# Coarsening dynamics of cocontinuous blends

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## 1. Summary

The time evolution of the interface shape of immiscible polymer blends with cocontinuous morphology was studied during annealing. Geometrical parameters of the interface of 50/50 blends made of fluorescently labeled polystyrene (FLPS) and styrene-ran-acrylonitrile copolymer (SAN) were obtained on the basis of differential geometry of 3D images. 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 interface curvature which is proportional to the coarsening driving force, i.e. the interfacial energy.

## 2. Introduction

A number of experimental studies have shown a linear growth of the characteristic size ($\lambda$) of cocontinuous blends [1-4]. Using scaling arguments, Siggia predicted a linear growth law, i.e. $\lambda$~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 SEM [1-2] or 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.

## 3. Experimental Part

FLPS was synthesized via free radical polymerization of styrene (S) with 1% of anthracenylmethyl methacrylate. SAN containing 9.6 %mole of acrylonitrile (AN) (measured via CHN analysis) was synthesized from a mixture of S and AN with monomer ratio: S/AN=4.1. Both polymerizations were performed at 60 °C with AIBN as initiator. The weight average of FLPS and SAN were 122,000 and 116,000, respectively [6].

A 50/50 w/w FLPS/SAN blend was prepared in a 4.3 $cm^3$ 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 µm 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].

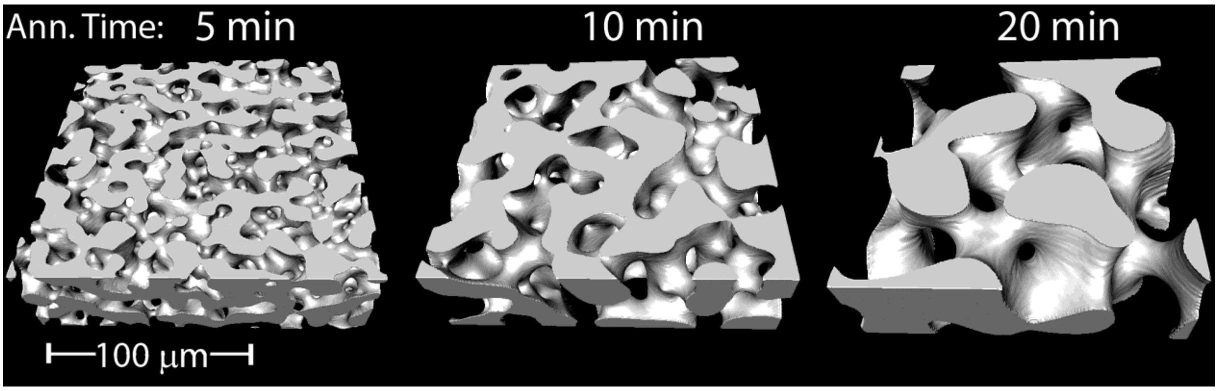


*Figure 1. 3D reconstructed image showing the time evolution of cocontinuous structures for the 50/50 FLPS/SAN blend. The solid part represents the FLPS phase and the transparent part the SAN phase.*

## 4. 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(a) shows the distribution of the mean curvature corresponding to the images shown in Figure 1. The probability density $P_H(H)$ is defined elsewhere [6]. 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.

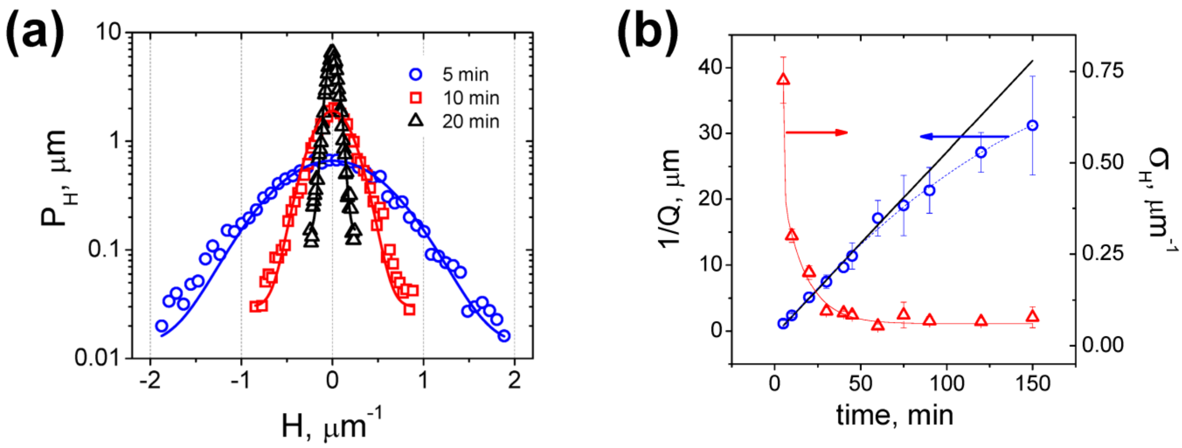


*Figure 2. a) Time evolution of the probability densities of the mean curvature and b) time evolution of 1/Q and $\sigma_H$ for the 50/50 FLPS/SAN blend. The solid lines in (a) represent fits with a Gaussian distribution function. The values of $\sigma_H$ in (b) are the standard deviation of these Gaussian distributions. The black line in (b) represents the initial linear growth and the dashed lines are to guide the eye.*

Figure 2(b) shows the time evolution of the reciprocal specific interfacial area (1/Q) and the standard deviation of the mean curvature distribution ($\sigma_H$). Values of $\sigma_H$ gives a measure of the curvedness of the interface [11] and are computed by fitting the curvature distribution data (from Figure 2(a)), with a Gaussian distribution function, i.e. $P_H(H) = \left(\sigma_H \sqrt{2\pi}\right)^{-1} \cdot e^{-(H-\mu_H)/(2\sigma_H)}$, where the mean value of H, $\mu_H$, 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 $\sigma_H$, while in the late stage a slowing down of the growth of 1/Q coincides with the time when $\sigma_H$ reaches a minimum plateau value.

Using scaling arguments, Siggia analyzed the time evolution of the characteristic length of spinodally decomposed systems above the percolation concentration [5]. For 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 $\lambda \sim (0.1 \cdot \Gamma/\eta) \cdot t$, where $\Gamma$ and $\eta$ 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 $\lambda$ slows down [8].

## 4. Summary

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 can be 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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