

TIME EVOLUTION OF INTERFACE SHAPE IN COCONTINUOUS BLENDS STUDIED BY 3D IMAGE ANALYSIS

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Abstract

The time evolution of the interface shape in a 50/50 PS/SAN cocontinuous blend was analyzed during annealing. The interface was tracked via LSCM (laser scanning confocal microscopy) coupled with 3D-image analysis. Images were analyzed for time evolution of interfacial area, curvature and curvature distributions. Two coarsening regimes were identified: an initial stage characterized by a linear growth of the characteristic size ($\lambda=1/Q$) followed by a slowing down of the size growth in the late stage. The decrease in coarsening rate was explained by the decrease of the interfacial energy which is proportional to the surface mean curvature.

Introduction

Due to the highly curved interface between the two phases in cocontinuous blends, a considerable amount of free energy is stored at the interface. Therefore the microstructure is not in thermodynamic equilibrium and will evolve into coarser structures when the temperature is above the glass transition of the components. A linear growth of the characteristic size (λ) of cocontinuous blends with time has been experimentally observed [1-4]. Using scaling arguments, Siggia predicted a linear growth law, i.e. $\lambda \sim t$, for the late stage of spinodal decomposition in systems with volume fractions above the percolation threshold [5]. Recent studies [2,6,7-8] showed a slowing down of the coarsening after an initial linear growth regime. This phenomenon is not well understood and is addressed here.

Direct observation and quantification of cocontinuous microstructures have been performed via 2D-imaging with, for instance, scanning electron microscopy (SEM) [1-2] or atomic force microscopy (AFM) [9-10]. However estimation of 3D geometrical parameters such as interfacial area per unit volume (Q) from 2D images leads to considerable errors [2]. Additionally, measurement of the surface curvature is not possible from 2D images. Analysis of 3D images allows accurate calculation of geometrical parameters of blend interfaces [4,6].

Laser scanning confocal microscopy (LSCM) allows one to obtain 3D images of polymer blends [4,6] and after an appropriate analysis to obtain the geometrical

parameters of the interface. Recently we proposed a simplified method to compute the mean (H) and Gaussian (K) curvatures from 3D images of immiscible blends [6]. In the present study we analyze the time evolution of $\lambda=1/Q$ and the distribution of H of the 50/50 FLPS/SAN blend. An initial linear growth of the microstructure characteristic size was observed. At later times a slowing down was observed and explained by the decrease in interface curvature.

Materials

Experiments were performed on a 50/50 wt% blend of fluorescently-labeled polystyrene (FLPS) and acrylonitrile-styrene copolymer (SAN) containing 9.6 % mole of acrylonitrile (measured via CHN analysis). Both polymers were synthesized by free radical polymerization in toluene at 60 °C with AIBN as initiator. 1% of a fluorescent monomer (anthracenylmethyl methacrylate) was used in FLPS synthesis [6]. SAN was synthesized from a mixture of styrene (S) and acrylonitrile (AN) with monomer ratio: S/AN=4.1. Table 1 shows the molecular weight and viscosity of the blend components.

Table 1. Properties of polymer blend components.

Polymer	Mw, kg/mole	η_0 , Pa-s
FLPS	122	1500
SAN	116	2300

Blending and Microscopy

The blend was prepared in a 4.3 cm³ twin screw microcompounder (Daca Instruments) at 180°C. After 10 min of mixing, the blend was extruded out of the mixer and quenched at room temperature. Small pieces of the extrudate were put in between a glass slide and a cover slip and annealed for different times at 200 °C. The annealed samples were imaged in a LSCM (Olympus Fluoview 1000) with an oil immersed 40X objective with an incident laser beam of 405 nm. About 100 2D image slices per sample were taken from 20 to 120 μ m away from the cover slip. The 2D images were deconvoluted, thresholded and reconstructed into 3D images (see Figure 1) and subsequently analyzed according to the same protocol described earlier [6].

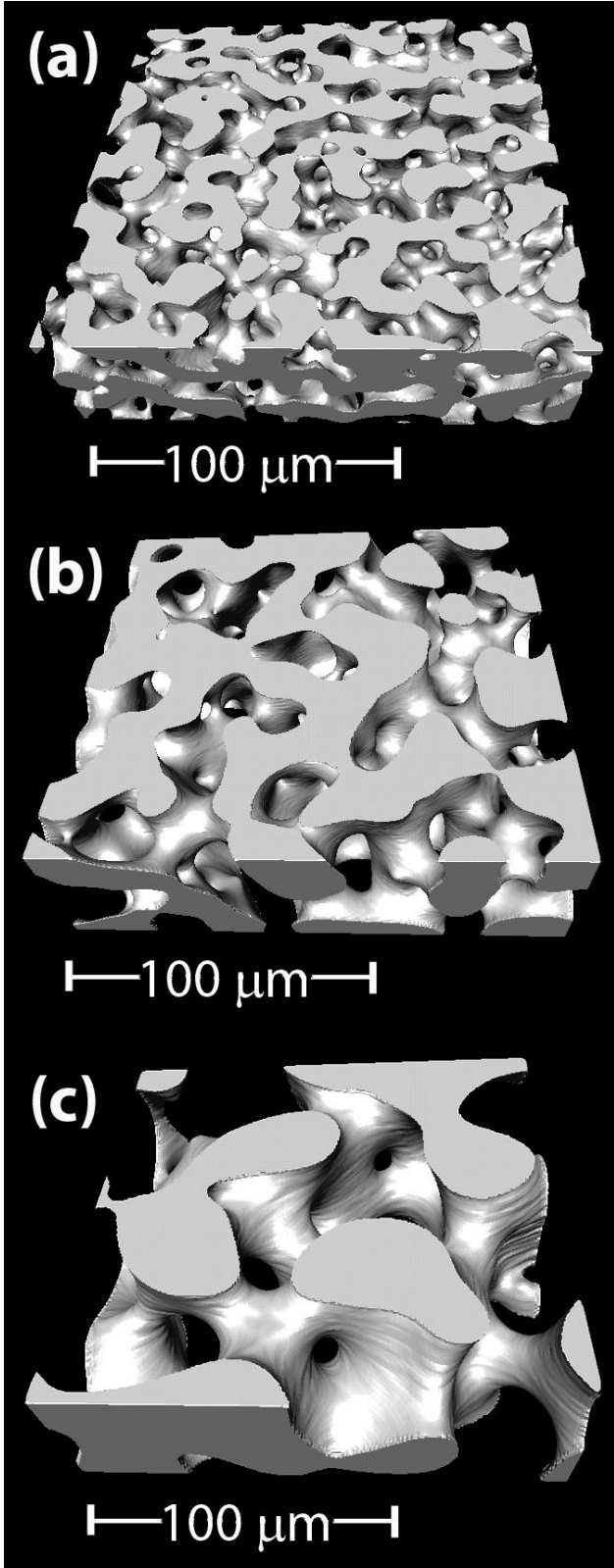


Figure 1. 3D reconstructed images of cocontinuous structures for the 50/50 FLPS/SAN blend at (a) 5 min, (b) 10 min and (c) 20 min. The solid part represents the FLPS phase and the transparent part the SAN phase.

Results and Discussion

Figure 1 shows 3D reconstructed images of the blend at three different annealing times. From the direct observation of these images, two facts are evident: one is the growth in size of the microstructure with time and second that the cocontinuous character remains during annealing.

Figure 2 shows the distribution of the mean curvature corresponding to the images shown in Figure 1. The probability density of the mean curvature, $P_H(H)$, is defined as [6]:

$$P_H(H) = \frac{\sum_{i=1}^N A[i | H - \Delta H / 2 \leq H_i < H + \Delta H / 2]}{\Delta H \sum_{i=1}^N A_i},$$

where H_i and A_i are the mean curvature and surface area of the i -th triangle, respectively. The term $A[i | H - \Delta H / 2 \leq H_i < H + \Delta H / 2]$ accounts for the surface area of all the triangles that satisfy the condition: $H - \Delta H / 2 \leq H_i < H + \Delta H / 2$. ΔH is the class interval of H . The term in the denominator is included to satisfy the normalization condition, i.e.

$$\sum_H P_H(H) \cdot \Delta H = 1.$$

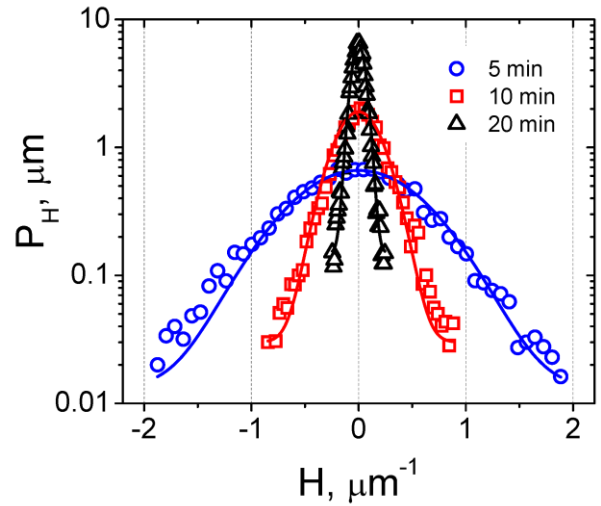


Figure 2. Time evolution of the probability densities of the mean curvature. The solid lines represent fits with a Gaussian distribution function.

Notice that the distributions are symmetrical and centered in $H=0$ at each time, evidence that the evolution of the interface progresses along a path of minimal energy. On the other hand, the width of the distribution decreases and its maximum value increases with time, which confirms that the interface evolves towards a more stable state by minimizing its curvature.

Figure 3 shows the time evolution of the reciprocal specific interfacial area ($1/Q$) and the standard deviation of the mean curvature distribution (σ_H). Values of σ_H gives a measure of the curvedness of the interface [11] and are computed by fitting the curvature distribution data (from Figure 2) with a Gaussian distribution function, i.e.

$$P_H(H) = \left(\sigma_H \sqrt{2\pi}\right)^{-1} \cdot e^{-(H-\mu_H)/(2\sigma_H)}, \quad \text{where the}$$

mean value of H , μ_H , is set to zero [8]. Two annealing stages were identified: In the early stage ($t \leq 60$ min) a linear growth of $1/Q$ is accompanied by an exponential decrease of σ_H , while in the late stage a slowing down of the growth of $1/Q$ coincides with the time when σ_H reaches a minimum plateau value.

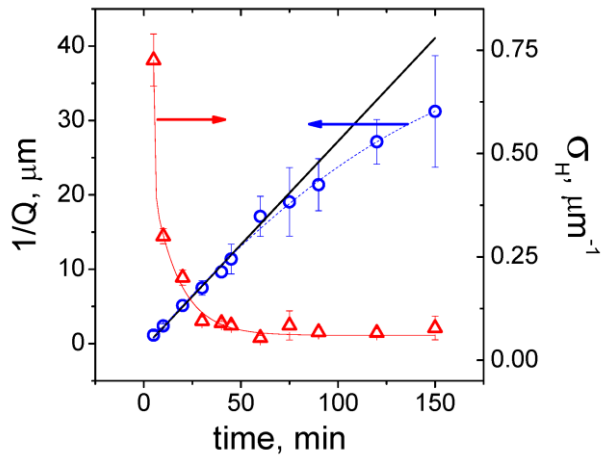


Figure 3. Time evolution of $1/Q$ and σ_H for the 50/50 FLPS/SAN blend. The values of $\square\sigma_H$ are the standard deviation of these Gaussian distributions. The black solid line represents the initial linear growth and the dashed lines are to guide the eye.

Using scaling arguments, Siggia analyzed the time evolution of the characteristic length of spinodally decomposed systems above the percolation concentration [5]. In his analysis, he considered the capillary flow within tubes formed by one of the phases. Using the Poiseuille flow equation and assuming that there is only one characteristic length, $\lambda \sim H^{-1}$, and one velocity, $d\lambda/dt$, he obtained the relation $\lambda \sim (0.1 \Gamma/\eta) \cdot t$, where Γ and η are the interfacial tension and the viscosity, respectively. The experimental evidence reported in the present work

confirms that these relations are valid in the early stage of coarsening but not at latter times. This can be explained by the fact that the coarsening is driven by the necessity to minimize the free energy stored at the interface between the phases. This interfacial energy is proportional to the quantity $\Gamma \cdot H$ [12]. As the annealing progresses, the value of H decreases and so does the coarsening driving force. Therefore the growth of λ slows down [8].

Conclusions

Interface shape of FLPS/SAN blends with cocontinuous morphology was characterized via laser scanning confocal microscopy coupled with 3D image analysis. Symmetric curvature distributions at different times showed that the evolution of the interface follows the path of least minimal energy. From the analysis of the time evolution of the interfacial area and curvedness, two coarsening regimes were identified, a linear growth of the characteristic length at early times followed by a slowing down. The slowing down was explained by the decrease in curvedness of the interface and its direct relation with the interfacial energy which in turn is the coarsening driving force.

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Key Words: 3D imaging, LSCM, Mean Curvature, Cocontinuous Blends.