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COMPATIBILITY OF POLYMER BLENDS EVALUATED BY CRYSTALLIZATION DYNAMICS

Simultaneous DSC-FTIR method

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Abstract

The mixing state of poly(vinylidene fluoride) (PVDF) and two amorphous polymers, poly(methyl methacrylate) (PMMA) and poly(isopropyl methacrylate) (PiPMA) were investigated from the viewpoint of crystallization dynamics using simultaneous DSC-FTIR method. The crystallization rate (R^*) and the growth rate of *trans-gauche-trans-gauche*' (*TGTG*') conformation (Rc^*) depended on both the blend content (ϕ) and the crystallization temperature for PVDF/PMMA. The temperature and ϕ dependency of R^* and Rc^* were almost the same for PVDF/PMMA. However, R^* and Rc^* depended scarcely on ϕ for PVDF/PiPMA, and the temperature dependency of R^* differed from that of Rc^* for PVDF/PiPMA. These results showed that PVDF and PMMA were miscible on molecular level, and that PVDF/PiPMA was immiscible and the concentration fluctuation existed in the PVDF-rich phase.

Keywords: conformation, crystallization, DSC-FTIR, miscibility, PiPMA, PMMA, polymer blend, PVDF

Introduction

In general, polymers scarcely mix with each other, because the combinational entropy between polymers is considerably low. As miscibility of polymers strongly depends on polymer–polymer interaction, a slight difference in conformation of polymer chain sometime affects the miscibility of blends. In the case of polymer blends containing crystalline polymer, the melting (or crystallization) temperature depression is observed by mixing with other polymer. The melting temperature depression in a miscible blend system is expressed by following equation [1].

$$\frac{1}{T_\mathrm{m}}+\frac{1}{T_\mathrm{m}^0}=-\frac{RV_2}{\Delta H_2 V_1}\left[\frac{\ln\phi_2}{n_2}+\left(\frac{1}{n_2}-\frac{1}{n_1}\right)\phi_1+\chi_{12}\phi_1^2\right] \tag{1}$$

where T_m, T_m^0, R, ΔH, V, ϕ, n and χ indicate the observed melting temperature, the equilibrium melting temperature, gas constant, melting enthalpy of repeating unit, volume of repeating unit, volume fraction, number of repeating unit and interaction parameter, respectively. The subscripts 1 and 2 denote amorphous and crystalline

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polymers, respectively. As a polymer crystal is in the metastable state, the melting temperature depends on its thermal history. Therefore the evaluation of equilibrium melting temperature of polymer crystal is difficult. Only a few polymer blend systems succeed in estimating χ_{12} value by using Eq. (1).

We have proposed the method evaluating a compatibility of polymer blend by analyzing crystallisation dynamics under isothermal condition using DSC [2, 3]. Crystal growth rate and surface free energy of crystallite in poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blend are influenced by PMMA content for a miscible blend system [2]. The miscibility of PVDF/PMMA blend depends strongly on PMMA tacticity [2].

The simultaneous DSC-FTIR method gives not only thermal changes but also conformational changes of polymeric materials [4, 5]. In this study, the miscibility of PVDF and poly(alkyl methacrylate)s were investigated by simultaneous DSC-FTIR measurements.

Experimental

PMMA (M_w=1.5·10^5) and poly(isopropyl methacrylate) (PiPMA) (M_w=2.0·10^5) were used for blend with PVDF (M_w=2.6·10^6). Blend samples were prepared by casting from N,N'-dimethylacetamide solution. The blend content of poly(alkyl methacrylate) (ϕ) was 0–0.4 in mass fraction. After drying, blend samples were pressed at 200°C and were quenched to ice water. The obtained blend film sandwiched with thin KBr disks and clumped in an aluminum vessel used for the DSC-FTIR measurement. Sample mass used was about 1.5 mg.

The simultaneous DSC [4] was set on JASCO FTIR 620 equipped with a MCT detector. DSC scanning rate was 5 K min^{-1}. Wavenumber and time resolutions of FTIR measurement were 2 cm^{-1} and 10 s, respectively. Blend samples were melted at 195°C for 5 min and then cooled to the fixed crystallization temperatures (T_c) at 5 K min^{-1}. During isothermal crystallization, DSC exotherm and FTIR spectra were recorded.

Results and discussion

Figure 1 shows the simultaneous DSC-FTIR results for PVDF/PMMA blend (ϕ=0.2) during isothermal crystallization at 149°C. The sample was held at 195°C for 5 min and cooled to 149°C at 5 K min^{-1}. The blank DSC run and temperature data are shown in the lower side. The expanded data during the isothermal crystallization is shown in the figure. DSC exothermic peak was observed at the time range from 16 to 28 min after the isothermal condition was established at 15 min. IR spectra of blend scarcely changed in the molten state, however, the absorbance of several IR bands increased following crystallization under isothermal condition. The bands at 795 and 763 cm^{-1} are assigned to rocking mode of CH_2 and bending mode of CF_2, respectively [6]. Both bands correspond to the *trans-gauche-trans-gauche*' (*TGTG*') conformation, a unique conformation of α-form of PVDF crystal [6].

Two characteristic times were evaluated from the exothermic DSC curve and the absorbance change at 763 cm^{-1}. The time required from establishing the isothermal condition to the occurrence of 50% of crystallization (t_{cry}) and the time needed to the formation of 50% of *TGTG*' conformation ($t_{TGTG'}$) were obtained. The reciprocals of t_{cry} and $t_{TGTG'f}$ were employed as crystallization rate (R^*) and growth rate of *TGTG*' conformation (Rc^*), respectively.

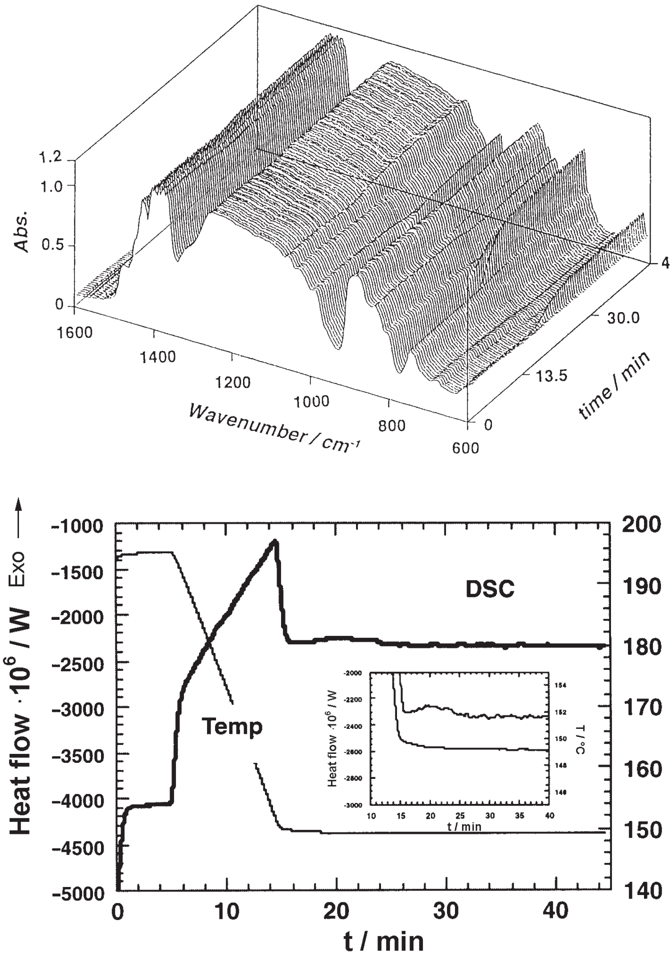

Fig. 1 Simultaneous DSC-FTIR results of PVDF/PMMA (ϕ=0.2). Time resolved IR spectra (upper) and DSC signal (lower) indicated the isothermal crystallization. Sample was held at 195°C for 5 min then cooled to 149°C at 5 K min^{-1}. The isothermal condition was established at 15 min, the crystallization occurred from 16 to 28 min

Figure 2 shows the temperature dependence of R^* (A) and Rc^* (B) for PVDF/PMMA as a function of blend content (ϕ). With the increase of ϕ, both R^* and Rc^* decreased extremely. Strong ϕ dependence of R^* indicates that PVDF/PMMA is in the miscible state as reported previously [2]. In polymer, the rate-determining stage is the diffusion of molecules to the crystal growth surface. If the diffusion process of the polymer was described by the reptation model [7], the diffusion distance is almost the same with the radius of gyration of polymer molecules ($R_g=N^{1/2}b$). Here, N and b indicate the number and length of the repeating unit, respectively. The R_g value evaluated from M_w of PVDF was 20 nm. Therefore, R^* is influenced by the average blend content in the area with a radius of 20 nm. On the other hand, a conformational ordering occurs as intramolecular phenomena. The rate of conformational ordering is influenced by few neighboring molecules. Therefore, Rc^* reflects the average blend content in the area within a radius of 1 nm. As shown in Fig. 2, PVDF/PMMA shows the same tendency of R^* and Rc^*. This fact indicates that PVDF and PMMA mix homogeneously in the distance from 1 to 20 nm.

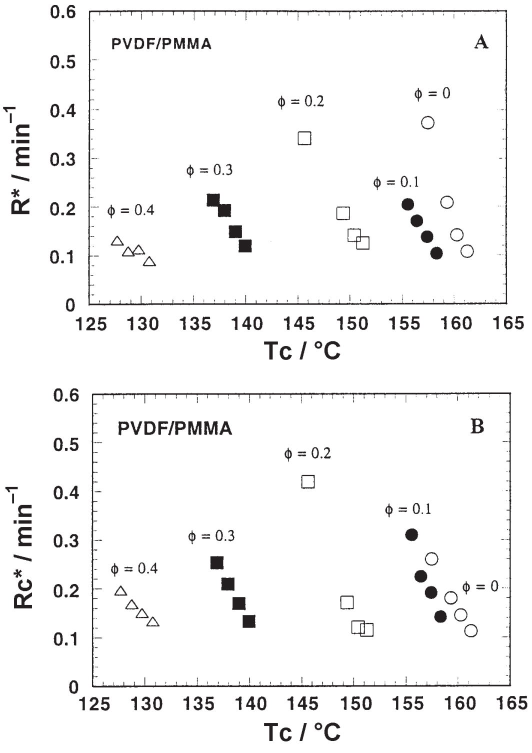

Fig. 2 Temperature dependence of crystallization rate, R^* (A), and growth rate of *TGTG'* conformation, Rc^* (B), for PVDF/PMMA system with various blend content; ϕ=0 (o), 0.1 (●), 0.2 (□), 0.3 (■) and 0.4 (Δ)

Figure 3 shows the temperature dependence of R^* (A) and Rc^* (B) for PVDF/PiPMA as a function of ϕ. Comparing with the results of PVDF/PMMA in Fig. 2, the crystallization temperature range is considerably narrower. The blend with ϕ=0.1 shows the ϕ dependency of R^* and Rc^*. However, the blends with ϕ above 0.2 show almost the same R^* and Rc^*. These results suggest that PVDF/PiPMA with ϕ=0.1 is in the miscible state, however, blends with ϕ above 0.2 are in the phase separated state. The temperature dependence of R^* differs from that of Rc^* for PVDF/PiPMA comparing with the case of PVDF/PMMA. These results suggest that the heterogeneity of PiPMA content exists in the scales between 1 and 20 nm. In spite of higher crystallization temperature, the crystallization rate of PVDF/PiPMA with ϕ above 0.2 is faster than that of PVDF/PMMA. In the phase separation system, the crystallization occurs in the PVDF-rich phase in which PiPMA content is lower than the initial fraction. However, the fast crystallization rate of PVDF/PiPMA was caused by the weaker interaction between PVDF and PiPMA.

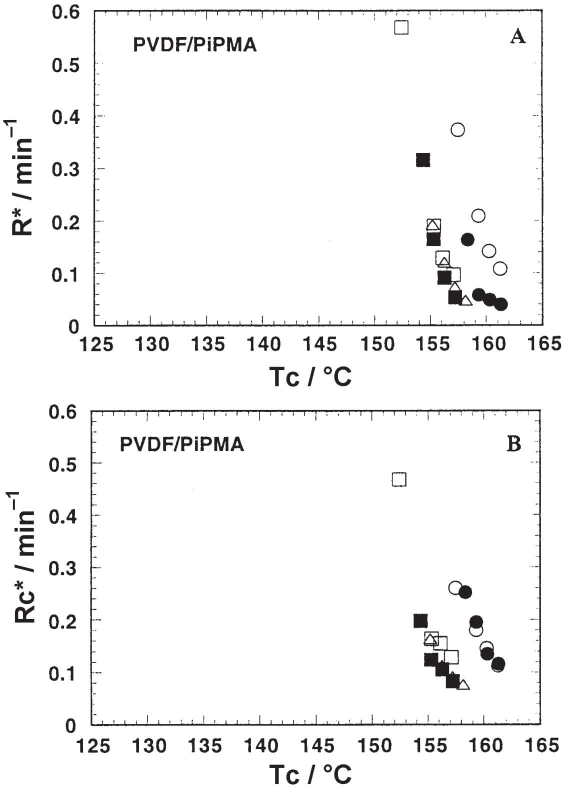

Fig. 3 Temperature dependence of crystallization rate, R^* (A), and growth rate of *TGTG'* conformation, Rc^* (B), for PVDF/PiPMA system with various blend content; ϕ=0 (o), 0.1 (●), 0.2 (□), 0.3 (■) and 0.4 (Δ)

From the results shown in Figs 2 and 3, the temperature at which R^* or Rc^* approached 0.15 min^{-1} ($T_{0.15}$) was evaluated for each blend content. The degree of super cooling ($\Delta T = T_m^0 - T_{0.15}$) for crystallization was described by the Eq. (2).

$$\frac{\Delta T}{T_m^0} = \frac{\Delta\mu}{\Delta H_m} \tag{2}$$

Here, T_m^0, $\Delta\mu$ and ΔH_m indicate the equilibrium melting temperature, the chemical potential difference between molecules in the liquid and the crystal states and the melting enthalpy of repeating unit, respectively. T_m^0 was evaluated by the extrapolation of the linear relationship between T_c and T_m observed by the DSC-FTIR method. Figure 4 shows the relationship between $\Delta T/T_m^0$ and ϕ for the case of R^* (A) and Rc^* (B). In other words, Figs 4A and 4B indicate the blend effect on chemical potential difference between molecules in the liquid and crystal states and between the random and TGTG' conformation, respectively. Both linear relationship evaluated by R^* and Rc^* are the same for PVDF/PMMA system due to the homogeneous miscible nature on molecular level. However, the different tendency observed in the relationship of R^* and Rc^* for PVDF/PiPMA suggest the concentration fluctuation exists in the scale between 1 to 20 nm in the PVDF-rich phase. The detailed discussion based on thermodynamics and kinetics will appear in the near future.

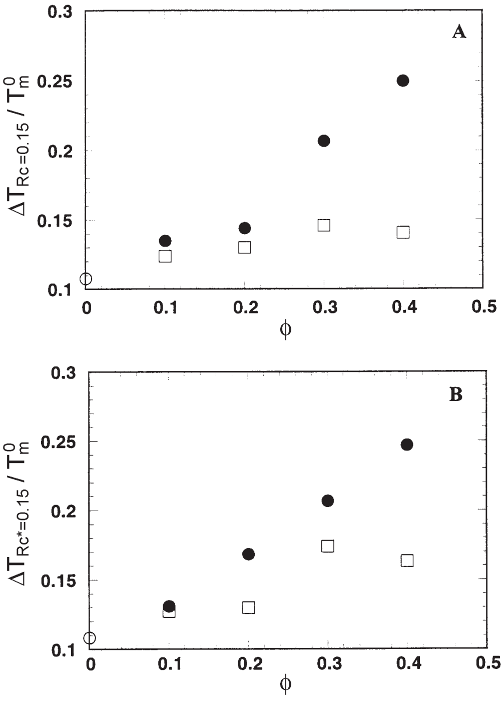

Fig. 4 Relationship between $\Delta T/Tm^0$ and ϕ obtained from R^* (A) and Rc^* (B) for PVDF/PMMA (●) and PVDF/PiPMA (❑)

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