Evaluation of Compatibility in Polymer Blend Systems By Simultaneous DSC-FTIR Measurement

H. Yoshida,

Graduate School of Urban Environmental Science, Tokyo Metropolitan University, Hachiouji, Tokyo 192-0397, Japan

CREST, JST, Japan

[Introduction] Compatibility of organic materials including polymers is essentially described by thermodynamics, such as Huggins-Flory [1] and Simha theory [2] for universal binary systems, and Nishi-Wang equation [3] for blend system with crystalline polymer. With increasing molecular weight of components, however, blend systems become difficult approaching the equilibrium state due to low diffusion coefficient. We have proposed "crystallization dynamics method" to evaluate the miscibility of binary polymer blend systems containing crystalline component [4]. In this method, the crystal growth rate and the surface energy of crystallites depend on blend content for the miscible systems, however, are independent on blend content for the immiscible systems. In this study, the crystallization dynamics method was extended to evaluate the concentration fluctuation in both miscible and immiscible binary systems using the simultaneous DSC-FTIR method.

Crystallization process consists of nucleation and crystal growth processes. Crystal growth proceeds by a supply of molecules from liquid state to growth surface of crystal by self-diffusion, and this diffusion process is a rate-determining process for organic molecules and polymers. The diffusion distance of molecules is estimated in the order of double radius of gyration (2Rg) of molecules considering the reptation mode [5]. The average crystal growth rate is influenced by diffusion coefficient of molecules. On the other hand, polymer molecules obtain three orderings, positional, conformational and orientation to crystallize from the isotropic state, and these ordering processes are observed as an endothermic process by thermal analysis. Conformational ordering process is intramolecular process, which is influenced by intermolecular interaction among closed neighboring molecules. In this study, both the crystal growth rate and the conformational ordering rate during the isothermal crystallization were determined simultaneously by DSC-FTIR for poly(vinylidene fluoride) and poly(alkyl methacryalte) blend systems in order to evaluate the compatibility of blend components.

[Experimental] PVDF supplied by Kureha Chemical Co. Ltd, atactic poly(methyl methacrylate) (PMMA) supplied by Mitsubishi Resin Co. Ltd, isotactic PMMA, syndiotactic PMMA and atactic Poly(alkyl methacrylate)s (alkyl = ethyl, isopropyl, tertiary butyl) were used in this study. Polymer blends were prepared by solvent casting method from N,N-dimethylacetamide solution. The blend content of poly(alkyl methacrylate)(ϕ) was 0 - 0.4 in weight fraction. After casting and drying, blend samples were pressed at 473 K and were quenched to ice water. The obtained blend films were further dried under vacuum at room temperature for 24 hours. Blend film sandwiched with two thin KBr dishes and cramped in an aluminum sample vessel was used for DSC-FTIR measurement. Sample weight used was about 1.5 mg.

The simultaneous DSC-FTIR measurement was carried out by setting the simultaneous DSC instrument [6] on the JASCO FTIR 620 with MCT (Mercury Cadmium Telluride) detector in the wavelength range between 650 cm^{-1} and 4000 cm^{-1}. The accumulation of one spectrum and the wavelength resolution were 2 times and 2 cm^{-1}, respectively. Under this condition, the time resolution of FTIR spectra was 15 sec. The scanning velocity and the time resolution of DSC were 5 $Kmin^{-1}$ and 1.0 sec, respectively. The sample was heated to 473 K and maintained at that temperature for 5 min, then quenched to a predetermined crystallization temperature (T_c).

[Results and Discussions] The crystallinity change at each Tc was determined by partial integration of exothermic DSC peak, and was plotted against time. The change of TGTG' conformation of PVDF was defined by the relative absorbance change at 763 cm^{-1}. The half time of crystallinity and TGTG' conformational changes were determined at each Tc, and the reciprocal half times were employed as the crystal growth rate (G*) and the conformational ordering rate (Gc), respectively.

From G* *vs.* Tc and Gc *vs.* Tc plots, a temperature (T*) at which G* or Gc established 0.005 s^{-1} were evaluated, and then $\Delta T_{G=0.05}$ (= T_m - T*) was obtained for each blend content. Gibbs energy for crystal growth is written by, $\Delta G = \frac{\Delta H_m \Delta T}{T_m}$, where ΔH_m is a latent heat of fusion. Fig. 1 shows relationship between Gibbs energy terms obtained for crystal growth (G*) and conformational growth (Gc) processes for the miscible blend systems, PVDF/at-PMMA, PVDF/syn-PMMA and PVDF/PEMA. For all miscible systems showed a good liner relationship with slope = 1. Fig.2 showed the same relationship with Fig.1 for the immiscible blend systems for PVDF/PiPMAA, PVDF/iso-PMMA and PVDF/PtBMA. All immiscible systems showed liner relationships with different slopes. The slope of PVDF/PiPMA was 1, however, PVDF/iso-PMMA showed small value of slope and PVDF/PtBMA showed larger value.

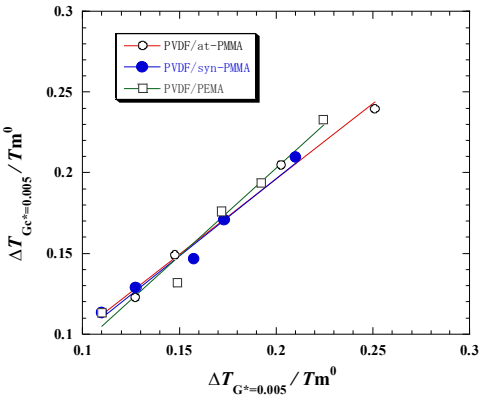

Fig.1 Relationship between Gibbs energy difference evaluated from G* and Gc for PVDF/at-PMMA, PVDF/syn-PMMA and PVDF/PEMA

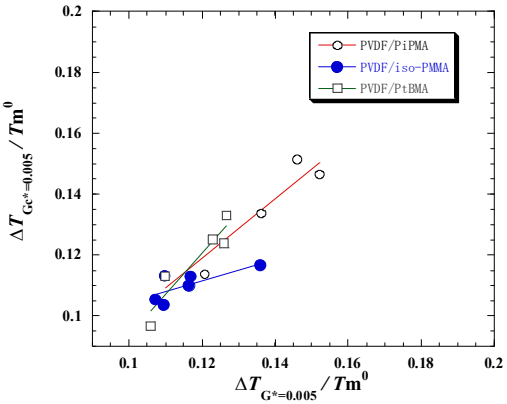

Fig.2 Relationship between Gibbs energy difference evaluated from G* and Gc for PVDF/PiPMA, PVDF/iso-PMMA and PVDF/PtBMA

G* indicated the diffusion process of molecules which reflected the concentration profile in the distance range of 2Rg, which evaluated from molecular weight of PVDF was 40 nm. Gc indicated the conformational change in molecules, which reflected the interaction among neighboring molecules in the range of 1 nm. For the miscible systems, PVDF molecules were existed in the same circumstances having similar interaction field both in the distance 1 and 40 nm. However, the crystallization occurred in the phase separated PVDF-rich phase for the immiscible systems. The conformational ordering occurred faster than the molecular diffusion for PVDF/iso-PMMA system. This fact indicated that the populations of iso-PMMA molecules in the range of 1 and 40 nm differed; in other words, the concentration fluctuation existed in the range between 1 and 40 nm for PVDF/iso-PMMA.

References

1. M. L. Huggins, J. Chem. Phys., 9, 440 (1941), P. J. Flory, *J. Chem. Phys*., **9**, 660 (1941)
2. R. K. Jain, R. Simha, *Macromolecules*, **13**, 1501 (1980)
3. T. Nishi, T. T. Wang, T. K. Kwei, *Macromolecules*, **8**, 227 (1975)
4. H. Sasaki, G. Bara, H. Yoshida, *Polymer*, **25**, 4805 (1995)
5. P-G. De Gennes,"Scaling Concepts in Polymer Physics", p.224, Cornell University Press (1979)
6. H. Yoshida, R. Kinoshita, Y. Teramoto, *Thermochimica Acta*, **264**, 173 (1995)