DIGITAL IMAGE ANALYSIS OF PHASE SEPARATION STRUCTURES IN SPINODAL DECOMPOSITION OF A POLYMER BLEND

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Key Words: Material, Phase Separation, Digital Image Analysis, Polymer Blend, Spinodal Decomposition, Interfacial Length, Fractal Dimensionality

Digital image analysis was applied to characterize structure growth in the phase separation of a poly(carbonate)/poly(methyl methacrylate) blend of a critical composition at various temperatures. Two-dimensional Fourier transformation was obtained from photographs of phase-separation structures. It was shown that the phase separation occurred in two stages. The first stage was characterized by a steady average domain distance during phase separation, and the second stage by the existence of a scaling law for structure growth. The fractal dimensionality and boundary length of the interfacial structures were also obtained during the second stage of the separation. The fractal dimensionality decreased with time, suggesting that the interface became smooth as the phase separation proceeded. The interfacial length obtained at various temperatures revealed a similar time-dependence which was approximated by a simple power law.

Introduction

Structure growth in spinodal decomposition of polymer blends has been the subject of extensive investigations. Small-angle light scattering has been the method most widely applied to the analysis of structures in the decomposition.

This method is suitable for semi-quantitative study of phase separation structures¹⁰⁾. In principle, however, small-angle light scattering is difficult to apply to the analysis of structures with domain sizes much larger than the wavelength of incident light.

Digital image analysis is expected to overcome such difficulty and to give detailed information on phase separation structures^{10,11)}. Furthermore, it is considered a useful tool for quantifying the relation between structure and physical properties. Recently, the authors¹²⁾ applied digital image analysis to characterize the phase separation structures of a poly (methyl methacrylate)/poly(vinyl acetate) blend. In the present work, digital image analysis is extended to study the evolution of structures of bisphenol A poly (carbonate) (PC) /poly (methyl methacrylate) (PMMA) in spinodal decomposition.

* Received May 8, 1992. Correspondence concerning this article should be addressed to S. Saito.

Fig. 1 Phase diagram: (—) Spinodal point, (---) Binodal point

1. Experiments

The polymers used were PC (Scientific Polymer Products, $M_w = 1.8 \times 10^4$, $M_w/M_n = 1.53$) and PMMA (Aldrich, $M_w = 5.1 \times 10^4$, $M_w/M_n = 2.5$), both of which were purified by precipitation from methanol. After purification the polymers were dried and dissolved in tetrahydrofuran at a concentration of 1.5 wt%. The polymer solution was cast on a slide glass, then evaporated in an oven kept at 30°C and maintained completely dry by vacuum-evaporation.

Prior to the phase separation experiments, the polymer film cast on the slide glass was used to determine the phase diagram of the polymer blend with the aid of a light-scattering method⁵⁾. Cloud points were measured by detecting light scattered from the polymer film at a slow heating rate of 1/12°C minute with a photodiode fixed at a scattering angle of 20°. Spinodal points were measured from the time variation of the scattered light intensity during phase separation of the specimen at various temperatures. The phase diagram is presented in Fig. 1. The critical point of the system was found to be at a PMMA weight fraction of 0.3.

The polymer film at this critical composition was used for the experiments in isothermal phase separation. The evolution of the phase separation was observed with an optical microscope equipped with a hot stage, and was photographed with a camera (Olympus PM-6) at appropriate intervals. The photographs were digitized with a TV camera possessing a spatial resolution of 640×400 pixel² and an intensity resolution of 256. An area of 256×256 pixel² was extracted for calculation of the two-dimensional Fourier transformation, in which the space resolution was $0.25 \mu\text{m}/\text{pixel}$. The boundary extraction method¹²⁾ was applied to calculate the interfacial length and fractal dimensionality of interfacial structures.

Fig. 2 Photographs of phase-separation structures in spinodal decomposition at 180°C: (a) 260 minutes, (b) 480 minutes

Fig. 3 Calculated results of two-dimensional Fourier transformation at 180°C: (—) 83, (---) 120, (---) 180, (---) 280 and (---) 420 minutes

2. Results

Figure 2 shows microphotographs taken at 260 and 480 minutes after the initiation of phase separation at 180°C. The interconnected structure of phase separation is observed at this temperature, and also appeared at other temperatures in the experiments.

Figure 3 shows the power spectra obtained from the two-dimensional Fourier transformation¹¹⁾ defined as

$$S(q) = \langle I(r)I(0) \rangle \exp + (-jqr) dr \quad (1)$$

where $I(r)$ is intensity at coordinate r , and q is Fourier wave number. To damp down the vibration of the Fourier profile, a multiple scanning method was applied which smoothed the profile by repeating the calculations 10 to 20 times after shifting the extracted area by 8 pixels in the x and y directions. The Fourier profile was further smoothed by averaging $S(q)$ circumferentially. Fig. 3 indicates that the wave number q_m which gives the maximum of $S(q)$ shifts toward a lower value with increasing time. The decrease in q_m corresponds to an increase in the domain distance of the phase-separated structure.

The development of q_m during phase separation at different temperatures is summarized in Fig. 4. In the early stage of phase separation at each temperature, the value of q_m remains relatively unchanged with time. In the late stage, however, q_m decreases with time. Thus, the

Fig. 4 Time-variation of q_m at phase-separation temperatures of (■) 215, (●) 204, (○) 195 and (▲) 180°C

phase separation of this system appears to be divided into two regimes: the early and late stages. No intermediate stage such as has been reported for some other polymer blends^{2,6)} was observed. The profile of the time-dependence of q_m in the present work is similar to that reported by Lim and Kyu^{7,8)} for the system of PC and PMMA. In their experiments a light-scattering technique was employed, and their relation of $q_m \propto t^{1/3}$ in the late stage is close to the present relation in Fig. 4.

It is interesting to compare the prediction from Furukawa's scaling theory^{3, 4)} for power spectra with the results obtained from digital image analysis. According to the theory, the power spectra for a critical mixture in the late stage of phase separation can be expressed in the following form:

$$S(q, t) = [q_m^{-d}(t) (1 + d) X^2] / [d + X^{2+2d}] \quad (2)$$

where

$$X = q/q_m \quad (3)$$

and d is dimensionality. In the literature, Furukawa's scaling theory was compared with the structure factor obtained from light-scattering experiments, but it has not yet been compared with that obtained from digital image analysis.

Figure 5 shows the plot of $S(q, t) q_m^2(t)$ against X after a phase separation time of 220 minutes at 180°C. The plot corresponds to the two-dimensional case described by Eq. (2). The solid curve shows calculated values from Eq. (2). Since the experimental values are shown in an arbitrary unit in the figure, the solid curve was shifted to fit the maximum of the solid curve to that of the experimental curve. The solid curve is wider than the experimental curve. However, in the regions of high and low X values the experimental dependence of $S(q, t) q_m^2(t)$ on X is fairly close to that predicted by Eq. (2). Although the plotted data do not show perfect agreement with the function in Eq. (2), it is important to note that the data are well correlated in the dimensionless form of $S(q, t) q_m^2$ versus X . This correlation suggests that a self-similarity in structures was maintained during phase separation in the late stage. On the other hand, the experimental results of $S(q) q_m^d(t)$ obtained in the early stage of phase separation were not scaled in the form of Eq. (2).

Fig. 5 Relation between $S(q) q_m^2(t)$ and X at 180°C: (●) 220, (○) 240, (□) 260, (■) 280 and (△) 300 minutes

Fig. 6 Relation between $S(q) q_m^2(t)$ and X at 195°C: (○) 35, (●) 45, (+) 53, (△) 60, (□) 70 and (■) 80 minutes

The data at 195°C after 35 minutes are plotted according to Eq. (2) in **Fig. 6**. Similarly to Fig. 5, the data in Fig. 6 are well correlated.

For characterization of interfacial structures, we attempted to determine the fractal dimensionality of the interface according to the following Richardson relation^{1,9)}:

$$N \propto L^{-D} \quad (4)$$

where N is the number of discs counted along each interfacial profile, L the disc radius, and D the fractal dimensionality. Since the boundary between the two phases became well-defined in the late stage of phase separation, the data in this stage were used for the analysis, in which the black-and-white treatment reported in a previous paper¹²⁾ was applied to boundary extraction.

Figures 7 and 8 present double-logarithmic plots of N versus L . In the range of small L , the data followed a relation of $N \propto L^{-1}$, which holds for a straight boundary. However, in the region of larger L the slope of the plotted data converged to a larger value, as seen in the figures. The values of the fractal dimensionality obtained from the

Fig. 7 Relation between N and L at 195°C: (a) 90 and (b) 180 minutes

Fig. 8 Relation between N and L at 215 °C: (a) 11 and (b) 60 minutes

slopes at 195°C were 1.39 at 90 minutes, 1.28 at 120 minutes and 1.24 at 180 minutes. The values at 215°C were 1.58 at 11 minutes, 1.51 at 20 minutes and 1.49 at 60 minutes, and those at 204°C were 1.38 at 30 minutes, 1.28 at 60 minutes and 1.23 at 90 minutes. Thus, the fractal dimensionality at each temperature decreased with phase separation time. This suggests that the interface became smooth as phase separation proceeded.

To measure the interfacial length of the phase separation, we should use a scale which is included in the range where the relation $N \propto L^{-1}$ holds. Accordingly, the interfacial length was measured with a scale less than 2 μm . The black-and-white method was applied to the determination of boarder lines, and the data in the late stage of phase separation were subjected to analysis. The results for the interfacial length per unit area at three temperatures are presented in **Fig. 9**. It is interesting to note that the dependence of interfacial length at each temperature is expressed by a similar power law: the exponent of time is about -0.4 .

Conclusion

In phase separation experiments using PC/PMMA with a critical composition, an interconnected phase separation structure was observed. The power spectra were obtained by two-dimensional Fourier transformation, which allowed the determination of q_m , consequently indicating that the process of the phase separation can be

Fig. 9 Revolution of interfacial length per unit area at temperatures of (●) 195, (○) 204 and (■) 215°C

divided into two stages. In the late stage the structure factor was found to be expressed by a scaling law. To characterize the interfacial structures of the phase separation, the fractal dimensionality defined by Richardson's equation was obtained. It tended to decrease with increase in phase-separation time. The interfacial length per unit area obtained at various temperatures revealed a similar time dependence, which was approximately expressed by the proportionality of 0.4 power of the phase-separation time.

Acknowledgment

The authors express sincere gratitude to Dr. Yoshiyuki Yamashita for his valuable advice regarding this work.

Nomenclature

D	= Fractal dimensionality	[-]
$I(r)$	= intensity of coordinate r	[-]
L	= disc radius	[m]
M_n	= number-averaged molecular weight	[kg/kmol]
M_w	= weight-averaged molecular weight	[kg/kmol]
N	= number of discs counted along interfacial profile	[-]
q	= Fourier wave number	[m ⁻¹]
q_m	= value of q giving maximum of $S(q)$	[m ⁻¹]
$S(q, t)$	= structure factor at time t	[m ²]
X	= variable defined by Eq. (3)	[-]

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