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STRUCTURE FORMATION OF PVDF/PMMA BLENDS STUDIED
Simultaneous DSC/FT-IR measurement

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Abstract

Conformational formation and crystallization dynamics of miscible PVDF/at-PMMA and PVDF/iso-PMMA polymer blends from the molten state were studied by the simultaneous DSC/FT-IR measurement. Formation of TGTG' conformation occurred before starting crystallization exothermic peak in the PMMA content (Φ_{PMMA}) range from 0 to 0.4 for both blends. The formation rate of TGTG' conformation, crystal growth rate and surface free energy of PVDF crystal in blends depended linearly on Φ_{PMMA} for PVDF/at-PMMA, however, those rates for PVDF/iso-PMMA slightly influenced by Φ_{PMMA}. These results suggested that the former was miscible blend in molecular level, however, the latter was a miscible blend with large concentration fluctuation or a partially segregated system.

Keywords: conformation, crystallization dynamics, miscibility, PVDF/PMMA blends, simultaneous measurement

Introduction

Miscibility state of polymer blends can be determined by various methods, such as thermal analysis, microscopic, spectroscopic (IR, NMR, etc.) and scattering methods. Concerning with thermal analysis, the estimation of polymer–polymer interaction parameter from the melting temperature depression [1] and/or the relationship between glass transition temperature and composition [2] are conventional methods to evaluate miscibility of polymer blends. However, some difficulty of the melting temperature depression method was pointed out [3].

We have proposed a new method to estimate the miscibility state of polymer blends including crystalline component from the view point of crystallization behavior for blends of poly(vinylidene fluoride) and poly(methyl methacrylate) (PVDF/PMMA) [4]. The miscibility of PVDF with PMMA depends on tacticity of PMMA. The growth rate (G) and the surface energy (σ) of PVDF crystal in PVDF/PMMA blend depend strongly on PMMA weight fraction (Φ_{PMMA}) for the miscible PVDF/atactic-PMMA system, however, G and σ are almost the same irrespective of Φ_{PMMA} for PVDF/isotactic-PMMA system [4].

PVDF, which shows polymorphism, forms α-form and ferroelectric β-form crystals by crystallization from the molten state and from the glassy state, respec-

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tively. Although the stable form is dependent on chain defect level [5], α-form, composed of anti-parallel packing of TGTG′ chains, is more stable than β-form composed of parallel packing of TT chains [6]. It is expected that the formation rate of TGTG′ conformation during crystallization gives the information of mixed state in molecular level, because the conformational change of molecules should be influenced by the circumstance around molecules. In this study, the structure formation process of PVDF/PMMA blends from the molten state was analyzed from the viewpoint of conformational formation and crystallization dynamics observed by the simultaneous DSC/FT-IR measurement.

Experimental

PVDF ($Mn=2.6\times10^6$) supplied by Kureha Chemical Co. Ltd., atactic PMMA (at-PMMA, $Mn=1.5\times10^5$) supplied by Mitsubishi Resin Co Ltd. and the ionic polymerized isotactic PMMA (iso-PMMA, $Mn=1.6\times10^5$) were used to prepare blend samples which were obtained by solvent casting method from these N,N′-dimethylacetamide solution at 333 K. The blend composition (Φ_{PMMA}) was indicated by the weight fraction of PMMA. The obtained blend films were further dried under vacuum at room temperature for 3 days.

The simultaneous DSC/FT-IR measurement was carried out by setting the simultaneous DSC/X-ray scattering measurement instrument [7] on Nicolet FT-IR 800. The detailed of the simultaneous measurement instrument and application of the simultaneous DSC/X-ray scattering measurement for melting behavior of polymers were already reported [7, 8]. Cooling rate was controlled by flowing liquid nitrogen through the cold path in the heat sink of DSC. Blend sample film with c.a. 3 mg was sandwiched with two KBr disks (0.1 mm in thickness and 6.5 mm in diameter) and was cramped in an aluminum sample vessel. Blend samples were heated to 10 K above these melting temperature (T_m) at 10 K min^{-1} and maintained at these temperatures for 5 min, then quenched to predetermined crystallization temperature (T_c) at 40 K min^{-1}. The heat of crystallization and FT-IR spectra at T_c were measured until the crystallization was completed. Accumulation and saving of one FT-IR spectra with 4 cm^{-1} accuracy required 55 s.

Results and discussion

Melting temperature depression by Φ_{PMMA} for PVDF/at-PMMA and PVDF/iso-PMMA systems were almost the same. The cloud-point *vs.* Φ_{PMMA} curve with the lower critical solution temperature (LCST) was closed to T_m *vs.* Φ_{PMMA} curve in the phase diagram of PVDF/iso-PMMA, however, the cloud-point curve of PVDF/at-PMMA was expected to exist at the temperature range above these thermal decomposition temperature [4]. As the phase separation temperature of PVDF/at-PMMA blend was sufficiently higher than T_m of blend, isothermal crystallization of PVDF occurred in the homogeneous mixed phase. In PVDF/iso-PMMA blend, temperature difference between the cloud-point and T_m was about 50 K and 10 K at 0.1 and 0.3 of Φ_{PMMA}, respectively. Crystallization occurred in the phase separated blend or in the blend with concentration fluctuation for PVDF/iso-PMMA with Φ_{PMMA} above 0.3, because the pre-set temperature in the molten state was above the cloud-point temperature. From X-ray diffraction study, α-form PVDF was obtained by isothermal crystallization from the melt in the Φ_{PMMA} range from 0 to 0.4 for both blend.

Changes of TGTG′ conformation (X_{TGTG}) and crystallinity (X_C) were evaluated from the changes of IR absorbance at 763 cm^{-1}, which was assigned as TGTG′ conformation of PVDF, and crystallization exothermic peak during isothermal crystallization as follows, since X-ray diffraction indicated no formation of the γ form which shares the 761 cm^{-1} band with the α form.

$$X_{TGTG'} = (A_t - A_{t0})/(A_{t\infty} - A_{t0}) \tag{1}$$

$$X_C = \frac{\int_0^t \left(\frac{d\Delta H}{dt}\right) dt}{\int_0^{t\infty} \left(\frac{d\Delta H}{dt}\right) dt} \tag{2}$$

Here, A_t, A_{t0} and $A_{t\infty}$ indicate absorbance at 763 cm^{-1} and $\Delta Ht/dt$ is DSC exothermic curve at corresponded time after isothermal condition was established.

Changes of X_{TGTG} and X_C were shown in Fig.1 for PVDF/at-PMMA with $\Phi_{PMMA}=0.2$ at 430 K. Generally X_C is corresponded to crystal growth process. For all crystallization condition, TGTG′ conformation was formed before DSC exothermic peak was observed. When polymer chain crystallized from random conformation, regular conformation was first formed and then molecules having regular conformation were aligned in crystal lattice. Similar experimental results were reported in the case of crystallization of high-density polyethylene by individual FT-IR and SAXS measurements [9] and by simultaneous DSC/FT-IR measurement [10]. Three characteristic times, TGTG′ conformation growth time, crystal growth time and crystal nucleation time, were evaluated by the half-times of X_{TGTG} and X_C, and the start time of crystallization exothermic peak from Fig.1. The reciprocal of these characteristic times gave the growth rate of TGTG′ conformation (G_C), the crystal growth rate (G) and the nucleation rate (N), respectively.

G_C and G showed good correlation with $\Delta T(=T_m - T_c)$ for PVDF and all blend samples. The relationship between G_C (or G) and ΔT for PVDF/at-PMMA depended strongly on Φ_{PMMA}, although the relationship between G_C (or G) and ΔT was almost the same in the Φ_{PMMA} range from 0 to 0.2 for PVDF/iso-PMMA. From the relationship between G_C (or G) and ΔT, the ΔT value at which sample obtained G_C (or G)$=0.2$ min^{-1} was estimated (ΔT_C and ΔT_G). In other word, the ΔT_C (or ΔT_G) value indicated the potential energy required to approach the constant G_C (or G). The ΔT_C (or ΔT_G) value thus obtained were shown as a function of Φ_{PMMA} in Fig.2 (a). For both G_C and G of PVDF/at-PMMA, ΔT_C (or ΔT_G) increase with the increase of Φ_{PMMA}, however, ΔT_C (or ΔT_G) was almost the constant irrespective of Φ_{PMMA} for PVDF/iso-PMMA.

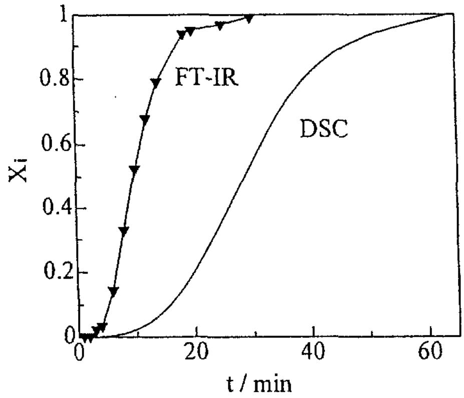

Fig. 1 Growth of TGTG′ conformation and crystal evaluated from changes of absorbance at 763 cm^{-1} and DSC exothermic peak during isothermal crystallization of PVDF/at-PMMA with $\Phi_{PMMA}=0.2$ at 430 K

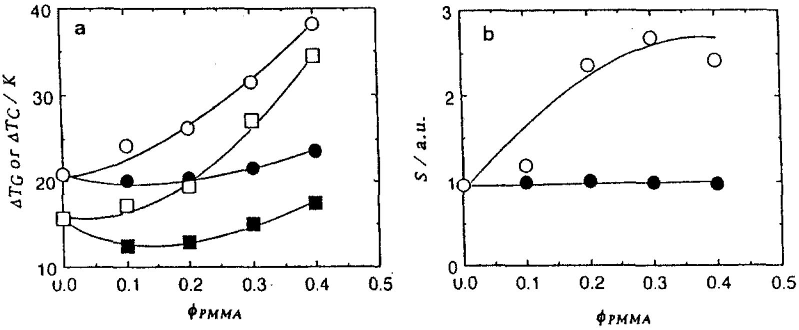

Fig. 2 Φ_{PMMA}, dependency of G and G_C (a) and of σ (b) for PVDF/at-PMMA and PVDF/iso-PMMA; G (○) and G_C (•) for PVDF/at-PMMA, G (□) and G_C (■) for PVDF/iso-PMMA, σ of PVDF/at-PMMA (○) and σ of PVDF/iso-PMMA (•)

In a miscible blend, the crystallization of PVDF was restricted by mixing of PMMA, because the diffusion process of PVDF to crystal surface was obstructed due to the attractive interaction with PMMA. The conformation growth process was also restricted by the attractive interaction with PMMA. Thus, G and G_C depended strongly on Φ_{PMMA} for PVDF/at-PMMA. As the cloud-point was closed to melting temperature in the PVDF/iso-PMMA system, the concentration fluctuation occurred before crystallization. In these blends with concentration fluctuation, the crystallization occurring in the PVDF-rich phase scarcely influenced by the weak interaction of PMMA.

According to the Turnbull-Fisher equation [11], the surface energy (σ) of crystal was given by nucleation rate (N) as follows:

$$\log N = N^{o} - STm^{2}/T_{C}\Delta T^{2} \qquad (3)$$

where

$$S = 2\sigma/R\Delta Hm^2 \quad (\text{for } \sigma >> \sigma_e) \tag{4}$$

The S value obtained from the linear relationship between log N and $T_m^2/T_C\Delta T^2$ was shown in Fig.2 (b) as a function of Φ_{PMMA}. The S value of PVDF/at-PMMA increased with the increase of Φ_{PMMA}, however PVDF/iso-PMMA showed the constant S value irrespective of Φ_{PMMA}. The σ value of the PVDF crystals in the blends depended on the concentration of PMMA in the amorphous region around crystallites. In a miscible blend, this PMMA concentration was thought to be equal to Φ_{PMMA}; therefore σ depended on Φ_{PMMA} for PVDF/at-PMMA. In an immiscible blend or the blend with concentration fluctuation, as crystallization occurred in the PVDF-rich phase, the PVDF crystal was surrounded by amorphous PVDF; therefore σ was independent of Φ_{PMMA}.

Conclusion

We have proposed new method to estimate the mixing state of polymer blend including crystalline polymer analyzing crystallization dynamics and conformational formation. In PVDF/PMMA blends, TGTG′ conformation proceeded the crystal growth during isothermal crystallization from the molten state. The Φ_{PMMA} dependency of G, G_C and σ suggested the different mixing state between PVDF/at-PMMA and PVDF/iso-PMMA blends.

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