The interface dynamics of bicontinuous phase separating structure in a polymer blend

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Abstract. The time evolution of the phase separating pattern during the spinodal decomposition (SD) of a specimen was observed at the same volume of the specimen using X-ray computerized microtomography (X-ray CT). A careful examination of time-dependent three-dimensional (3D) images revealed that bridge-like domains played an important role in the phase separation dynamics. In the course of the SD, some bridge-like domains became thicker, while the others became thinner. It was found that the pressure difference across the interface, which is quantified through the mean curvature of the interface, influences such interface dynamics.

1. Introduction

Pattern formation and interface dynamics during phase separation have long been the focus for many experimental and theoretical studies on nonlinear and non-equilibrium phenomena [1–2]. When a binary mixture is rapidly quenched from a single-phase to the spinodal region of a phase diagram by changing thermodynamic variables such as temperature or pressure it becomes thermodynamically unstable and then separates into two phases via spinodal decomposition (SD) [1–3].

A considerable number of scattering studies have been conducted on polymer blend systems to investigate pattern ordering in Fourier space by using light scattering (LS) [6–7] and small-angle neutron scattering (SANS) [8–9]. These studies have yielded the following principles of phase-separating structures during SD: (i) the evolution of concentration fluctuations in the early stage of SD can be well described by the linearized theory [10–11], and (ii) the phase separating structure grows with dynamic self-similarity in the later stages of SD [12–13].

Apart from the above mentioned scattering studies, studies were also conducted on the time evolution of the three-dimensional (3D) interface of a phase separating pattern by laser scanning confocal microscopy (LSCM). On the basis of the obtained 3D images, we can demonstrate both the dynamic self-similarity of the time evolution of the local interface during SD, and the global structure [14–16]. Further, a statistical analysis of the LSCM images was carried out to propose basic processes of the pattern evolution of the phase separating structure. However, a fundamental aspect of SD that has not yet been examined is the actual interface dynamics, which can be elucidated only by in situ observations. Nevertheless, such examinations have not yet been carried out because of difficulties such as the high chemical reactivity of the ultraviolet (UV) laser used in the LSCM; the UV laser causes cross-linking or degradation of polymers.

In order to examine interface dynamics, in this study, we use X-ray computerized tomography (X-ray CT) [17]. The radiation source is an X-ray with high penetrating power and low chemical reactivity with polymers. The spatial resolution of an X-ray CT has currently improved up to 1 µm. In this study, the time evolution of the
interface development of a specimen during SD was observed at its original volume; an in situ observation was carried out; that is, an in situ observation was carried out using X-ray CT. The interface dynamics is discussed in the following sections.

2. Experimental

A polymer blend system of polystyrene (M_w = 200,000) and polymethylmethacrylate (PMMA) (M_n = 60,000) was used for the X-ray CT observations. In order to enhance the absorption contrast for the X-ray, 30% of the para position of styrene unit was brominated using the pre-existing procedure [18]. Poly(styrene-co-4-bromostyrene) (PS-Br) and PMMA thus obtained, were then dissolved in toluene to obtain a 5% solution and lyophilized. The volume fraction of PS-Br was 0.5. The obtained homogeneous blend was vacuum-pressed at 180°C to remove low-molecular impurities. The present blend system phase separated via the SD at 180°C. Hence, it was deduced that the onset of phase separation was at the beginning of the vacuum pressing. In order to prevent the occurrence of a volume change of the sample due to heat and contact with open air, the obtained polymer blend was cut further and embedded in an epoxy resin at 60°C. A small amount of Cu powder was dispersed in the epoxy resin as a position marker for the same-volume observation. The temperature for the epoxy embedding was well below the glass transition temperatures of the constituent polymers (107°C for PS-Br and 100°C for PMMA).

The obtained specimen was observed using X-ray CT at room temperature (nano focus ELESCAN, Nittetsu Elex Co., Ltd). The tube voltage, tube current, increment angle, and magnification were observed to be 40 kV, 150 mA, 1200 projections/tomograph, and 50 × , respectively. The time evolution of the phase separating pattern was observed by carrying out heat treatments repeatedly at 180°C and subsequently carrying out rapid quenching to room temperature. The phase separation time t of the obtained specimen was recorded at 180, 225, 240, 255, 270, 285, 300, 380, 385, 390, 395, 400, 405, 410, 415, 420 min. The obtained projections were subjected to correction for the fan-type beam of X-ray CT [19] and were reconstructed using the filtered back-projection method [20]. The series of sliced images was volume-rendered by the Marching Cubes algorithm. Further, the obtained 3D images were subjected to coordinate conversion in order to align the positions with the aid of Cu powders dispersed in the epoxy resin.

3. Results and Discussion

Figure 1 shows the time evolution of the phase separating patterns of the PS-Br/PMMA blend obtained by X-ray CT observations. The white-colored areas in the figure show the PMMA phase, while the empty-looking spaces show the PS-Br phase. The interface dynamics was successfully observed in the same field of view for the first time. The periodic length of the phase separating pattern was observed to be 38.5 μm at t = 180 min; it further escalated to 86.3 μm at t = 420 min. The volume fractions of the PMMA phase were observed to be constant at around 0.5 within 1% errors over the observation time. Therefore, the local compositions of the polymers are assumed to attain the corresponding equilibrium values as described by the phase diagram.

Fig. 1 shows the periodicity of the interface: The elliptic interface denoted by red circles transformed into a flat interface.

Figure 1. 3D phase separating patterns of PS-Br/PMMA blend obtained by X-ray CT observations. The white phase is the PMMA phase; the transparent phase is the PS-Br phase.
The hyperbolic interface marked by blue circles, which has bridge-like shape, was pinched off and relaxed to flatter interface. These observations are consistent with the predictions previously proposed by Jinnai et al. [16]. Interestingly, some bridge-like domains denoted by green circles were observed to become thicker.

While the thickening bridges concur with the overall tendency of the increase in the size of the polymers, the thinning bridge does not. On the basis of the concept that the difference between the thickening and thinning bridges should account for the intriguing behavior of SD, we calculated the curvature distributions at the interface [21]. SD exhibits a bicontinuous pattern and sustains self-similarity, though the pattern itself is not fractal architecture. The details on the curvature measurement are described elsewhere [16].

The geometry around the point of interest on a surface can be categorized by the sign of Gaussian curvature $K$. Surfaces with positive $K$, $K = 0$, and negative $K$ are considered as elliptic, parabolic, and hyperbolic surfaces, respectively. The Gaussian curvature of the interface of phase separating pattern was plotted on the interface as depicted in Fig 2. Though slightly on the negative side, the value of $K$ is approximately 0 on a greater part of the interface. Regardless of its thickening or thinning behavior, the bridge-like domains are identified as interfaces with negative $K$.

The mean curvature appears to be negative on most of the bridge-like domains. Considering their time evolution, the thickening bridge has positive $H$ (see also Fig. 4(a)) and the thinning bridge has negative $H$ (see also Fig. 4(b)). Then, we can consider the Laplace equation [22],

$$\Delta P = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = 2\sigma H$$  \hspace{1cm} (1)

where $H$ is related to the interface pressure difference $\Delta P$ and the interfacial tension $\sigma$. Since the compositions of the coexisting phases already attain equilibrium, $\sigma$ becomes a constant in the later stages of SD. Therefore, the interfacial pressure difference is proportional to the mean curvature at a given point.

On the thickening bridge, a positive mean curvature is observed, this indicates a positive interfacial pressure difference $\Delta P$. In other words, the pressure of the PMMA phase is higher than that of the PS-Br phase. In order to relax the local pressure difference, the interface is presumed to change its shape so that there is a decrease in the positive $H$, resulting in the thickening of bridge-like domains. It encourages the local flow of PMMA into the bridge-like domain. On the other hand, a negative mean curvature is observed at the thinning bridges. The pressure of PS-Br phase is noted to be higher than that of the PMMA phase, and the pattern of local flow of PS-Br is observed to be opposite to that of the local flow of PMMA, i.e., the local flow is observed to be out of the bridge-like domain.
domains. Thus, by using curvature, the interfacial dynamics was found to be reasonably correlated with the interfacial geometry.

The bicontinuous structure can be regarded as the architecture of thickening and thinning bridges. The criterion for the thickening or thinning behavior of the bridges was determined to be the sign of mean curvatures. Therefore, development of the phase separating pattern can be considered to occur on the sacrifice of relatively thinner bridge-like domains with negative $H$. The separated bridge-like domains eventually become flatter in order to reduce interfacial energy. The procedure progresses regardless of the absolute value of the structural dimension, thus the phase separating pattern develops with self-similarity.

The interface curvature and the hydrodynamic flow steer each other. Their relation can be effectively described by the Laplace equation. However, in order to comprehend the phase separation dynamics completely, we would require a clear explanation of both interface curvature and the hydrodynamic flow. An in situ observation would help in the differential analysis of the interface. It would elucidate the yet ambiguous reality of the hydrodynamic flow and the physics behind the time evolution of the phase separating pattern during the later stages of SD.

4. Conclusions

Time evolution of a three-dimensional (3D) interface of phase separating pattern was observed in a mixture of poly(styrene-co-4-bromostyrene) (PS-Br) and polymethylmethacrylate (PMMA) for the first time in the same field of view by using X-ray computerized tomography (X-ray CT). The analysis of the interface curvature revealed that the interface dynamics can be accounted for by the pressure difference across the interface. The interface dynamics can be measured using the curvatures of the interface between the two coexisting phases.

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