Phase Separation Behavior of Blends of Poly(vinylidene fluoride-co-tetrafluoroethylene) and Poly(methyl methacrylate) by Differential Scanning Calorimetry

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ABSTRACT: Miscibility and phase separation were investigated in the blend of poly(vinylidene fluoride-co-tetrafluoroethylene) (P(VDF-TFE)) and poly(methyl methacrylate) (PMMA). The blends showed the single glass transition and melting point depression for all blend compositions, indicating that they are miscible. The phase separation behavior of a blend was elucidated by differential scanning calorimetry (DSC). On heating the blend samples, an endothermic peak in DSC thermogram appeared at the cloud point which was obtained from the change of optical transmittance of samples. The area under the endothermic curve was assumed to be the heat of demixing. It showed a maximum near 50 wt% of P(VDF-TFE). From the heat of demixing, the compositional dependence of interaction parameter was calculated and it was an increasing function of P(VDF-TFE) content.

KEY WORDS Polymer Blend / Phase Separation / Differential Scanning Calorimetry / Interaction Parameter /

Poly(vinylidene fluoride) (PVDF) is well known to be miscible with poly(methyl methacrylate) (PMMA) in the amorphous phase over an entire composition of two components.^{1–3} Many investigators have studied the melting behavior,⁴ morphology,^{5,6} crystallization kinetics,⁷ and thermodynamic interaction parameter of PVDF/PMMA blend.^{1,3} PVDF has been also reported to be miscible with poly(ethyl methacrylate), poly(ethyl acrylate), poly(vinyl methyl ketone), etc.^{8–10} It is generally accepted that miscibility arises from specific interactions between the dipole moment in PVDF and the carbonyl oxygen in the partner polymers.

The miscibility of polymer blend is attributed to the negative interaction parameter between the component polymers. In order to determine the interaction parameter, various methods have been used: melting point depression,^{1,9}

vapor sorption¹¹, calorimetric measurement of analog compound,¹² inverse-phase gas chromatography,¹³ and light scattering methods.¹⁴ Among these, differential scanning calorimetry (DSC) has been often carried out. The interaction parameter in the case of blend consisting of crystalline/amorphous polymers can be obtained from analysis of melting point depression. According to Nishi and Wang,¹ the interaction parameter in PVDF/PMMA blend is -0.265 at 160°C , whereas Wendorff³ reported the composition dependence of interaction parameter in that blend system. It was also reported that the interaction parameter can be determined from the values of glass transition temperature (T_g) and the difference in molar heat capacity at T_g s of component polymers by DSC measurement.

In this study, the miscibility and phase separation of a polymer blend are investigated

from DSC measurement. No observation of phase separation behavior using DSC measurement has been yet done in the study of a polymer blend. The blend in this study consisted of poly(vinylidene fluoride-*co*-tetrafluoroethylene) (P(VDF-TFE)) and PMMA. Calculation of enthalpy change due to phase separation of DSC measurement makes the quantitative evaluation of phase separation possible and leads to the determination of compositional dependence of interaction parameter between two components.

EXPERIMENTAL

Sample Preparation

P(VDF-TFE) was the random copolymer of 80 mol% vinylidene fluoride and 20 mol% tetrafluoroethylene and was supplied from Daikin Kogyo Co., Ltd. Atactic PMMA was supplied from Mitsubishi Rayon, Co., Ltd. Table I lists molecular weight distribution data from the gel permeation chromatography.

Using methylethylketone as a common solvent, homogeneous mixtures of P (VDF-TFE) and PMMA were obtained at various weight percents at room temperature. From the homogeneous mixture, films were cast at room temperature and dried at 80°C for 2 days. The films were subjected to further drying in a vacuum oven at 160°C for 3 days. The average thickness of sample ranged from 30 to 50 μm .

Measurements

Thermal properties were measured by DSC (Rigaku TG-DSC) with a sample of 10 ± 1 mg. A heating rate of $20^\circ\text{C min}^{-1}$ was used for the thermal analysis. Certain samples were also measured at rates ranging from 3 to 100°C

min^{-1} . Peak temperature was taken as a melting temperature (T_m) of sample.

X-Ray diffractions of samples were measured with a Rigaku SG-9 type X-ray diffractometer, using Ni filtered $\text{CuK}\alpha$ radiation at 35 kV and 30 mA at a scan speed of 2θ $2^\circ/\text{min}^{-1}$.

Cloud point measurements were carried out in the apparatus set up by our laboratory. The cloud point could be observed by measuring the change of optical transmittance of sample on heating and the apparatus was in principle similar to the apparatus of others.⁸ The transmittance of the sample was measured by using a CdS of which electrical resistance changed with the intensity of illuminated light through the sample. The electrical resistance of CdS was quite linear to the light intensity. The heating rate of 5°C min^{-1} was used in the measurement of cloud points. The temperature at which the transmittance began to drop rapidly on heating was taken as a cloud point.

The refractive index was measured with an Abbe refractometer by using a test piece of refractive index of 1.74 and by using methylene iodide as a contact liquid.

RESULTS AND DISCUSSION

Miscibility

All cast films of the blends were optically

Figure 1. Refractive indices of samples versus blend composition.

Table I. Molecular weight characteristics of samples

Polymer	$M_n \times 10^5$	$M_w \times 10^5$	M_w/M_n
P(VDF-TFE)	1.03	1.90	1.85
PMMA	1.20	2.70	2.25

Figure 2. X-Ray diffraction curves of samples for various weight compositions.

transparent at room temperature. The refractive index changed continuously with blend composition as shown in Figure 1. But two different refractive indices were observed in the blend films as the sample was heated to above the phase separation temperature. This indicates that P(VDF-TFE) and PMMA are miscible at room temperature but the phase separation occurs above the high temperatures.

Figure 2 shows the X-ray diffraction curves of blends having various compositions. Pure P(VDF-TFE) has a strong intensity at $2\theta = 20^\circ$. It is reflected by crystals of Form I similar to that of PVDF.¹⁵ A blend containing 70 wt% of P(VDF-TFE) also shows a strong peak near $2\theta = 20^\circ$ but its intensity decreases with the addition of PMMA. But for blends containing 50 wt% of P(VDF-TFE) or less, only an amorphous halo appears and it is shifted toward a smaller diffraction angle with increase of wt% of PMMA.

Miscibility is also evidenced by the existence of single T_g between each T_g of polymers. Figure 3 shows a plot of T_g and T_m versus blend

Figure 3. Composition dependence of melting (T_m) and glass transition temperatures (T_g).

Figure 4. DSC thermograms scanned at a heating rate of $20^\circ\text{C min}^{-1}$.

composition from DSC thermogram shown in Figure 4. Only single T_g was observed for all the samples. This indicates the miscibility of P(VDF-TFE) and PMMA. On the other hand, melting temperatures were observed for the P(VDF-TFE) rich blend due to the existence of

crystals for the sample containing 60 wt% of P(VDF-TFE) or more. This is in good agreement with the X-ray diffraction results. Melting temperature decreases with increase of weight percent of PMMA. It is usually well explained with the melting point depression phenomenon which appears in the case of a miscible blend of crystalline and amorphous polymers such as in the blend of PVDF/PMMA.¹⁻³

Phase Separation

In the DSC thermograms in Figure 4, an explanation for the endothermic peak near 200°C is required. It is below the degradation temperature. Designating the onset temperature of endothermic peak near 200°C as T_c , the relation between T_c and blend composition is shown in Figure 5. T_c curve is regarded as having some concern with the cloud point curve. That is, they may stem from the same origin. A slight mismatch between two curves could be ascribed to differences of heating rate of DSC (20°C min⁻¹) and cloud point (5°C min⁻¹) measurements. Phase separation behavior by cloud point measurement showed lower critical solution temperature behavior and was reversible during heating and cooling through the cloud point. The T_c curve was also very reproducible in DSC measurements

during heating or cooling. It implies that the endothermic peak near 200°C on DSC thermogram results from phase separation of the blend.

By visual observation, the transparent sample took on a faint blue color near phase separation temperature and on further heating, the sample turned out to be completely opaque. This was already reported in the blend of polystyrene/poly(vinyl methyl ether) (PS/PVME)¹⁶ and may be characteristic of the phase separation. But in the case of PS/PVME blend, no evidence of phase separation of DSC measurement was observed, through similar visual observation appeared in the PS/PVME blend. The sample in this study is a blend system similar to the blend of PVDF/PMMA. No detection of endothermic peak due to phase separation in DSC measurement of the PVDF/PMMA blend is perhaps ascribed to the fact that the phase separation of PVDF/PMMA blend occurs above the degradation temperature.

Endothermic enthalpy change due to phase separation was obtained from the area under DSC curve. A plot of the enthalpy change versus blend composition is shown in Figure 6. According to the Flory-Huggins-Scott expression, the enthalpy change (ΔH_c) with mixing is represented as

Figure 5. Plot of T_c (●) and cloud point (○) versus blend composition.

Figure 6. Compositional dependence of enthalpy change due to phase separation.

Figure 7. Compositional dependence of interaction parameter.

$$\Delta H_c = NRT \chi_{12} V_1 V_2 \quad (1)$$

where ΔH_c is the heat of mixing (cal g^{-1}), N is the number of moles of the segment in the system, R is the gas constant, T is the absolute temperature (K), χ_{12} is the interaction parameter and V_1 and V_2 are volume fractions of P(VDF-TFE) and PMMA, respectively. Assuming additivity of density so that the specific volume of sample is nearly proportional to the composition, eq 1 can be rewritten as

$$\Delta H_c = -\Delta H_{\text{sep}} = NRT \chi_{12} V_1 (1 - V_1) \quad (2)$$

where ΔH_{sep} is the enthalpy change due to phase separation. In this study, enthalpy change on phase separation show a maximum value near the composition of 50 wt% of P(VDF-TFE). The interaction parameter estimated by eq 2 is shown in Figure 7. The values of interaction parameters are negative for all compositions and close to zero for samples containing rich PMMA. This means that the interactions are stronger for samples containing rich P (VDF-TFE) than in the PMMA rich system. This is similar to that of the PVDF/PMMA blend elucidated using SAXS measurement.³ The interaction parameter in this study is smaller than that of -0.295 at 160°C obtained from the PVDF/PMMA blend by Nishi *et al.*¹ and the phase separation temperature is lower. This is ascribed to the effect of tetrafluoroethylene units in the copolymer

CONCLUSIONS

From DSC measurement of miscible blend of P(VDF-TFE) and PMMA, phase separation behavior was elucidated. The phase separation temperature observed as an endothermic peak on heating was almost equal to a cloud point. The enthalpy change due to phase separation was calculated from the area under the phase separation curve on a DSC thermogram. This led to determination of the compositional dependence of the interaction parameter. The value of the interaction parameter was negative for all compositions and indicated that the blend is miscible for all compositions and that the blend with rich P (VDF-TFE) has stronger interaction between two components.

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