Dynamical study on the late stage of demixing in poly(methyl methacrylate) and poly(vinyl acetate) blends

M. Konno, Z.-Y. Wang and S. Saito*

Department of Molecular Chemistry and Engineering, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai 980, Japan

A dynamical study was made on demixing of an immiscible polymer blend, whose specimens were prepared by solvent casting and had very finely phase separated structures in the initial stage of the demixing. Light scattering experiments showed the applicability of a scaling rule to the later stage of the growth of phase separation structures. The demixing can be described by a scaling theory proposed by Furukawa.

INTRODUCTION

The dynamics of demixing in polymer blends has been the subject of extensive research in recent years. Most work has been devoted to studying the early stage of spinodal decomposition for a number of polymer pairs with phase diagrams[1-4]. Recently, Hashimoto et al. have reported experimental work on demixing of some immiscible systems, such as polypropylene (PP)/ethylene–propylene random copolymer (EPR)[5] and polybutadiene (PB)/styrene–butadiene (SBR) random copolymer[6]. For the PB/SBR system extremely slow demixing was observed in the early stage[5], and a pinning down in structure growth was found for off-critical compositions in the late stage[7]. This peculiar behaviour implied a complex demixing mechanism in immiscible blend systems. Other experimental work on the polymer blend system, poly(methyl methacrylate) (PMMA)/poly(vinyl acetate) (PVAc), which is known to be an immiscible system, has been done by the present authors[8,9]. In our study it was observed that an interconnected phase separation structure formed in the early stage of the demixing process and then increased in size with demixing time. However, it is unclear whether the demixing of this system follows critical or off-critical behaviour. This aspect is worthy of exploration by testing with the new scaling law of Furukawa for the shape of the structure function.

In this work we report on demixing of PMMA/PVAc blends in the late stage of spinodal decomposition and compare the experimental results with predictions from Furukawa's scaling rule[10,11].

EXPERIMENTAL

Commercial polymers were used (Wako Pure Chemical Industries Ltd; $M_n = 5.1 \times 10^4$, $M_w/M_n = 1.9$ for PMMA; $M_n = 7.1 \times 10^4$, $M_w/M_n = 3.0$ for PVAc). PMMA and PVAc were dissolved in the common solvent chloroform at a total polymer content of 10 wt% and at PMMA/PVAc weight ratios of 1:1, 2:3 and 3:7. The solution was cast on a slide glass at room temperature and the solvent was evaporated naturally for two days. Subsequently, the solvent-cast film was completely dried in a vacuum oven and a transparent polymer film of thickness of 100–150 μm was obtained.

The polymer films prepared were subjected to demixing experiments performed using small-angle light scattering apparatus equipped with a programmable heating chamber and a He–Ne laser source. The isothermal demixing processes of the polymer blends at different compositions were observed by a light-scattering technique after the temperature had been rapidly raised to a desired value. Details of the experimental procedure are given in a previous work[8].

As previously reported[8], polymer film specimens had phase separation structures, which might affect the demixing processes of the polymer blend. To check the reproducibility of the experiments, polymer films of the same blend were also prepared with toluene as casting solvent and subjected to demixing experiments.

RESULTS AND DISCUSSION

Figure 1 shows the transient distributions of intensities of light scattered from a specimen with 50 wt% PVAc at 168°C plotted as a function of the scattering vector, q, defined as

$$q = (4\pi/\lambda) \sin(\theta/2) \qquad (1)$$

where λ is the wavelength of light and θ the scattering angle. With increasing demixing time, the peak of the distribution moves towards a smaller scattering vector, corresponding to the smaller scattering angle. This indicates the growth of the domains of phase separation structure during the demixing.

Figure 2 shows the time dependence of the scattering vector, q_m, at which the maximum intensity of the scattered light appears. The experimental data were obtained at temperatures of 168 and 153°C with specimens cast from both chloroform and toluene solutions. The
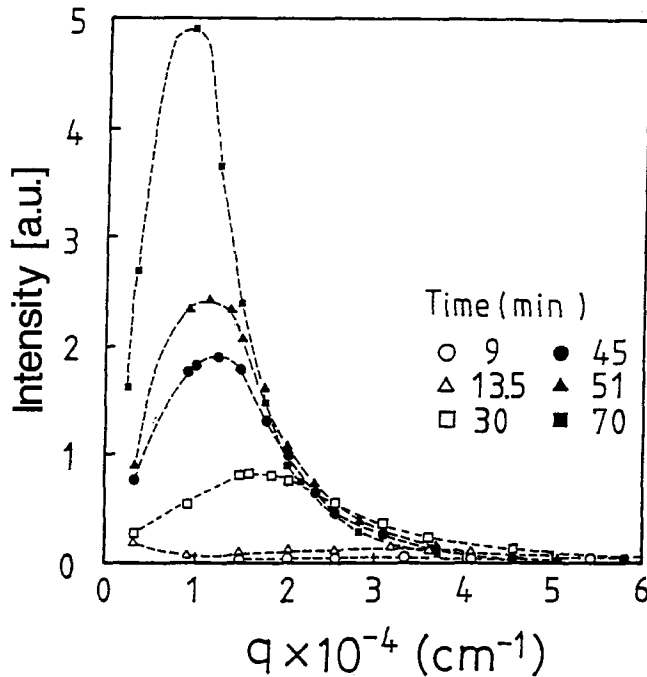
---

* To whom correspondence should be addressed

Figure 1 Time evolution of intensity distributions of scattered light from a blend of PMMA/PVAc (2:3) at 168°C

where I_m is the maximum intensity of scattered light, d the spatial dimensionality, and α and β are exponents. *Figure 3* shows logarithmic plots of I_m against demixing time t under experimental conditions corresponding to *Figure 2*. *Figures 2* and *3* show that q_m and I_m can be well expressed by the functional forms of equations (2) and (3). *Table 1* summarizes the values of α and β obtained in all experiments. The values of α were in the range 0.5–0.8 and those of β in the range 1.4–2.2, corresponding to a change in β/α from 2.8 to 2.7. The values of β/α are close to the theoretical value of 3 predicted from the above equations with $d = 3$, which is a major prerequisite for the application of Furukawa's model.

Before comparing experimental results with predictions obtained from Furukawa's model, it is interesting to compare the values of α and β with those obtained in the spinodal decomposition of miscible polymer blends. Hashimoto et al.[13,14] reported experimental results in both the intermediate and late stages of spinodal decomposition with a polystyrene and poly(vinyl methyl ether) system. In the intermediate stage, α ranged from 0.2 to 0.3 and β from 1.0 to 1.2, whereas in the late stage α ranged from 0.5 to 0.8 and β from 1.5 to 2.0. The values of α and β obtained in the present work are close to those in the late stage of spinodal decomposition, in which the
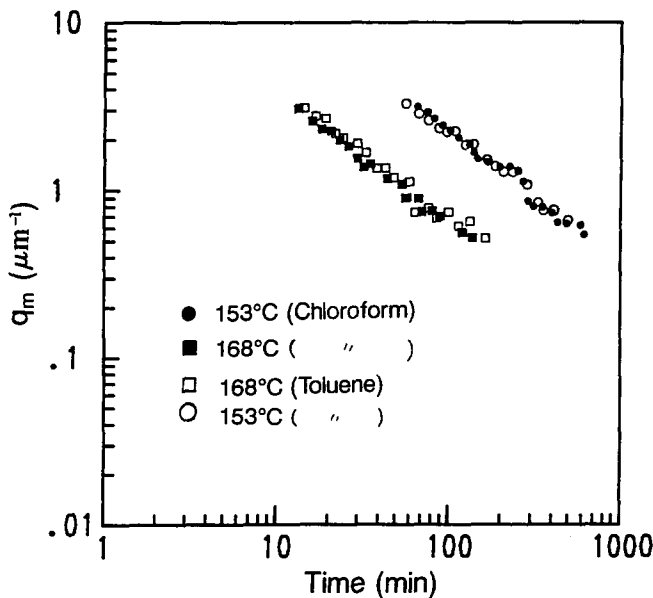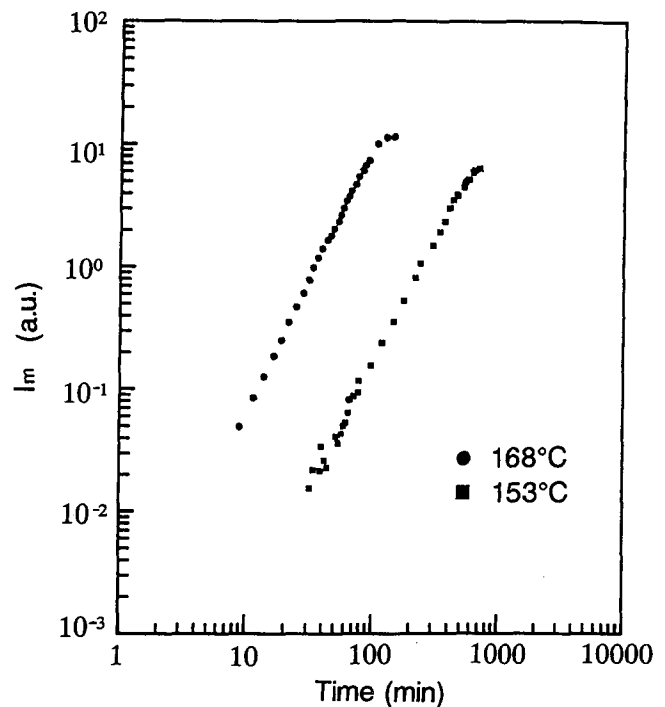

Figure 2 Logarithmic plot of q_m versus time with specimens cast from chloroform and toluene solutions at 153 and 168°C

figure shows that the choice of casting solvent has no effect on the variation of q_m with time. This suggests that the phase separation structure of the specimens used were too fine to retain their effects in the later stage of the demixing.

Binder and Stauffer[12] proposed scaling rules, assuming that clusters aggregate by a diffusion process and coalesce into larger clusters, resulting in the growth of phase separation structures that keep 'self-similarity'. They hold the evolution of the demixing process to be characterized by only a single parameter $R(t)$, which represents the average domain distance of the phase separation structures, and eventually derived the following equations:

$$q_m \propto R(t)^{-1} \propto t^{-\alpha} \tag{2}$$

$$I_m \propto R(t)^{-d} \propto t^{\beta} \tag{3}$$

Figure 3 Logarithmic plot of I_m versus time for PMMA/PVAc (1:1) at 153 and 168°C

Table 1 Values of α and β in power law expressions for q_m and I_m against t

Composition (PMMA/PVAc)	Temp. (°C)	α	β	β/α
1:1	168	0.80	2.2	2.8
	158	0.71	1.6	2.7
	153	0.71	2.1	3.0
2:3	168	0.80	2.1	2.6
3:7	168	0.79	1.7	2.6

applicability of Furukawa's model to the miscible system was confirmed. Gilmer *et al.*[15] reported similar values of α and β with a polystyrene and poly(o-chlorostyrene) system.

According to Furukawa[10,11], the following scaling law can be expected in the late stage of spinodal decomposition when self-similarity in structure is maintained during the process:

$$S(X) = X^2/(\gamma/2 + X^{2+\gamma}) \qquad (4)$$

where

$$X = q/q_m \qquad (5)$$

and $S(X)$ is a scaled structure function, which is related to scattered light intensity by the following equation:

$$S(X) = q_m^3 I(q, t) \qquad (6)$$

The value of γ equals $d + 1$ ($=4$) for off-critical composition (cluster regime) and $2d$ ($=6$) for critical composition (percolation regime). In the region of sufficiently large
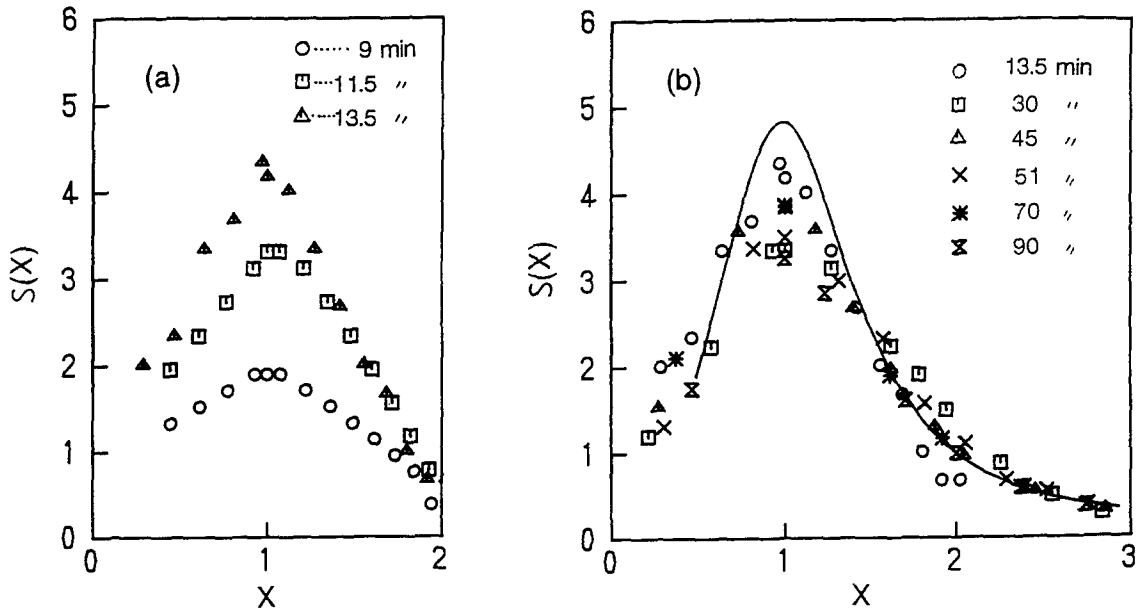

Figure 4   Scaled structure function in different time regions for PMMA/PVAc (1:1) at 168°C
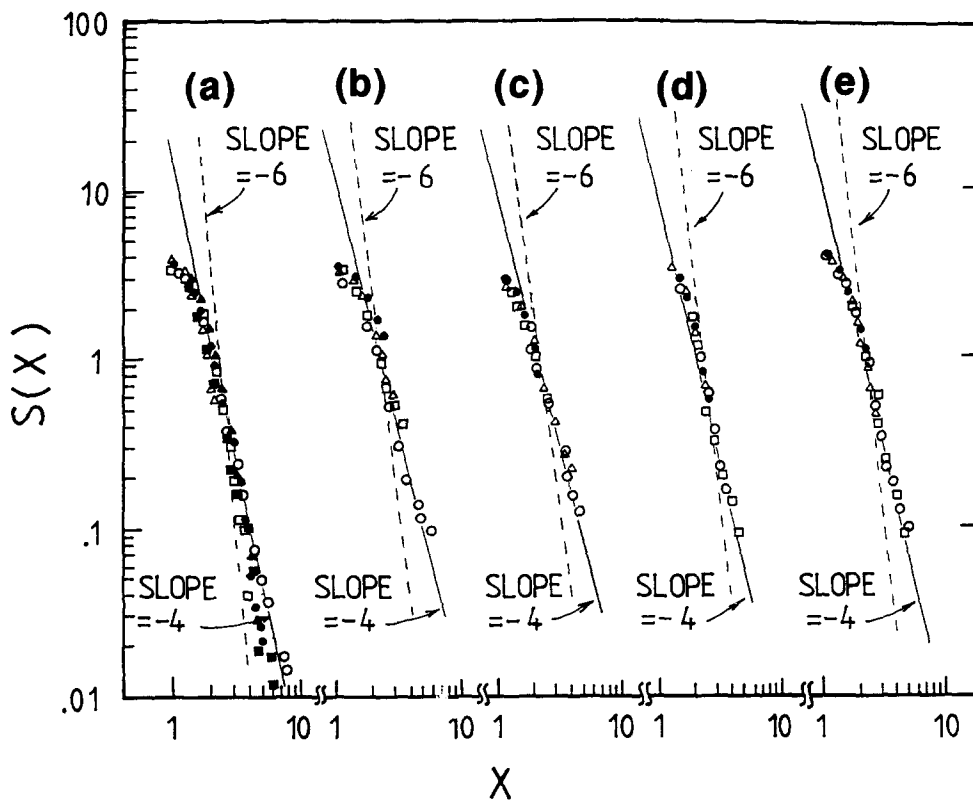

Figure 5   Logarithmic plots of $S(X)$ versus X for $X > 1$ for specimens under experimental conditions corresponding to *Table 1*. (a), (b) and (c) 1:1 Blend; 168, 158 and 153°C, respectively; (d) 168°C, 2:3 blend; (e) 168°C, 3:7 blend

X, a simple relation $S(X) \propto X^{-\gamma}$ can be expected from equation (4).

From the measurements of the scattered light intensity values of $S(X)$ were calculated from equation (6). *Figure 4* shows the plots of $S(X)$ during the early and late stages of the demixing at 168°C and a PMMA/PVAc weight ratio of 1:1. At each scattering vector the experimental value of $S(X)$ increases with time in the early stage before 15 min, as shown in *Figure 4a*, where both the dominant wavelength and the amplitude of composition fluctuations may be considered to grow with time, resulting in a breakdown in dynamic scaling, as pointed out by Hashimoto *et al.*[13]. On the other hand, in the late stage shown in *Figure 4b* the data indicate the applicability of the scaling law to the immiscible polymer blend. It appears that the experimental results are correlated by equation (4) by taking $\gamma = 4$ rather than $\gamma = 6$.

To show this conclusion more clearly, all the data are plotted on double logarithmic scales in *Figure 5*. The slopes of the experimental curves of $S(X)$ come close to 6 rather than 4 in regions of large X. This implies that the demixing of the immiscible polymer system in the later stage follows the mechanism of cluster coarsening. It seems, then, reasonable to regard an immiscible mixture as an off-critical rather than a critical mixture. Therefore, it is more plausible that the present experimental results for demixing are consistent with the prediction in which γ is taken to equal 4, while those for the critical mixture reported by Hashimoto *et al.*[13] compared well with a prediction that took γ as equal to 6.

ACKNOWLEDGEMENT

REFERENCES

1 Hashimoto, T., Kumaki, J. and Kawai, H. *Macromolecules* 1983, **16**, 641
2 Snyder, H. L., Meakin, P. and Reich, S. *Macromolecules* 1983, **16**, 757
3 Han, C. C., Okada, M., Muroga, Y., McCrackin, F. L., Bauer, B. J. and Tran-Cong, Q. *Polym. Eng. Sci.* 1986, **26**, 3
4 Sato, T. and Han, C. C. *J. Chem. Phys.* 1988, **88**, 2057
5 Inaba, N., Sato, K., Suzuki, S. and Hashimoto, T. *Macromolecules* 1986, **19**, 1690
6 Izumitani, T. and Hashimoto, T. *J. Chem. Phys.* 1985, **83**, 3694
7 Takenaka, M. and Hashimoto, T. *Polym. Prepr. Jpn* 1988, **37**(7), 2085
8 Wang, Z.-Y., Konno, M. and Saito, S. *J. Chem. Eng. Jpn* 1989, **22**, 429
9 Wang, Z.-Y., Konno, M. and Saito, S. *J. Chem. Phys.* 1989, **90**, 1281
10 Furukawa, H. *Prog. Theor. Phys.* 1978, **59**, 1072
11 Furukawa, H. *Physica* 1984, **123A**, 497
12 Binder, K. and Stauffer, D. *Phys. Rev. Lett.* 1974, **33**, 1006
13 Hashimoto, T., Itakura, M. and Hasegawa, H. *J. Chem. Phys.* 1986, **85**, 6118
14 Hashimoto, T., Itakura, M. and Shimidzu, N. *J. Chem. Phys.* 1986, **85**, 6773
15 Gilmer, J., Goldstein, N. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 2219