APPLICATION OF DIGITAL IMAGE ANALYSIS TO THE CHARACTERIZATION OF PHASE-SEPARATED STRUCTURES IN POLYMER BLEND

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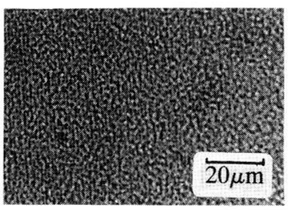
Introduction

Phase separation by spinodal decomposition has been attracting considerable interest as a method for controlling the structures and properties of multicomponent polymeric materials. It is important from both scientific and industrial viewpoints to correlate quantitatively the morphological characteristics of phase-separated structure with various conditions of phase separation, because the physical properties of polymer blends, such as electrical and mechanical properties, are well-known to be strongly dependent on their high-order structures. In a previous paper[6], we reported the experimental results of phase separation on polymethyl methacrylate (PMMA) and polyvinyl acetate (PVAc) blend by using a small-angle light-scattering (SALS) technique. The light-scattering method is valid for giving information about overall structures, but is not applicable to a structure of large scale compared with the wavelength of the light and is difficult to use for extracting local information on morphology. Recently, a digital image-processing technique has shown its utility in analyzing the pattern formation in polymer systems[2-5]. The purpose of the present work is to apply the digital image technique to the characterization of phase-separated structures in PMMA/PVAc blend. In particular, we attempt to quantify the morphology of phase-separated structure by applying fractal dimensionality.

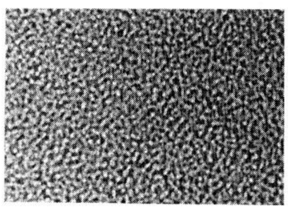
1. Experimental

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 chloroform as common solvent at a total polymer content of 10 wt%. The solution was cast onto 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 with a thickness of 100–150 μm was obtained.

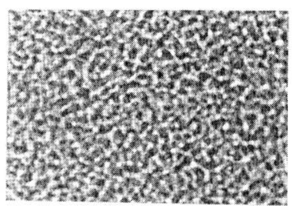
Isothermal phase separation processes of PMMA/PVAc films were observed with a phase-contrast optical microscope (Olympus BH-2) equipped with a heating stage. Details of phase separation experiments were presented in previous papers[6,7]. The time development of the phase-separated structures was recorded by using a camera (Olympus PM-6) mounted on the microscope. The micrographs obtained at different times were digitized by use of a TV camera with a spatial resolution of 512 × 512 and an intensity resolution of 256. The overall spatial resolutions of the image analysis system are 0.51 μm/pixel for the treatment of Fourier transformation and 0.15 μm/pixel for the calculation of fractal dimensionality. Various operations were carried out on a personal computer. The boundary extraction method was used for calculation of fractal dimensionality.



(a) 13 min



(b) 39 min



(c) 192 min

PMMA/PVAc (50/50) 150°C

Fig. 1. Temporal evolution of phase-separated structure observed by optical microscope

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2. Results and Discussion

Figure 1 shows the temporal evolution of a phase-separated structure observed at 150°C for the 50wt% PVAc system. Initially no structure was observed, but a finely interconnected structure was observed after 10 minutes, followed by a coarsening process with the characteristic of spinodal decomposition. The coarseness of the interconnected phase domains increases with time, as seen in Fig. 1.

Figure 2 shows the power spectra of one-dimensional Fourier transformation corresponding to the phase-separated structures of Fig. 1. The window function of Hanning was used to damp down the vibration of the Fourier profiles. The profiles in Fig. 2 directly correspond to that of SALS. A maximum can be observed in each power spectrum, indicating the existence of periodicity in the phase-separated structures. The positions of the maximum shift toward the lower wave number. This implies that the scale of phase separation becomes larger with lapse of time. These results are in good agreement with that of the SALS experiment[6,7].

In the later stage of spinodal decomposition the phase-separated structure changes from a interconnective domain to a cluster with closed region. By extracting the boundary of the region we can quantitatively analyze the shape of the region. Recently, the concept of fractals has been used successfully to characterize the morphological features of shape in the natural world. If we assume similarity in the morphology of clusters, the fractal dimensionality D used in this work can be defined as[1]

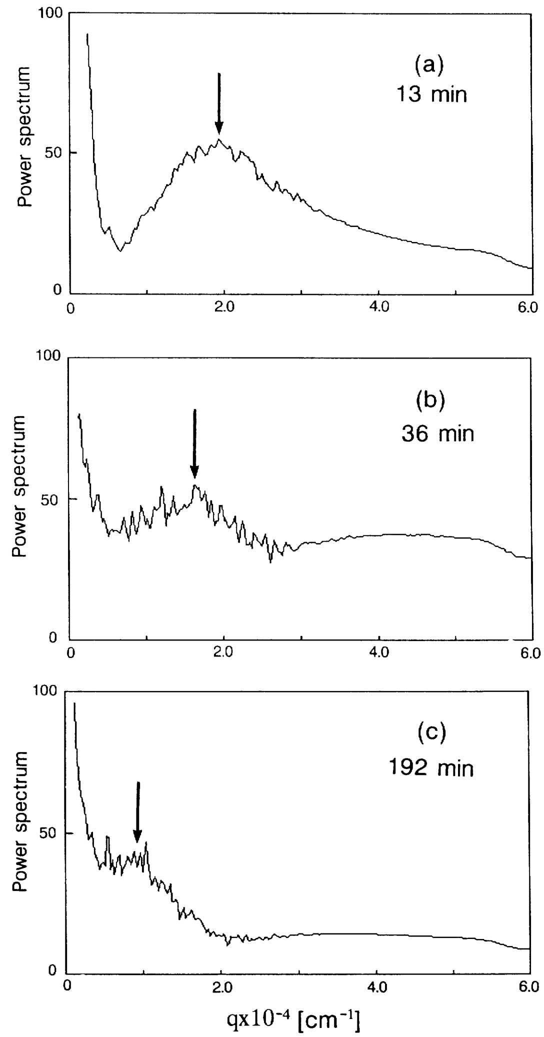

Fig. 2. Power spectra of phase-separated structure in Fig. 1 for PMMA/PVAc (50/50) blend at 150°C

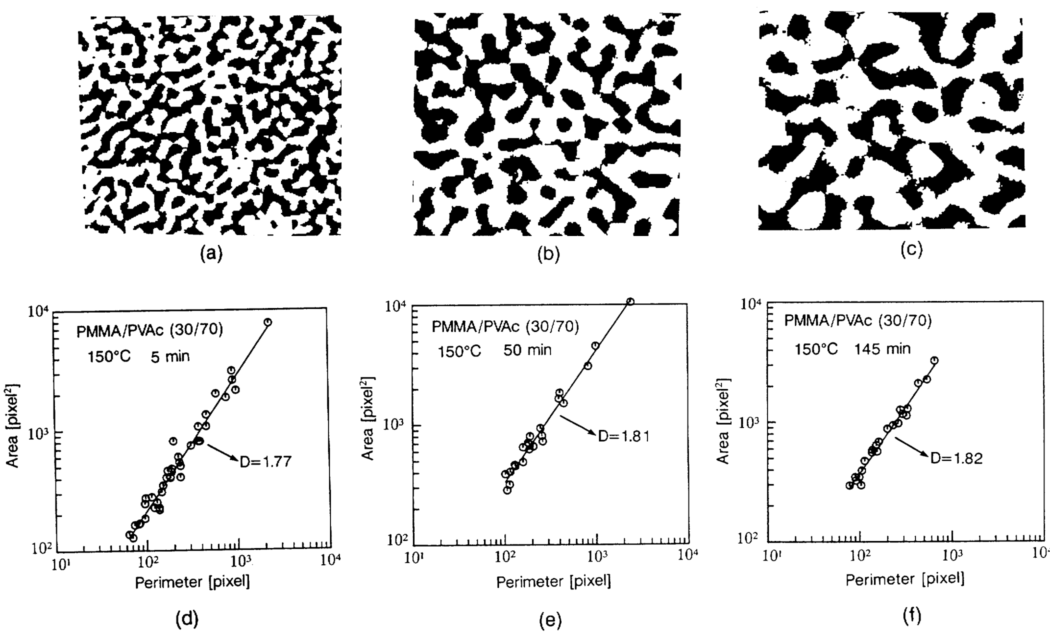

Fig. 3. Digital images of phase-separated structures ((a), (b) and (c)) and corresponding plots of area versus perimeter for determining fractal dimensionality ((d), (e) and (f))

$$S^{1/2} \propto P^{1/\boldsymbol{D}} \tag{1}$$

where S and P are the area and perimeter of cluster, respectively. Because each image is represented by a 512×512 pixel matrix, we can calculate the values of S and P by counting the number of pixels that constitute a cluster.

Figure 3 shows a typical series of images of phase-separated structures with black-and-white treatment. These structures were observed at 150°C for the 70 wt% PVAc system, and are regarded as structures formed through intermediate to late stage. The corresponding double-logarithmic plots of area versus perimeter are shown in Figs. 3(d), (e) and (f). Standard deviations for these plots were respectively 0.078 (d), 0.058 (e) and 0.045 (f) at log-scale. It was found that the relation expressed by Eq. (1) holds satisfactorily in these figures. Accordingly, the fractal dimensionality defined by Eq (1) may be considered as a parameter which can characterize the shape of the phase-separated clusters. The value of fractal dimensionality $\boldsymbol{D}$ can be determined from the slope through the relation $\boldsymbol{D}=2/(\text{value of slope})$, and is indicated in each figure. A trend observed in these plots is that the value of $\boldsymbol{D}$ increases significantly from intermediate to late stage (Figs. 3(d), and (e), (f)), and remains almost constant in the late stage (Figs. 3(e) and (f)). This may imply that the clusters grow from a branched structure to a spherulite-like structure.

Acknowledgement

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Literature Cited

1) Mandelbrot, B. B.: "*The Fractal Geometry of Nature*", W. H. Freeman and Company, New York (1977).
2) Reich, S.: *Phys. Letts.*, **114A**, 90 (1986).
3) Tanaka, H., T. Hayashi and T. Nishi: *J. Appl. Phys.*, **59**, 653 (1986).
4) Tanaka, H., T. Hayashi and T. Nishi: *J. Appl. Phys.*, **59**, 3627 (1986).
5) Tanaka, H. and T. Nishi: *Phys. Rev. Lett.*, **59**, 692 (1987).
6) Wang, Z.-Y., M. Konno and S. Saito: *J. Chem. Eng. Japan*, **22**, 429 (1989).
7) Wang, Z.-Y., M. Konno and S. Saito: *J. Chem. Phys.*, **90**, 1281 (1989).