Notes

Light Scattering Studies on the Phase Structure of Ethyl Acetate Casting PMMA/PVAc Blends

Chang-Sik Ha*, Won-Ki Lee, and Won-Jei Cho

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

T. Ougizawa and T. Inoue[†]

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152, Japan

Received October 20, 2000

Abstract : In this work, we present the development of phase structure of the poly(methyl methacrylate) (PMMA)/ poly(vinylacetate)(PVAc) mixtures in ethyl acetate solution by light scattering. The PMMA/PVAc blends cast from ethyl acetate solutions exhibited fine "modulated structures" over broad blend composition ranges, which originated from the spinodal decomposition of the ternary polymer solutions at low polymer concentrations during the casting. The periodic distance was depended on the blend compositions and evaporation times.

Introduction

Many experimental works have been conducted on the demixing processes of polymer blends to control the phase separation structure of polymer mixtures.[1-5] However, most of these works have been limited to the thermally-induced phase transitions in polymer-polymer systems, such as poly (methyl methacrylate)/poly(styrene-co-acrylonitrile) and poly(vinyl methyl ether)/polystyrene(PS) having the lower critical solution temperature(LCST) and poly(methyl phenyl siloxane)/PS having the upper critical solution temperature (UCST). Instead, very few works have been reported on the phase separation structure of the blends during solution casting.[6-8]

In general, the phase separation structures of polymer blends have poor regularity in shape and size. Particularly, the solution casting of an incompatible polymer blend usually results in the two-phase morphology having irregular shape and size

of domains. Inoue *et al.*, however, reported[6] that a regularly phase-separated structure with a periodic distance of 1.4 μm was found in a 50/50 blend of poly(vinyl chloride)(PVC) and poly(acrylonitrile-co-butadiene)(NBR) having 26 wt% of acrylonitrile when they were cast from tetrahydrofuran (THF) solutions. They defined the structure with the periodicity and the dual connectivity of the phases, which are similar in appearance to the phase structure formed by spinodal decomposition, as "modulated structure". They also studied the casting process from the ternary solution(A polymer/B polymer/solvent) to dry film by using the light scattering technique to answer two fundamental questions (1) why and how does the modulated structure develop and (2) what the molecular and thermodynamic factors affecting the modulated structures.[6,7]

Recently, Kano *et al.* also reported that a gradient domain morphology was developed for poly (2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate)/poly(vinylidene fluoride-co-hexafluoacetone) blends during solution casting according to both spinodal decomposition and nucleation and growth mechanism when they were cast from THF

*e-mail : csha@hyowon.pusan.ac.kr
[†]present address : Department of Polymer Science and Engineering, Yamagata University, Yamagata 992, Japan

solutions.[8,9]

In this work, we found that the poly(methyl methacrylate) (PMMA)/ poly(vinylacetate) (PVAc) blends cast from ethyl acetate solution also showed such modulated structure over all the blend compositions. We report, here, the development of phase structure of the PMMA/PVAc mixtures in ethyl acetate solution by light scattering.

Experimental

The characteristics of the polymers used in this study are summarized in Table I. Weighed PMMA and PVAc of various compositions were dissolved at 20 wt% of total polymer in ethyl acetate. The solution was poured into a shallow glass dish (7 mm deep and 50 mm in diameter) with a flat glass cover. Both the cover and bottom are made of optically-flat glass. The depth of solution in the dish was ca. 2 mm. The rate of evaporation was controlled by adjusting the gap between the cover and dish. The polymer concentration during the casting process was monitored by measuring the weight of the whole dish. The dish was set horizontally on the light scattering stage, as in Figure 1. The radiation of He-Ne laser of 632.8 nm wavelength was applied vertically to the bottom of the dish. A goniometer trace of the intensity of

scattered light from the solution was given by the light scattering apparatus shown in Figure 1. Thus, the change of light scattering profile was observed during the evaporation(casting) process at room temperature.

Results and Discussion

Figure 2 shows a typical light scattering profile from the cast films of 7/3 PMMA/PVAc blend obtained for various rates of solvent (ethyl acetate) evaporation. The evaporation time is given in the right upper table inside the figures. The scattering peaks appearing initially at early evaporation time, i.e. low polymer concentrations, shifts to smaller scattering angles during evaporation. This implies some degree of coarsening of the structure. After the polymer concentration had passed 70 wt% and the rate of evaporation had slowed, the concentrated solution was further dried under vacuum for 10 hrs. The structure of the dried film was observed by placing a white paper beneath the film. For all the blend films in this work, clear ring patterns were projected on the paper, which can be easily observed by naked eyes. The results mean that all the ethyl acetate cast PMMA/PVAc blends possess a highly interconnected two-phase morphology with uniform domain size, i.e. "modulated

Table I. Materials and Their Characteristics

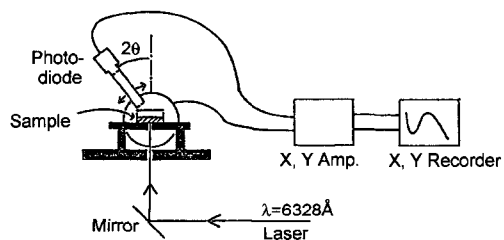| Material	Properties	Source
PMMA	$M_w = 99,300$	LG Chem. Ltd.
	$M_w/M_n = 1.53$	Polym. Res. Center
PVAc	$M_w = 78,800$	Junsei Co.
	$M_w/M_n = 1.46$	

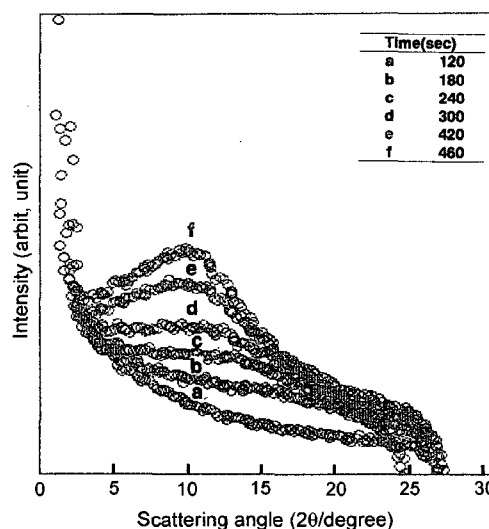**Figure 1.** Schematic diagram of light scattering apparatus in this work.

Figure 2. Change of light scattering profile during casting process for the 7/3 PMMA/PVAc blend film. The evaporation time is given in seconds inside the figure.
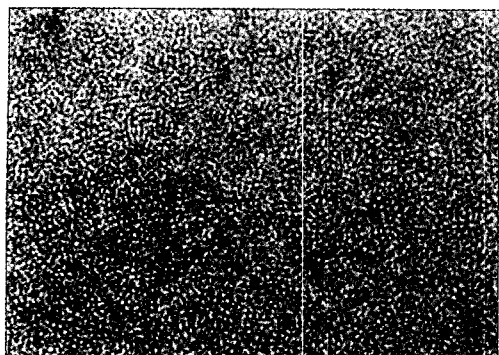
Figure 3. Optical micrograph of the ethyl acetate cast 50/50 PMMA/PVAc blend film, taken after completely dried, showing a typical phase-separation morphology of spinodal decomposition in polymer blends.

structure", a characteristic morphological feature similar in appearance to the structure formed by spinodal decomposition, as demonstrated in thermally-induced phase transitions in polymer-polymer systems. The morphology of spinodal decomposition can be easily identified if one takes optical micrographs of the dried blend films. Figure 3 shows the ethyl acetate cast 50/50 PMMA/ PVAc blend film, taken after completely dried. The micrograph clearly illustrates a typical phase-separation morphology of spinodal decomposition in polymer blends. Saito *et al.* systematically investigated the thermally-induced demixing process of PMMA/PVAc blends cast from chloroform at the temperatures above their LCST.[10-13]

Figure 4 shows the effect of blend ratio on the development of modulated structure. Regularly

phase-separated structures with various periodic distances were found in the blends, depending on the blend compositions and evaporation times. For example, the 40/60 blend of PMMA and PVAc showed a periodic distance of 1. 52 μm when the evaporation time was 120 sec. The periodic distance varied from1.5 to 5.0 μm in the evaporation time ranges from 200 to 1,000 sec for 3/7 compositions; from 2 to 6 μm in the range from 30 to 40 sec for 5/5 compositions; 1.5 to 2.5 μm from 200 to 500 sec.

Figure 4 shows that the larger the deviation of the blend ratio from symmetry (e.g. from 5/5 to 7/ 3 or 3/7), the slower the rate of phase separation and the higher the concentration at which the scattering peak was initially detected and the higher the angle of final scattering peak, suggesting a shorter periodic distance in the modulated structure. In the case of symmetrical blend (5/5 blend system), the scattering peak initially appears at the lowest concentration and the final scattering peak is at the lowest scattering angle, suggesting the longest periodic distance in the modulated structure. The results are coincident with the PVC/ NBR cast from THF solution, reported by Inoue *et al.*[6,7] They interpreted the results in terms of the phase separation kinetics based on the Flory-Huggins theory.

The kinetics of the phase separation is based on the maximum rate constant of fluctuation growth, R_m. One of the most characteristic features of the spinodal decomposition elucidated by the linearized theory is the exponential nature of the
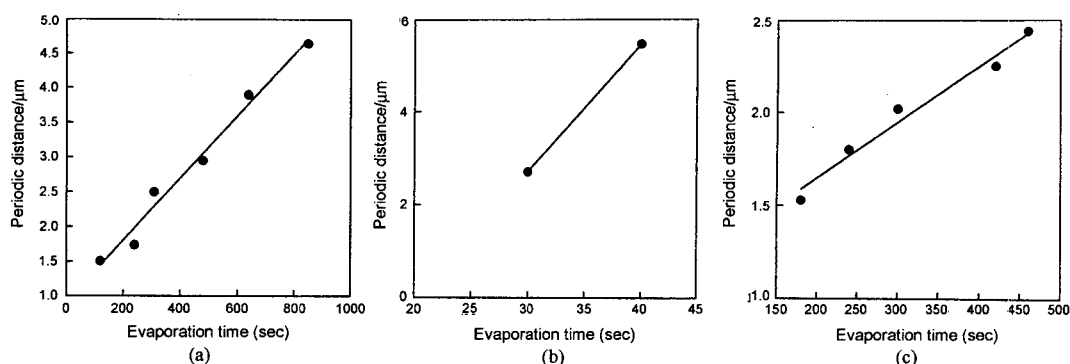

Figure 4. Dependence of periodic distance on the rate of solvent evaporation for the (a) 3/7, (b) 5/5, and (c) 7/3 PMMA/PVAc blend film obtained by a casting process(solvent; ethyl acetate).

growth rate of the composition fluctuation: that is, the periodic distance of the fluctuation should be dominated by R_m.

When R_m can be assumed to be a rate constant of phase separation, the following relationship holds between $\theta_A(t)$ and R_m as follows;

$$| \; \theta_A(t) - \theta_A(t=0) \; | \; \propto \; exp(R_m \cdot t) \tag{1}$$

where θ_A is a volume fraction of polymer A and t is a time.

The R_m parameter is a function of Flory interaction parameter, χ_{AB}, relative volume fractions of polymer A and B, θ_A, θ_B, and spinodal volume fraction of total polymers, $\varphi_p{}^s$, as follows;

$$R_m = f(\chi_{AB}, 1/N) \; \varphi \; (\varphi_p - \varphi_p^s)^2 \tag{2}$$

Where N is the degree of polymerization and φ_p is a volume fraction of total polymers.

Also, the Flory-Huggins theory on the free energy of mixing gives

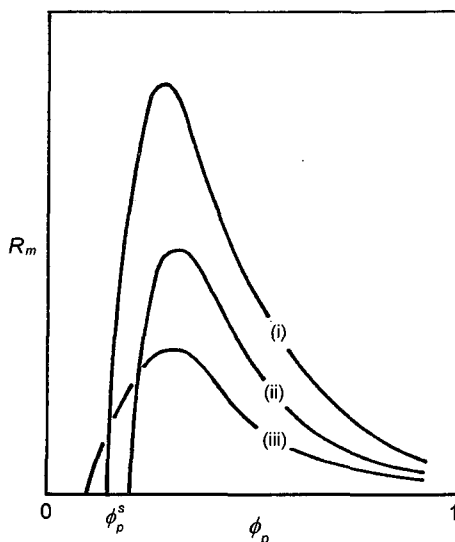$$\varphi_p^s \propto (\chi_{AB}\theta_A\theta_B)^{-1} \tag{3}$$

Figure 5. Concentration dependence of R_m, showing the effects of χ_{AB}, blend ratio $\theta_A\theta_B$, and degree of polymerization N. (i) larger χ_{AB}, $\theta_A \doteq \theta_B$, (ii) small χ_{AB}, $\theta_A < \theta_B$, and (iii) large N.

Schematic curves in Figure 5 show the change of R_m- φ_p relation with various factors such as the polymer-polymer interaction parameter, blend ratio and degree of polymerization, which was drawn according to equations (1) through (3).[6,7] Equation (3) shows that for a symmetrical polymer pair, the larger the χ_{AB}, the smaller the $\varphi_p{}^s$. The symmetrical blend of $\theta_A = \theta_B$; 50/50 blend) gives the maximum of the product $\theta_A\theta_B$. The larger the deviation from the symmetry, the smaller the product θ_A and θ_B, and hence the larger the R_m. Therefore, the deviation of blend ratio from symmetry shifts the R_m- φ_p curve from I to II.

When the rate of solvent evaporation is small, appreciable phase separation is expected to occur at low concentration but when the rate of evaporation is large, appreciable phase separation is not expected to occur at low concentration and instead to occur at higher concentration. That is, when the evaporation rate is fairly high, appreciable phase separation cannot occur during casting even in the unstable region, until the evaporation proceeds to the higher polymer concentration. Therefore, the larger the rate of solvent evaporation, the smaller the periodic distance in the modulated structure. If the evaporation is much faster, appreciable phase separation fails to occur even at the concentration.

For the 2/8 and 8/2 compositions, the periodic distance varied from 2.8 to 3.2 μm in the range of 200 to 600 sec and 1.2 to 1.9 μm in the range of 200 to 1400 sec, respectively.

In summary, the PMMA/PVAc blends cast from ethyl acetate solutions exhibited fine "modulated structures" over broad blend composition ranges, which originated from the spinodal decomposition of the ternary polymer solutions at low polymer concentrations during the casting. The larger the deviation of the blend ratio from symmetry (e.g. from 5/5 to 7/3 or 3/7), the slower the rate of phase separation and the higher the concentration at which the scattering peak was initially detected and the higher the angle of final scattering peak, suggesting a shorter periodic distance in the modulated structure. In the case of symmetrical blend (5/5 blend system), the scattering peak initially appears at the lowest concentration and the final scattering peak is at the lowest scattering angle,

Korea Polym. J., Vol. 9, No. 1, 2001

69

suggesting the longest periodic distance in the modulated structure.

In our previous works, we found that the miscibility of the solution-casting PMMA/PVAc blends strongly depends on the choice of solvents.[13,14] It should be noted that the construction of a ternary phase diagram based on the polymer(1)/polymer(2), polymer(1)/solvent, and polymer(2)/solvent interaction parameters is quite necessary to interpret quantitatively the exact phase behavior of the polymer-polymer-solvent ternary system using a theoretical solution thermodynamics such as the Scott-Tompa theory.[15] Therefore, more detailed phase behavior and phase structure of the PMMA/PVAc blends cast from other various solvents as well as ethyl actate with some theoretical approaches are now underway and will be reported elsewhere.

References

(1) Z. Liu and Q. Guo, *J. Therm. Anal. Calor.*, **59**, 101 (2000).

(2) W. K. Lee, W. J. Cho, A. Takahara, T. Kajiyama, and C. S. Ha, *Polymer*, **36**, 1229 (1995).

(3) P. L. Rinaldi, T. Wagler, C. D. Han, and H. Chun, *Macromolecules*, **33**, 1778 (2000).

(4) W. B. Liau and C. F. Chang, *J. Appl. Polym. Sci.*, **76**, 1627 (2000).

(5) Q. Guo, S. Zheng, J. Huang, and J. Li, *J. Appl. Polym. Sci.*, **69**, 675 (1998).

(6) T. Inoue, T. Ougizawa, O. Yasuda, and O. Miyasaka, *Macromolecules*, **18**, 873 (1985).

(7) O. Yasuda, T. Ougizawa, T. Inoue, and K. Miyasaka, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 813 (1983).

(8) Y. Kano, H. Sato, M. Okamoto, T. Okamoto, T. Kotaka, and S. Akiyama, *J. Adhes. Sci. & Technol.*, **13**, 1243 (1999).

(9) S. Akiyama, Y. Kano, M. Inoue, I. Akiba, H. Sano, and H. Yui, *J. Adhes. Sci. & Technol.*, **12**, 415 (1998).

(10) M. Konno, Z. Y. Wang, and S. Saito, *Polymer*, **31**, 2330 (1990).

(11) Z. Y. Wang, M. Konno, and S. Saito, *J. Chem. Phys.*, **90**(2), 1281 (1989).

(12) Z. Y. Wang, M. Konno, and S. Saito, *J. Chem. Eng. Jpn.*, **22**, 429 (1989).

(13) W. K. Lee and C. S. Ha, *Polymer(Korea)*, **18**, 793 (1994).

(14) C. S. Ha, W. K. Lee, and W. J. Cho, *Macromol. Symp.*, **84**, 279 (1994).

(15) L. Zeman and D. Patterson, *Macromolecules*, **5**(4), 513 (1972) and references therein; especially including (a) R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949) and (b) H. Thompa, *Trans. Fraday Soc.*, **45**, 1142 (1949).

70

Korea Polym. J., Vol. 9, No. 1, 2001