

Note

APPLICATION OF TIME-TEMPERATURE SUPERPOSITION PRINCIPLE TO EVALUATION OF SCATTERING INTENSITY EVOLUTION IN PHASE SEPARATION FOR PMMA/SAN BLENDS*

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Abstract Spinodal phase separation behavior of poly(methyl methacrylate)/poly(styrene-co-acrylonitrile) (PMMA/SAN) blends was investigated by the time-resolved small angle light scattering (SALS) technique. It was found that the influence of temperature on the scattering intensity evolution followed the time-temperature superposition principle. The relationship between temperature and the relaxation time of scattering intensity $I(t)$ can be well described by the Williams-Landel-Ferry (WLF) function.

Keywords Spinodal decomposition mechanism, Small angle light scattering, Time-temperature superposition principle

INTRODUCTION

Thermally induced phase separation of low critical solution temperature (LCST) type polymer blends has attracted extensive attention because of its great significance in optimizing the mechanical properties of polymer blends. In case the polymer pairs have enough difference in refractive index, the small angle light scattering (SALS) technique is available for determining the weak concentration fluctuation at the very early stage of phase separation. Hence, in the 1980's, SALS was introduced into the study of thermally induced phase separation kinetics of LCST-type polymer blends. It has been found that the phase separation of most LCST-type polymer blends follows the spinodal decomposition (SD) mechanism in the unstable temperature region and the linearized Chan-Hilliard theory can successfully describe the intensity evolution in early stage SD^[1, 2]. However, the influence of temperature on the phase separation behavior of LCST-type polymer blends has not been entirely elucidated to date. Recently we found experimentally that the time-temperature principle is applicable in describing the scattering intensity evolution during SD of some polymer blends. In this paper, poly(methyl methacrylate)/poly(styrene-co-acrylonitrile) (PMMA/SAN) was selected as a model to study the influence of temperature on the phase separation behavior of LCST type polymer blends.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) ($M_n = 8 \times 10^4$, $M_w/M_n = 2.1$) and poly(styrene-co-acrylonitrile) (SAN) ($M_n = 4.5 \times 10^4$, $M_w/M_n = 2.2$, PN-127H, Qimei Co., Ltd., Taiwan) with AN content of 32 wt% were both available commercially.

PMMA and SAN were dissolved in dichloromethane (CH_2Cl_2) to form a homogeneous solution. The solution was then cast on the surface of microscope slides preheated to 32°C. After the solvent evaporated at ambient environment, the samples were further dried at 80~90°C in a vacuum oven for at least 24 h to ensure that

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no residual solvent exists. The sample films with a thickness of about 40 micrometers were homogeneous and transparent.

Time-Resolved Small Angle Light Scattering (SALS)

A time-resolved SALS apparatus similar to that described in many earlier papers^[2-4] was used in this work. The scattering patterns with a resolution of $540 \times 660 \times 24$ bits were captured in realtime by a Charge Coupling Digital (CCD) camera (MTV-1802CB, MINTRON, Taiwan), then imported into the computer memory at the minimum time interval of 2 s through a video capturing board (VIDEO VESA, Daheng, Beijing). On-line circular averaging of each radially symmetric scattering pattern was performed to obtain the intensity distribution, namely the relationship between intensity and scattering angle. The intensity at the beginning of examination was subtracted from the intensity measured at later time as background to avoid the negative effects of parasitic light, thermal fluctuation in the homogeneous samples and the dark current of the CCD camera. The recording intervals can be changed at the beginning of the experiment according to different phase separation speed, which is determined by the experimental temperature and the compositions of the samples.

The temperature of the hot stage usually returned to equilibrium within 10–40 s after the samples were placed on it, depending on the set temperature. In most cases, the time for temperature recovery is negligible compared with the entire experimental time. The temperature was controlled to within $\pm 0.2^\circ\text{C}$.

RESULTS AND DISCUSSION

The samples used in the experiments exhibited some diversity due to the difference in concentration inhomogeneity and thickness for various samples. Hence, the normalized intensity $I(t)/I_0$ is employed instead of using $I(t)$ directly. I_0 is the initial intensity at the start of experiment. Figure 1 presents the semi-logarithmic plots of $I(t)/I_0$ versus time at $q = 6.0 \mu\text{m}^{-1}$ of isothermal annealing experiments at different temperatures. It is noted that the plots of $I(t)/I_0$ versus time for different temperatures are nearly parallel to each other, indicating that they can superpose with each other and form a master curve by horizontal shifting, namely, the time-temperature superposition principle can be applied in this case.

The glass transition temperature T_g of PMMA/SAN (60/40) obtained from dynamic mechanical analysis (DMA) measurement is about 110°C . Therefore, we set 160°C as the reference temperature T_r , being about 50°C higher than the T_g . Then the logarithmic shifting factor, $\lg \alpha_T = \lg(\tau/\tau_r)$, can be calculated from Fig. 1, in which τ is the relaxation time defined as the onset time at which the scattering intensity starts a sharp ascent as shown in Fig. 2, τ_r is the relaxation time at the reference temperature. Figure 2 presents the plots of shifting factor α_T versus temperature. It is interesting that α_T decreases almost exponentially with temperature, similar to that of the well-known viscoelastic behavior that follows the time-temperature superposition behavior. The inset of Fig. 2 presents the perfect linearity relationship described through the plots of $1/\lg \alpha_T$ versus $1/(T - T_r)$. Thus, we can obtain the WLF-like function:

$$\lg \alpha_T = \lg \frac{\tau}{\tau_r} = \frac{-C_1(T - T_r)}{C_2 + T - T_r} \quad (1)$$

in which the constants C_1 and C_2 are 8.76 and 135.8, respectively. It is interesting that the values of C_1 and C_2 are close to the empirical constants, 8.86, 101.6 of the universal WLF function for polymer melt viscosity, respectively, at the reference temperature of 50 K higher than T_g . This indicates that the phase separation behavior of PMMA/SAN blends also follows the time-temperature superposition principle. It should be pointed out that Eq. (1) is also valid for other scattering vectors within the observation temperature range with almost the same C_1 and C_2 values, meaning that Eq. (1) can be applied universally to all scattering vectors.

We are very interested in the phase separation behavior of PMMA/SAN (60/40) at lower temperatures. The τ over a very wide temperature range can be calculated by using Eq. (1). It was found that the τ values increased rapidly as the temperature decreased. For example, at 145°C , about one week is required to observe obvious scattering pattern. To confirm the validity of Eq. (1), we performed the experiment at 145°C , 150°C and 155°C ,

respectively and obtained the corresponding α_T . As shown by the solid points in Fig. 2, the shifting factors α_T obtained experimentally for 155°C, 150°C and 145°C are in good correspondence with the calculated results. Therefore, function (1) is applicable at least at temperatures higher than 145°C. It should be emphasized that, no detectable thermal degradation and oxidation of PMMA or SAN occurred during the long-term observation at the experimental temperatures.

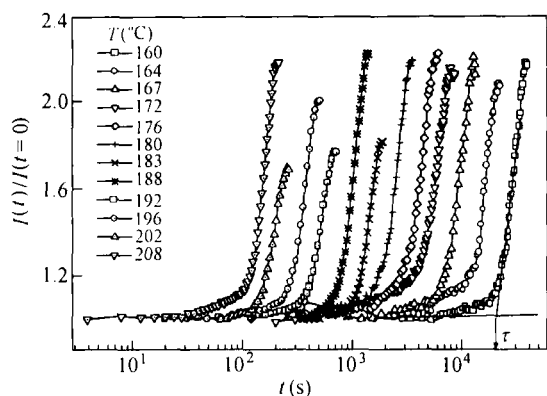


Fig. 1 Evolution of normalized scattering intensity at various temperatures of PMMA/ SAN (60/40) blends

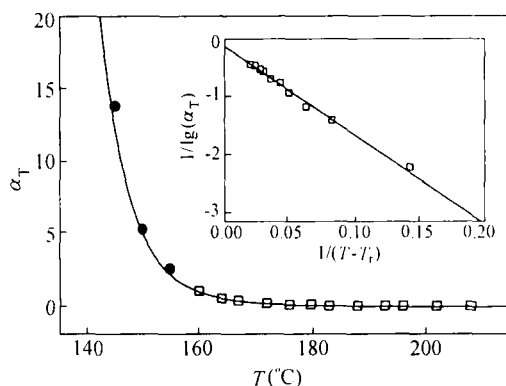


Fig. 2 Relationship between shifting factor α_T and temperature for PMMA/SAN (60/40) blends
The inset presents the plots of $1/\lg \alpha_T$ versus $1/(T - T_g)$

As reported by most literature references^[3-5], the spinodal curves of PMMA/SAN blends are usually 40–80°C higher than the T_g -composition curve, depending on the composition, the molecular weight and AN content of SAN copolymer. However, one can find from the above discussion that the phase diagram of PMMA/SAN is strongly dependent on the observation time. According to the prediction of Eq. (1), phase separation can be observed at temperatures very close to T_g , if the observing time is sufficiently long. Strictly speaking, τ should be infinite at critical SD temperature, namely, at the equilibrium phase separation temperature. It is notable that in Eq. (1), τ approaches infinity only when the experimental temperature approaches $T_g - C_2$. This means that the equilibrium SD temperature may be $T_g - C_2$, about 40 K lower than the T_g in the present system. But unfortunately this conclusion cannot be confirmed directly by experiment due to the overlong experimental time. Furthermore, even if the long-term experiment could be realized, phase separation would not be observed because macromolecular chains are frozen at temperatures under T_g . Therefore, the equilibrium phase separation temperature can not be obtained for the present PMMA/SAN (60/40) blends. However, it is still reasonable to state that the use of time-temperature superposition principle for describing the scattering intensity evolution is of great importance in predicting the phase separation behavior of binary LCST-type polymer blends during thermal annealing and melt mixing over a wider temperature range.

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