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Phase structure development in poly(styrene-*co*-acrylonitrile)/poly(methyl methacrylate) blend under elongational flow

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Abstract

Elongational flow behaviour of a poly(styrene-*co*-acrylonitrile) (SAN)/poly(methyl methacrylate) (PMMA) blend of a near critical composition (~40/60) was examined below and above its lower critical solution temperature $T_s(= 195°\mathrm{C})$ via elongational flow opto-rheometry (EFOR) which enabled us to simultaneously monitor transient tensile stress $\sigma(\dot{\varepsilon}_0; t)$ and birefringence $\Delta n(\dot{\varepsilon}_0; t)$ as a function of time *t*. Thus the stress optical rule (SOR) was tested on the blend below and above T_s. The morphology change with time *t* was examined by ex situ transmission electron microscopy (TEM) and the resulting TEM pictures were subjected to a fast Fourier transform (FFT) analysis.

In the miscible region at 150°C, the stress optical coefficient of the blend C_{Blend} $[\equiv \Delta n(\dot{\varepsilon}_0; t)/\sigma(\dot{\varepsilon}_0; t)]$ was found to be constant ($\cong -1.2 \times 10^{-9}\ Pa^{-1}$) independent either of the strain rate $\dot{\varepsilon}_0$ the Hencky strain $\varepsilon(\equiv \dot{\varepsilon}\cdot t)$ or $\sigma(\dot{\varepsilon}_0; t)$. At 215°C above T_s, however, the sign of C_{blend} changed from negative to positive in the early stage of elongation and the value itself increased as the blend was stretched to a larger extent. Under such a condition the SOR was clearly violated, for which a large contribution of *form* birefringence was responsible due to the highly oriented and elongated domain structure, as revealed by TEM-FFT analysis, of the SAN phase with a large optical anisotropy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: SAN/PMMA blend; Stress optical rule; Form birefringence

1. Introduction

The structural change and phase transition of polymer blends under shear fields have been extensively investigated in both academic and industrial perspective during the past two decades [1]. For some blends, shear-induced mixing was reported, but for some other blends, shear-induced demixing was observed. Poly(styrene-*co*-acrylonitrile) (SAN)/poly(methyl methacrylate) (PMMA) blends [2,3] are an especially interesting system to be studied which exhibits the lower critical solution temperature (LCST)-type phase behaviour and possesses dynamic symmetry [4] due to almost the same high glass transition temperatures T_g of the components. Much published literature data are now available on the blends including the thermodynamics interaction parameter values [5,6] and easy observation of the internal structure is also possible.

In this communication, we report a preliminary result on the effect of transient elongational flow on the phase structure development in a near critical SAN/PMMA blend below and above its critical temperature T_s. We employed elongational flow opto-rheometry (EFOR) [7] and transmission electron microscopy (TEM) combined with fast Fourier transform (FFT) analysis of the TEM pictures. EFOR is a new technique of optical rheometry which enables us to simultaneously monitor transient tensile stress $\sigma(\dot{\varepsilon}_0; t)$ and birefringence $\Delta n(\dot{\varepsilon}_0; t)$ as a function of time *t* for polymeric liquids under constant Hencky strain rate $\dot{\varepsilon}_0$. We discuss here the validity of the stress optical rule (SOR) [7,8] for the SAN/PMMA blend under elongation below and above its T_s, and also discuss the contribution of *form* birefringence $\Delta n_f(\dot{\varepsilon}_0; t)$ due to the phase separated structure with a large optical anisotropy.

2. Experimental

SAN with 26.9 wt% AN content, $M_n = 7.2 \times 10^4$ and $M_w/M_n = 2.6$, and PMMA with $M_n = 3.8 \times 10^4$ and $M_w/M_n = 1.8$ used were supplied by Asahi Chemical Industry Co., Ltd. The SAN/PMMA 40/60 (w/w) with a critical composition was prepared by melt mixing, using a Kneader

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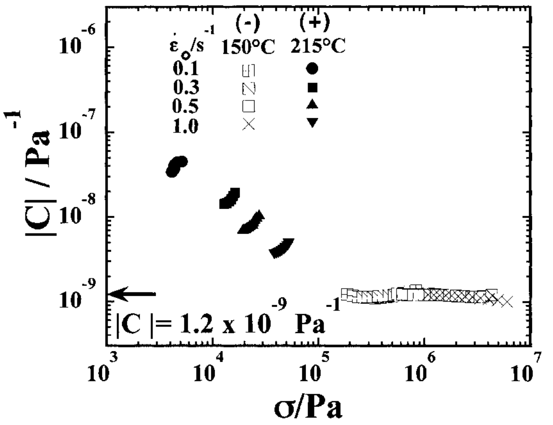

Fig. 1. Plots of absolute stress optical coefficient $|C(\dot{\varepsilon}_0;t)|$ ($\equiv |\Delta n(\dot{\varepsilon}_0;t)|/\sigma(\dot{\varepsilon}_0;t)$) vs tensile stress $\sigma(\dot{\varepsilon}_0;t)$ for SAN/PMMA 40/60 blend at 150°C (below T_s) and 215°C (above T_s). The arrow indicates the calculated value of $C(= -1.2\times10^{-9}\ \mathrm{Pa}^{-1})$ for one phase blend.

(S-1 KRC, Kurimoto Ltd.) operated at 180°C (below critical temperature $T_s = 195$°C). The melt mixed blend was quickly quenched in water to freeze the structure. The quenched transparent blend was placed between two cover glasses and remoulded at 180°C for 30 s on a hot stage to a thin film of ca 20 μm thick. The molten blend was quickly transferred to the hot chamber of a light scattering apparatus as described in the previous article [9] and subjected to time-resolved light scattering measurement at various temperatures ranging from 190 to 250°C. To estimate the critical temperature T_s, we determined the temperature dependence of the apparent mutual diffusion coefficient D_{app} in the early stage of phase decomposition on the basis of the linearized Cahn–Hilliard theory [9,10]. By the intercept of the temperature T-axis at $D_{\mathrm{app}}/T = 0$, the obtained T_s value was 195°C for 40/60 blend.

We conducted simultaneous measurements of $\sigma(\dot{\varepsilon}_0;t)$ and $\Delta n(\dot{\varepsilon}_0;t)$ via EFOR [7] in the miscible state at 150°C and the immiscible temperatures ranging from 195 to 215°C under uniaxial elongation by varying the tensile strain rate $\dot{\varepsilon}_0$ from 0.1 to 1.0 s^{-1} to determine the obtained stress optical coefficient $C(\dot{\varepsilon}_0;t)[\equiv \Delta n(\dot{\varepsilon}_0;t)/\sigma(\dot{\varepsilon}_0;t)]$. In each EFOR run the blend was annealed in situ for 115 s at a desired temperature before starting the run. During 115 s annealing, spinodal decomposition (SD) in the early stage takes place immediately. The elongated specimens were recovered at various stages of elongation and the developed phase structure was observed by transmission electron microscopy (TEM), using a Hitachi EMH-300 (75 kV) with a microtomed-thin section (ca 70 nm) stained with ruthenium tetroxide ($\mathrm{RuO_4}$). For better understanding of the obtained TEM pictures, we carried out a FFT analysis on digitally saved TEM images with commercial image analysis software (Ultimage®, Graftek France).

3. Results and discussion

Fig. 1 summarizes the double logarithmic plot of the absolute value of $|C(\dot{\varepsilon}_0;t)|$ vs $\sigma(\dot{\varepsilon}_0;t)$ for the 40/60 critical blend at 150 ($<T_s$) and 215°C ($>T_s$). In the miscible region at 150°C, the SOR is nicely valid and the value of $|C(\dot{\varepsilon}_0;t)|$ is independent of $\dot{\varepsilon}_0$, strain ε or $\sigma(\dot{\varepsilon}_0;t)$. Here, the value of $C(\dot{\varepsilon}_0;t)$ is given by the simple additivity rule [11] as $C_{\mathrm{Blend}} = C_{\mathrm{SAN27}}\phi_{\mathrm{SAN27}} + C_{\mathrm{PMMA}}\phi_{\mathrm{PMMA}}$ with ϕ_i, volume fraction of i polymer, $C_{\mathrm{SAN27}} = -2.6\times10^{-9}\ \mathrm{Pa}^{-1}$ and $C_{\mathrm{PMMA}} = -0.2\times10^{-9}\ \mathrm{Pa}^{-1}$ [11]. The calculated value of C_{Blend} $(= -1.2\times10^{-9}\ \mathrm{Pa}^{-1})$ is indicated with an arrow in Fig. 1. This suggests that $\sigma(\dot{\varepsilon}_0;t)$ of dissimilar polymers in the one-phase liquid does not behave independently but cooperatively, due presumably to the dynamic symmetry [4], i.e. $\sigma_{\mathrm{SAN27}}(\dot{\varepsilon}_0;t) = \sigma_{\mathrm{PMMA}}(\dot{\varepsilon}_0;t) \equiv \sigma(\dot{\varepsilon}_0;t)$.

Above T_s, the absolute value of C_{Blend} increases as the blend is stretched to a larger extent. The SOR is clearly violated, especially under low $\dot{\varepsilon}_0(= 0.1\ \mathrm{s}^{-1})$ elongation, $|C_{\mathrm{Blend}}|$ rapidly increases to a level well above that of

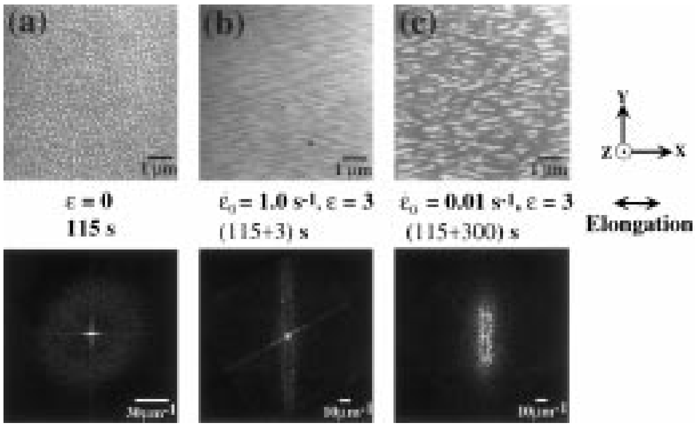

Fig. 2. TEM micrographs showing elongated SAN/PMMA blend at 215°C with: (a) before elongation ($\varepsilon = 0$); (b) $\dot{\varepsilon}_0 = 1.0\ \mathrm{s}^{-1}$ up to $\varepsilon = 3.0$; and (c) $\dot{\varepsilon}_0 = 0.01\ \mathrm{s}^{-1}$ up to $\varepsilon = 3.0$. The time elapsed during elongation is shown in the parentheses. Corresponding lower pictures in each micrograph are computed FFT spectra.

the one-phase region. Interestingly, at 215°C with $\dot{\varepsilon}_0 = 0.1$–$1.0\ \mathrm{s}^{-1}$, the sign of C_{Blend} changes from negative to positive in the first stage of the elongation, implying that the large contribution of $\Delta n_{\mathrm{f}}(\dot{\varepsilon}_0; t)$ of the phase-separated structure induced by SD become prevailing. This point becomes clear by TEM observation.

Fig. 2 shows typical TEM micrographs of specimens elongated at 215°C up to $\varepsilon(\equiv \dot{\varepsilon}_0 t) = 3.0$ (stretching ratio $\lambda = 20$). The SAN phase is stained with RuO_4. The lower pictures are FFT analysis on digitally saved TEM images. A TEM picture in Fig. 2a shows a bi-continuous structure and a circular spinodal ring appears in the FFT spectrum, implying that the demixed structure of the blend by SD has isotropic feature before elongation ($\varepsilon = 0$).

In Fig. 2b, the elongated morphology at high $\dot{\varepsilon}_0$ ($= 1.0\ \mathrm{s}^{-1}$) up to $\varepsilon = 3.0$ ($\lambda = 20$) exhibits the highly oriented modulated structure with regularity, whereas that at low $\dot{\varepsilon}_0$ ($= 0.01\ \mathrm{s}^{-1}$) elongation under same ε (Fig. 2c) shows weak deformed domains and retains its regularity fairly well, the only stretching direction is seen as two-wing-like patterns in FFT spectrum. For low $\dot{\varepsilon}_0$ elongation, due presumably to long time stretching, domain growth and breaking up of the interconnected domains took place. This suggests that the flow condition affects the internal structure developed in the competitive process between deformation due to elongation and the domain growth (coarsening) induced by SD. The large deviation from the SOR in low $\dot{\varepsilon}_0$ elongation ($\dot{\varepsilon}_0 = 0.01\ \mathrm{s}^{-1}$) indicates that during the elongation SD developed further, accompanying structure coarsening and leading to a large difference in the refractive indices between the two phases as compared to the high $\dot{\varepsilon}_0$ elongation.

For better understanding of the competitive coarsening and structural change of interconnected domains of the blend, we designed and carried out an analysis of the morphology development of the demixed blend, which was first annealed at 215°C for 10 min in the static state, elongated at 150°C (below T_s), where no effect of the time variation of the phase-separated domain coarsening, but only observation of the deformation manner of the domains was possible [12].

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