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Elongational flow birefringence of poly(methyl methacrylate)/poly(vinylidene fluoride-co-hexafluoro acetone) blends

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Abstract

For blends of a poly(methyl methacrylate) (PMMA) and a poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)], we examined phase behavior and crystalline melting (T_m) and glass transition (T_g) temperatures. In the range 130–160°C, which is a miscible one-phase region between their lower critical solution temperature (LCST: $T_c = 220°C$; $\phi_c \cong 0.5$) and T_m ($\cong 120°C$) of P(VDF-HFA), simultaneous measurements of transient tensile stress σ(t) and birefringence $\Delta n(t)$ were conducted via elongational flow opto-rheometry (EFOR) on the blends under uniaxial elongation at constant Hencky strain rates. The stress optical coefficient $C(t)(\equiv \Delta n(t)/\sigma(t))$ increased monotonically with increasing volume fraction $\phi_{P(VDF-HFA)}$ of P(VDF-HFA) in the blend. Molten PMMA/P(VDF-HFA) blends in the one-phase region appear to follow the stress optical rule with $C(t)$ obeying the simple additivity: $C(t) = C_{P(VDF-HFA)}\phi_{P(VDF-HFA)} + C_{PMMA}\phi_{PMMA}$ with the suffices being relevant to each component. The value of $C(t)$ extrapolated to $\phi_{P(VDF-HFA)} = 1$ yielded $C_{P(VDF-HFA)} = 6.5 \times 10^{-9}\ Pa^{-1}$. The $C(t)$ vs $\phi_{P(VDF-NFA)}$ behavior suggested that $C(t)$ can be zero for the (97/3) blend or the addition of only 3% P(VDF-HFA) to PMMA makes the blend non-birefringent. Thus, P(VDF-HFA) can be an optimal modifier when PMMA is used as a high-technology optical material, e.g., optical discs and lenses. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Blend; Elongational viscosity; Birefringence modifier

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1. Introduction

Poly(vinylidene fluoride-co-hexafluoro acetone) [P(VDF-HFA)] [1] and poly(methyl methacrylate) (PMMA) is an interesting combination for preparing partially miscible blends of a lower critical solution temperature (LCST) type. Because P(VDF-HFA) exhibits positive birefringence while PMMA has a small negative birefringence, the blends may be a non-birefringent one-phase material at a certain composition. Hahn [2] and Inoue [3] reported for a PVDF/PMMA blend at 20/80 composition that such behavior was certainly the case. To explore this possibility of P(VDF-HFA)/PMMA blends, we examined their phase behavior, including composition dependencies of the glass transition T_g and melting temperature T_m of P(VDF-HFA) crystallites. In particular, by using recently developed elongational flow opto-rheometry (EFOR) [4] which enabled us to perform simultaneous measurements of transient tensile stress $\sigma(t)$ and birefringence $\Delta n(t)$ as a function of time t under uniaxial elongation with constant Hencky strain rates $\dot{\varepsilon}_0$, we tested the validity of the stress–optical rule, [5] and looked for the P(VDF-HFA) content where the stress optical coefficient $C(t)(\equiv \Delta n(t)\sigma(t))$ may vanish. On the other hand, if the blends are in a two-phase state, the contribution of form-birefringence of the segregated domains may prevail even when the contrast factor of the two components are negligible [6].

2. Experimental

The miscibility of PMMA and P(VDF-HFA) was examined by temperature-modulated differential scanning calorimetry (TMDSC) [7,8], cloud point observation, optical microscopy and dynamic mechanical spectroscopy. As the results, we constructed on LCST type phase diagram with T_g and T_m vs the volume fraction $\phi_{P(VDF-HFA)}$ curves. Then, we conducted simultaneous measurements of $\sigma(t)$ and $\Delta n(t)$ via EFOR [4][6] on the blends in the miscible state from 130 to 160°C under uniaxial elongation by varying the tensile strain rate $\dot{\varepsilon}_0$ from 0.1 to $1.0\ s^{-1}$ to determine $C(t)$. For comparison, steady and dynamic shear viscosities were

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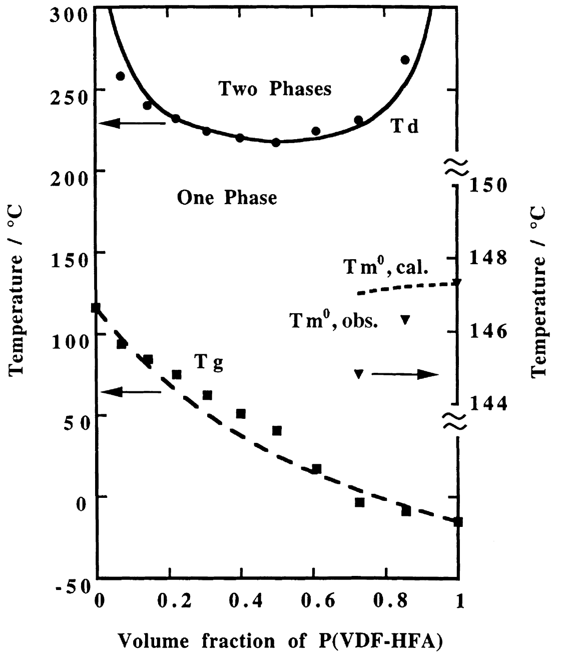

Fig. 1. A phase diagram of the PMMA/P(VDF-HFA) blends, representing phase dissolution temperatures T_d (solid circles), melting temperatures T_m (triangles) and glass transition temperatures T_g (squares). The solid line represents the binodal curve calculated using the Flory–Huggins expression and the dashed line is the Fox equation for T_g of a homogeneous mixture.

also determined on a cone-and-plate type rheometer (Rheometrics Dynamic Analyzer RDA II) within angular frequencies ω of 0.1 to 100 rad/s or shear rates $\dot{\gamma}$ of 0.001 to $1.0\,s^{-1}$. The details were described elsewhere [4][9][10][11].

The blends tested were composed of a PMMA with Mn = 56 000 and Mw/Mn = 1.5 and a P(VDF-HFA) with 8 mol% HFA content, Mn = 52000 and Mw/Mn = 2.5. The molecular weights were determined on a gel permeation chromatograph (Tosoh HLC-803D) for ~0.1 (wt%) THF solution with polystyrene elution standards. The test specimens were prepared by casting from ~10 wt% THF solution, dried at 50°C in vacuum for more than 7 days and annealed at 160°C ($> T_m$) usually for 2 h. For TMDSC (TA Instruments, TA2920) measurement the annealed specimen was quenched in liquid nitrogen and subjected to the test in a nitrogen stream with the modulation amplitude and period of ± 0.5°C and 60 s, respectively, under a constant heating rate of 10°C/min. Cloud points (T_d) were determined on quenched specimens by raising T at a heating rate of 1°C/min and observing changes in the intensities of transmitted light from a He–Ne gas laser sourse.

For EFOR, the annealed specimen was molded on a hot-press at 190–240°C for 0.5–3 min, cut into strips of appropriate size (usually $\sim 0.1–0.4 \times 7.0 \times 60\,mm^3$). In each EFOR run a sample strip set at a desired temperature between 150 and 170°C was annealed in situ for 90 s before starting the run. For shear viscosity measurements the annealed specimen was molded at 170–200°C for 3 min, and then cut into disks of 25 mm diameter and 0.8–2.0 mm thickness to be mounted on the rheometer.

3. Results and discussion

3.1. Thermal and phase behavior

The phase behavior of the blends is summarized in Fig. 1, in which T_d, T_g and T_m are plotted against volume fraction $\phi_{P(VDF\text{-}HFA)}$ of P(VDF-HFA). Clearly, the blends exhibit LCST-type phase behavior. Above T_c ($\cong$ 220°C; $\phi_c \cong$ 0.5) the blends exist in a liquid–liquid two-phase state. The solid curve labeled with T_d is a theoretical spinodal curve based on the Flory–Huggins theory [12] taking the free energy parameter χ as an adjustable parameter assigned as [13][14];

$$\chi = 0.016 - 52.5/RT \tag{1}$$

where R is the gas constant and T the absolute temperature. The value of χ at 160°C was estimated to be $-$ 0.045. For the blends of two P(VDF-HFA) rich (20/80 and 30/70) compositions, the equilibrium melting temperatures T_m^0 were determined by Hoffman and Weeks analysis [15]. The T_m^0 clearly exhibits a tendency of melting point depression, implying the two components are miscible, as pointed out earlier by Nishi and Wang [13] on the PVDF/PMMA blend. However, the theoretical melting point depression predicted by using the interaction parameter χ determined for the cloud point curve was too small as compared with the observed depression, as shown by the dotted line labelled T_m^0, cal. in Fig. 1.

In any case, below T_m^0, the blends of P(VDF-HFA) rich composition may exist in a liquid/crystalline two-phase state, whereas PMMA-rich blends exist in a liquid or glassy single-phase state depending, respectively, on T being above or below T_g of the blend. Therefore, the T_g vs composition curve of the miscible blends can be well approximated with Fox Eq. (2) [16] :

$$Tg^{-1} = (W_{PMMA}/Tg_{PMMA} +) + (W_{P(VDF-HFA)}/Tg_{P(VDF-HFA)}) \tag{2}$$

where W_{PA} with PA = PMMA or P(VDF-HFA) is the weight fraction and $T_{g_{PA}}$ the glass transition of the pure polymer PA ($T_{g_{PMMA}}$ = 389 K and $T_{g_{P(VDF-HFA)}}$ = 257 K). In Fig. 1, the dashed curve is the T_g vs $\phi_{\{P(VDF\text{-}HFA)}$ curve calculated by Eq. (2).

3.2. Elongational flow birefringence

From the thermal and phase behavior of the blends, we see that in the temperature range from 130 to 220°C on the molten blends are a one-phase liquid at all compositions, and hopefully the PMMA-rich blends may form a one-phase homogeneous glass even below the T_gs.

To test this expectation, we conducted EFOR tests

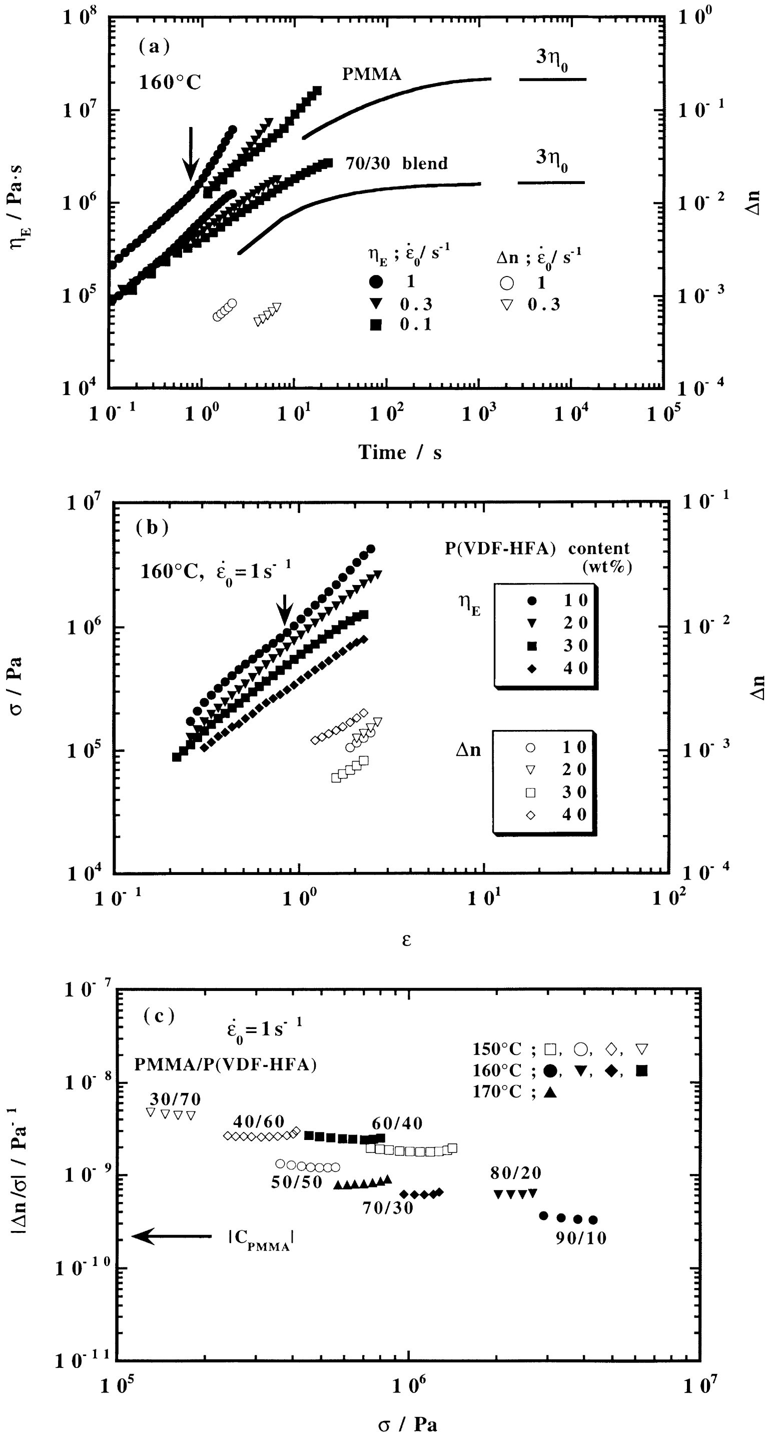

Fig. 2. (a) Double logarithmic plots of elongational viscosity $\eta_E(t) = \sigma(t)/\dot\varepsilon_0$ and birefringence $\Delta n(t)$ vs time t for PMMA and PMMA/P(VDF-HFA) 70/30 blend at 160°C. The solid curves are the three times transient shear viscosity $3\eta_0(t)$ at a constant shear rate $\dot\gamma = 0.001$ s^{-1} (determined on RDA II); (b) double logarithmic plots of $\sigma(t)$ and $\Delta n(t)$ against Hencky strain $\varepsilon \cong \dot\varepsilon_0 \cdot t$ (with $\dot\varepsilon_0 = 1$ s^{-1}) at 160°C for the 90/10, 80/20, 70/30, and 60/40 blends; and (c) the stress optical coefficient $C(t)$ ($\equiv \Delta n(t)/\sigma(t)$) vs $\sigma(t)$ with $\dot\varepsilon_0 = 1$ s^{-1} at 160°C obtained from the same data shown in Fig. 2b. For PMMA [17] the absolute value of reported $C_{PMMA} = -0.2 \times 10^{-9}$ Pa^{-1} is indicated with the arrow.

involving simultaneous measurements of tensile stress $\sigma(t)$ and birefringence $\Delta n(t)$ on the molten blends of 100/0 (PMMA) to 60/40 composition in the miscible state of (T_g, T_m $<$) 150–170°C ($<$ T_d of the blends). Fig. 2 summarizes the results: (a) the elongational viscosity $\eta_E(t) \equiv \sigma(t)/\dot\varepsilon_0$ and birefringence $\Delta n(t)$ vs time t for PMMA and the PMMA/P(VDF-HFA) 70/30 blend measured at 160°C with the dotted experimental results (determined on EFOR) and solid lines being the three times transient shear viscosity $3\eta(t)$ at a constant

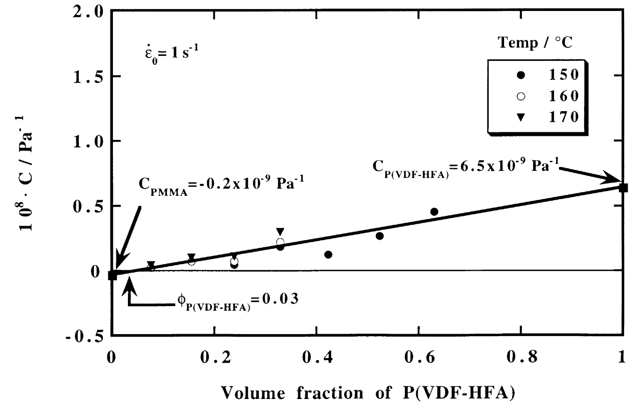

Fig. 3. Plots of *C(t)* ($\equiv \Delta n(t)/\sigma(t)$) vs P(VDF-HFA) volume fraction $\phi_{(VDF-HFA)}$ for all the single-phase blends obtained at 150, 160, and 170°C. The solid line indicates Eq. (3): $C(t) = C_{P(VDF-HFA)}\phi_{P(VDF-HFA)} + C_{PMMA}\phi_{PMMA}$ with a literature value [17] of $C_{PMMA} = -0.2 \times 10^{-9}\ Pa^{-1}$, yielding $C_{P(VDF-HFA)} = 6.5 \times 10^{-9}\ Pa^{-1}$ at $\phi_{P(VDF-HFA)} = 1$.

rate of $\dot{\gamma} = 0.001\ s^{-1}$ and zero-shear viscosity $3\eta_0$ (determined on RDA II); (b) plots of *σ(t)* and *Δn(t)* against Hencky strain $\varepsilon \cong \dot{\varepsilon}_0 \cdot t$ (with $\dot{\varepsilon}_0 = 1\ s^{-1}$) at 160°C for the blends of 90/10, 80/20, 70/30, and 60/40 composition; and (c) the stress optical coefficient $C(t)(\equiv \Delta n(t)/\sigma(t))$ vs *σ(t)* collected again with $\dot{\varepsilon}_0 = 1\ s^{-1}$ at 160°C from the same data shown in Fig. 2b. For PMMA, we see that $\eta_E(t)$ exhibits a tendency of so-called strain-induced hardening [18] that is upward deviation from the $\dot{\varepsilon}_0$-independent portion of the $\eta_E(t)$ curves (which is often referred to as the linear region), as shown with an arrow for the curve with $\dot{\varepsilon}_0 = 1.0\ s^{-1}$ in Fig. 2a. On the other hand, for the PMMA/P(VDF-HFA) 70/30 blend, the strain-induced hardening is rather suppressed and $\eta_E(t)$ and/or *σ(t)* increases more slowly with increasing P(VDF-HFA) content, as seen in *σ(t)* vs *ε* plots in Fig. 2b.

For ordinary homopolymer gels, the coincidence between $\eta_E(t)$ and time development of $3\eta(t)$, the so-called extended Trouton rule [19] is generally valid. In the 70/30 blend, the difference between the early stage of $\eta_E(t)$ and $3\eta(t)$ profiles seems to be rather larger than that for PMMA. At present, we are not sure whether the difference is true or just an artefact.

For PMMA we employed a literature value [17] of $C_{PMMA} = -0.2 \times 10^{-9}\ Pa^{-1}$, for which the absolute value is indicated with the arrow. From Fig. 2c we see that the *C(t)* vs *σ(t)* plot of each blend is independent of *σ(t)*, implying that the single phase blends obey the stress optical rule, although we have obtained *Δn(t)* data only in a very limited time span.

Fig. 3 shows the plot of $C(t)(\equiv \Delta n(t)/\sigma(t))$ vs $\phi_{P(VDF-HFA)}$ for the single-phase blend obtained at 150, 160, and 170°C. The birefringence of a biphasic system usually contains a contribution of form-birefringence of the existing domains, which can, however, be neglected. On the other hand, if strong nematic-like interactions prevail between the component segments, additivity in the birefringence may not hold. However, neither of these contributions are unlikely in the present PMMA/P(VDF-HFA) blend in the miscible, single-phase state. Thus, the simple additivity may hold and *Δn(t)* is given by:

$$\Delta n(t) = \Delta n^0_{P(VDF-HFA)}\phi_{P(VDF-HFA)} + \Delta n^0_{PMMA}\phi_{PMMA} \qquad (3)$$

Then if $\sigma(t) \equiv \sigma_{PMMA}(t) = \sigma_{P(VDF-HFA)}(t)$, the simple additivity may hold also for the stress optical coefficient *C(t)* which thus reads:

$$C(t) \equiv \Delta n(t)/\sigma(t) = C_{P(VDF-HFA)}\phi_{P(VDF-HFA)} + C_{PMMA}\phi_{PMMA} \qquad (4)$$

where $C_{P(VDF-HFA)}$ and C_{PMMA} are the stress optical coefficients of P(VDF-HFA) and PMMA homopolymers, respectively. The solid line in Fig. 3 was obtained by the method of least squares, and extrapolation of *C(t)* to $\phi_{P(VDF-HFA)} = 1$ leads to the value of $C_{P(VDF-HFA)} = 6.5 \times 10^{-9}\ Pa^{-1}$.

The *C(t)* vs $\phi_{P(VDF-HFA)}$ behavior in Fig. 3 suggests that *C(t)* may vanish for the PMMA/P(VDF-HFA) (97/3) blend. This finding may not be surprising because PMMA originally has a small negative birefringence, but it means that the addition of only 3 wt% P(VDF-HFA) to PMMA makes the matrix non-birefringent, while keeping the system in a single-phase state. Zero birefringence has already attained for the PMMA/PVDF 80/20 blend [2] and the PMMA/P(VDF-co-trifluoro ethylene) 90/10 blend [3]. Thus, P(VDF-HFA) is an optimal modifier of PMMA when PMMA is to be used as a high-performance optical material such as optical discs and plastic lenses.

In this study, EFOR measurements were carried out on the blend with P(VDF-HFA) contents varied from 0 to 40 wt%, because the blends with more than 50 wt% P(VDF-HFA) contents were too soft to be handled on EFOR in the 150 to 170°C range. If we lower the temperature below this level, effects of solid/liquid phase separation due to the crystallization of P(VDF-HFA) may prevail. This crystallization should complicates the problem. If, on the other hand, the EFOR test on the blend could be conducted at a temperature above the LCST, we will face a problem of elongational flow birefringence of complex multiphase liquid, such as that seen in some block copolymer liquids [20].

References

[1] Central Glass Co. Japanese Patent 63-117085, 1963.
[2] Hahn BR, Wendorff JH. Polymer 1985;26:1619.
[3] Saito H, Inoue T. Polym J Sci, Part B, Polym Phys 1987;25:1629.
[4] Kotaka T, Kojima A, Okamoto M. Rheol Acta 1997;36:646.
[5] Doi M, Edwards SF. The theory of polymer dynamics. Oxford: Clarendon Press, 1986.
[6] Okamoto M, Kojima A, Kotaka T, Munstedt H. Macromolecules, 1998, in press.
[7] Sauerbrunn S, Gill P. Am Lab 1993;25:54.
[8] Wunderlich B, Jin Y, Boller A. Thermochim Acta 1994;238:277.
[9] Kubo H, Sato H, Okamoto M, Kotaka T. Polymer 1998;39:501.
[10] Okamoto M, Kojima A, Kotaka T. Polymer 1998;39:2149.
[11] Okamoto M, Kubo H, Kotaka T. Polymer 1998;39:3153.

[12] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.
[13] Nishi T, Wang TT. Macromolecules 1975;8:909.
[14] Nishi T, Wang TT. Macromolecules 1977;10:421.
[15] Hoffman JD, Weeks JJ. J Res Natl Bur Stand, Sect A 1962;66:13.
[16] Fox TG. Bull Am Phys Soc 1956;1:123.
[17] Read BA. J Polym Sci Part C 1887;1967:16.
[18] Larson RG. J Rheol 1984;28:545.
[19] Trouton FT. Proceedings of the Royal Society 1906;A77:426.
[20] Kojima A, Okamoto M, Kotaka T. Macromolecules, 1998, submitted for publication.