maximum $R(q_m)$ for the growth rate $R(q)$ which characterizes the growth behavior. The maximum $R(q_m)$ was obtained with light scattering technique as shown in Figure 4.

Figure 5 shows the plot of $R(q)/q^2$ vs. q^2 based on Cahn-Hilliard theory. The result shows that the experimental data did not satisfy the condition that the plot of $R(q)/q^2$ vs. q^2 should be linear. Generally, the dynamical equation of phase separation includes linearization term and non-linearization term. Cahn-Hilliard theory only considered the linearization term. In fact in the process there exists the effect of non-linearization on the dynamics.

The phase structure of the spinodal decomposition was confirmed by optical microscope. Figure 6 shows the morphology of the sample of PEO:PES = 70:30 at 120 °C for

21 min (a) and 27 min (b) The development of the separated structure can be clearly seen.

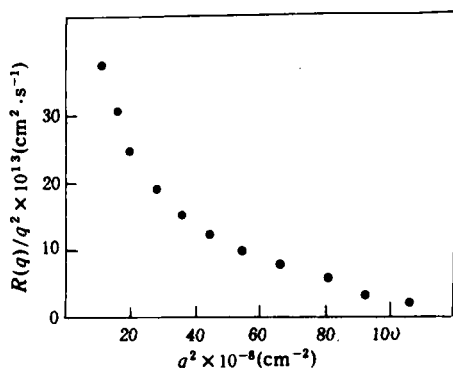


Fig 5 $R(q)/q^2$ vs q^2 at 97 °C in the early stage of phase separation

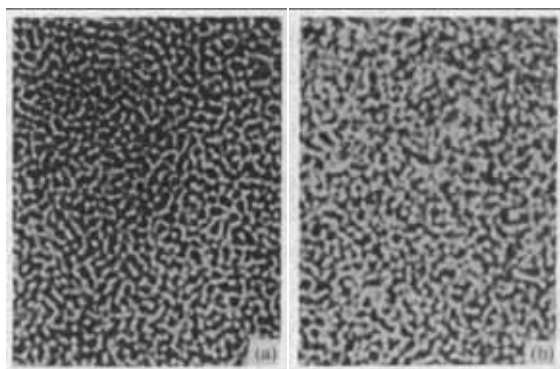


Fig 6 Optical microscope picture of PEO:PES= 70:30 at 120 °C for 21 min (a) and 27 min (b), respectively

For the samples unmixed for 30 min at 120 °C and annealed to 30 °C for three hours the morphology of the samples is shown in Figure 7, where a, b and c, d are crossed polar and optical micrographs, respectively. These micrographs clearly show that the dish structure was formed and the modulated structure disappeared which originated from the spinodal decomposition. The dish structure may result from modulated structure.

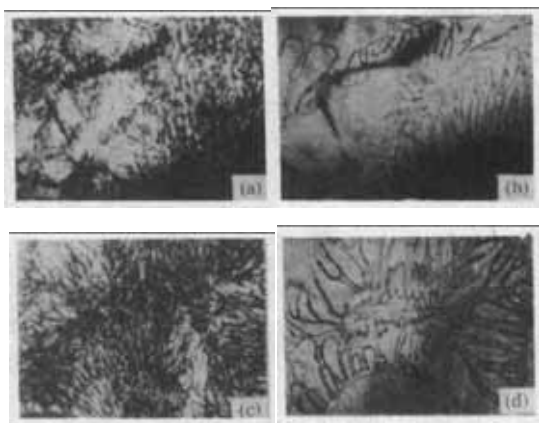


Fig 7 The crossed polar and optical micrographs for the sample (70:30=PEO:PES) unmixed for 30 min at 120 °C and annealed at 30 °C for three hours, respectively

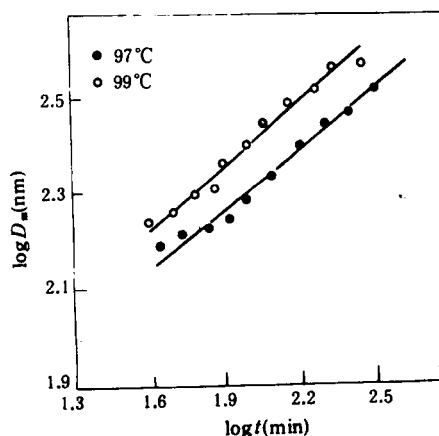


Fig 8 Time dependence of correlation length

Figure 8 represents the different logarithmic plots of average domain sizes against time t at different temperatures. The experimental data can be correlated with a straight line which expresses the power-law relation, $D_m \sim t^\alpha$.

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