Notes

Chain Relaxation Behavior in Single-Phase Mixtures of Dissimilar Polymers

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For binary mixtures of homologous polymers, e.g., low and high molecular weight polystyrenes, the stress relaxation studies by Watanabe et al.[1-3] revealed that similar polymers with different chain lengths relax independently. They found three peaks in the relaxation spectra and these were assigned to the entanglements between short chains, between long chains, and between short and long chains, respectively.

For the single-phase mixture of dissimilar polymers, such as poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride) (PVDF) system, we[4] investigated the chain orientation relaxation behavior by the infrared dichroism and shear stress relaxation measurements. The dissimilar polymers showed an identical time variation of the normalized Hermans orientation function. The mixture showed a relaxation spectrum with a single characteristic relaxation time, depending on the composition. The results suggest that the dissimilar polymers do not relax independently but cooperatively.

Thus the stress relaxation behavior in the binary mixture of dissimilar polymers seems to be different from that of the homologous mixture. As is well known, the miscibility between dissimilar polymers with high molecular weights arises from the specific interactions between them, such as hydrogen bonding and weak charge complex formation.[5] So, individual chains are expected to relax under a constraint caused by the interactions. This may yield relaxation behavior different from that of the homologous polymer mixtures.

On the other hand, our depolarized light scattering studies on the single-phase mixtures of dissimilar polymers showed that the effective mean-square optical anisotropy γ^2 of the mixture was much higher than that estimated by the simple additivity of γ^2 of component polymers.[6,7] This suggests formation of local ordering in the mixtures, i.e., nematic alignments of the locally stretched dissimilar chains (compared with random coil chains; see Figure 1). (The local ordering implies the reduction in entanglements with mixing, as suggested by the dynamic viscoelastic studies by Wu.[8,9]) With decreasing temperature, the degree of ordering and the degree of specific interactions by FT-IR increased, suggesting that the local ordering is caused by the specific interactions.[7]

To get a deeper understanding of the cooperative relaxation in relation to the specific interactions and the nematic ordering, in this article we carried out simultaneous measurement of stress and birefringence as a function of time after shear deformation for the melts of PMMA/PVDF blends.

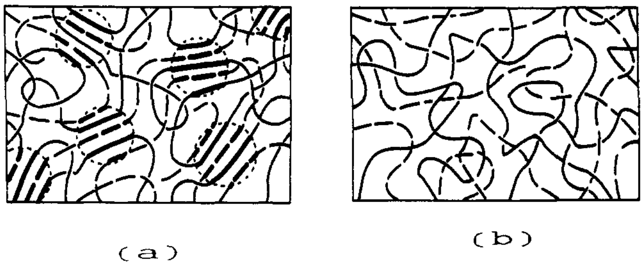

Figure 1. Chain conformations in the single-phase mixture of dissimilar polymers: (a) locally ordered chains[7] and (b) random coil chains.

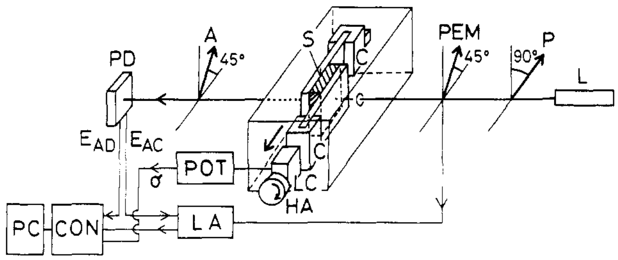

Figure 2. Apparatus for simultaneous measurment of the stress and birefringence relaxations after shear deformation: L, laser (2 mW; GL G5370, NEC); P, polarizer; PEM, photoelastic modulator (ADR-200, ORC); S, specimen between parallel glass plates; C, clamp; LC, load cell; HA, handle; POT, potentiometer; A, analyzer; PD, photodiode; LA, lock-in amplifier (5610B, NF Elec. Inst.); CON, A/D converter (ADR-16, Contec); PC, personal computer (PC-9801 VM, NEC). The photoelectric signal detected by PD contains two components; AC amplitude E_{AC} with the frequency of 50 kHz modulated by PEM and the DC one E_{DC} which is independent of the AC signal. E_{AC} is analyzed by LA and sent to PC through CON. E_{DC} is analyzed directly by CON and sent to PC.

Polymer specimens used in this study, PMMA and PVDF, were commercial polymers. PMMA was supplied by Aldrich Chemical Co. (M_w = 36.9 × 10^4, M_n = 12.1 × 10^4). PVDF was by Kureha Chemical Industry Co., Ltd. (KF 1000, M_w = 7.0 × 10^4).

PVDF and PMMA were dissolved at 10 wt % of total polymer in *N,N*-dimethylacetamide. The solution was cast onto a glass plate. After the solvent had been evaporated at room temperature, the cast film was further dried under vacuum (10^{-4} mmHg) for 2 days, and then at 170 °C for 1 day. A stack of thin-cast films was compression molded into a film of 0.8-mm thick. The thick film was put between two parallel glass plates (see Figure 2) and held at 170 °C for a day to ensure strong adhesion between the glass and film.

Figure 2 shows an apparatus designed for simultaneous measurement of stress and birefringence as a function of time after shear deformation. Shear deformation was caused by quickly sliding one of the glass plates. The applied shear strain γ was 0.8. The shear relaxation modulus curve $G(t) = \sigma(t)/\gamma$ was obtained at a fixed temperature and then the relaxation spectrum $H(\tau)$ was calculated by the Schwartzl–Staverman second-order

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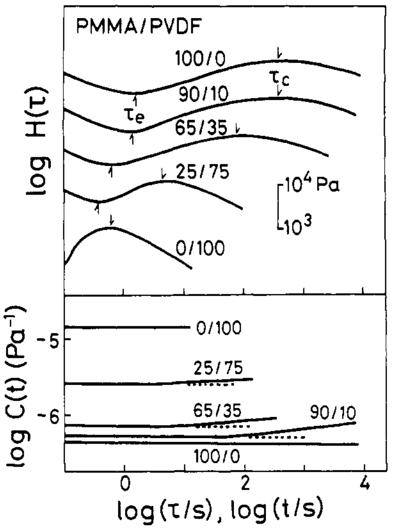

Figure 3. Relaxation spectra $H(\tau)$ and time variations of stress-optical coefficient $C(t)$ of PMMA/PVDF mixtures with various compositions at 170 °C; τ_c, relaxation time at peak maximum of $H(\tau)$; τ_e, relaxation time at minimum of $H(\tau)$.

approximation:[10]

$$H(\tau) = -G(t)[\mathrm{d}\log G(t)/\mathrm{d}\log t - (\mathrm{d}\log G(t)/\mathrm{d}\log t)^2 - (1/2.303)\,\mathrm{d}^2\log G(t)/\mathrm{d}(\log t)^2]|_{t=2\tau} \quad (1)$$

(Note that the familiar time-temperature superposition procedure for a series of $G(t)$ curves observed at different temperatures is not adequate for the specimen with strong temperature dependence of the specific interactions.[7] Hence, $H(\tau)$ in this study was obtained by a $G(t)$ curve at a fixed temperature for long time.)

Precise measurement of birefringence was carried out by employing a photoelastic modulator (PEM)[11,12] as shown in Figure 2. A He-Ne laser was passed through a Gran-Thomson polarizer and PEM. The PEM produces a sinusoidal retardation $\delta_0 = A_{\mathrm{PEM}} \sin \omega t$ with high frequency (ω = 50 kHz) and adjustable amplitude A_{PEM}. Then the modulated light was applied to the specimen. After passing through a Gran-Thomson analyzer, the light was detected by a photodiode. In the optical arrangement shown by arrows in Figure 2, the retardation Δ by the specimen is given by[12]

$$\Delta = \sin^{-1}[E_{\mathrm{AC}}/(2J_1(\delta_0)E_{\mathrm{DC}})] \quad (2)$$

where E_{AC} and E_{DC} are AC and DC amplitudes of the detected light, respectively, and $J_1(\delta_0)$ is the first Bessel function which is experimentally determined as a calibration constant. Then birefringence Δn is given by

$$\Delta n = (\Delta \cdot \lambda d)/2\pi \quad (3)$$

where λ is the wavelength of light and d is the thickness of specimen.

Figure 3 shows the relaxation spectra $H(\tau)$ and the time variations of stress-optical coefficient $C(t) = \Delta n(t)/\sigma(t)$ at 170 °C. The $H(\tau)$ spectra are shifted vertically for clarity. PMMA has a long characteristic relaxation time τ_c, while PVDF has a short one. In spite of the big difference in τ_c between component polymers, the blend shows $H(\tau)$ with a single τ_c as in the case of a single polymer system, and the τ_c systematically varies with the blend composition, suggesting the cooperative chain relaxation, as discussed in our previous papers.[4]

The most interesting is that the $C(t)$ of the blend is constant for a while and then starts to increase, while those of neat PMMA and PVDF maintain constant throughout the relaxation process. That is, the stress-optical law, which claims C being maintained constant,[13] does not hold in the blends. Similar behavior was observed at other temperatures, as shown in Figure 4. The deviation from the stress-optical law could be interpreted by taking into account the local ordering as follows.

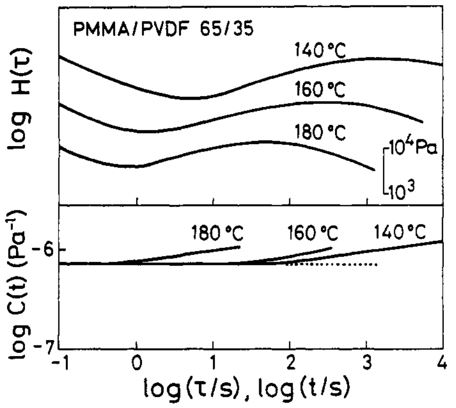

Figure 4. Relaxation spectra $H(\tau)$ and time variation of stress-optical coefficient $C(t)$ of a 65/35 PMMA/PVDF mixture at various temperatures.

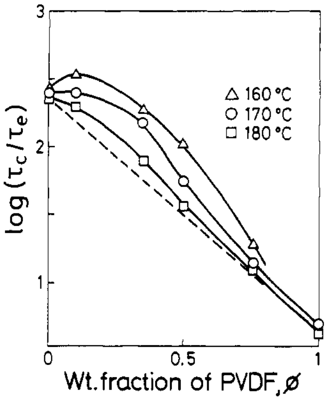

Figure 5. log (τ_c/τ_e) as a function of weight fraction of PVDF ϕ at various temperatures. Broken line is by simple additive rule.

When the ordered domains exist, overall Δn induced by the deformation of specimen will be enhanced by the large excess Δn due to the nematic alignment of stretched chains in the domain.[14] On the other hand, σ will be reduced by the ordering which reduces the number of entanglements, as discussed by Wu.[8,9] Thus, the effect of the nematic ordering on Δn will be different from that on σ. The difference will yield the change in the ratio of Δn and σ with time after the deformation, resulting in the deviation from the stress-optical law. For example, when chains in a disordered region relax faster than those in the ordered domain and the domains, being still oriented, relax very slowly, the ratio C is expected to increase with time. Actually, such a situation seems to be plausible also from the $H(\tau)$ results as follows.

To discuss the relaxation rate, it is convenient to employ the normalized characteristic relaxation time (τ_c/τ_e); τ_e being the relaxation time of entanglement strand estimated from the minimum of relaxation spectrum (see Figure 3).[10] The values of τ_c/τ_e are plotted as a function of weight fraction of PVDF ϕ in Figure 5. A 90/10 PMMA/PVDF mixture shows larger τ_c/τ_e than that of the slow component polymer PMMA at 160 °C, indicating that the chains in the mixture relax more slowly than the slow component. In other mixtures with various compositions, the observed values of τ_c/τ_e are larger than those estimated by the simple additive rule: $\tau_c/\tau_e = (\tau_c/\tau_e)_{(PMMA)}(1-\phi) + (\tau_c/\tau_e)_{(PVDF)}\phi$, e.g., as shown by broken line in Figure 5. The upward deviation could be ascribed to a restriction caused by the nematic ordering. That is, the relaxation of individual chains in a long time scale of τ_c would be restricted by the ordering because, to attain to the fully relaxed state, the domain should disappear (to be organized into a new one) or the orientation of the domain should relax as a whole; both would be very slow rate processes.

Further, note that the lower the temperature is, the bigger the deviation becomes from the additive rule in Figure 5, suggesting the greater restriction at the lower temperatures. As discussed before,[7] the degree of ordering is higher at lower temperature. Hence, the highly ordered domain at lower temperature is expected to restrict more the chain relaxation and render the larger τ_c.

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Registry No. PMMA (homopolymer), 9011-14-7; PVDF (homopolymer), 24937-79-9.