

Morphology and Rheology of Cocontinuous Blends

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Abstract. The time evolution of the elastic modulus and the geometrical parameters of interfaces in a 50/50 PS/SAN cocontinuous blend are analyzed during annealing. The interfaces were tracked via LSCM (laser scanning confocal microscopy) coupled with 3D-image analysis. The evolution of G' and the geometrical variables can be described with power laws. Experiments reveal that interfaces relax faster ($dQ/dt \propto Q^{2.4}$) than predicted by the Doi-Ohta theory ($dQ/dt \propto Q^2$) [1]. Rheological behavior is a result of interfacial relaxation which includes interface expansion and curvature relaxation.

Keywords: Cocontinuous blends, Rheology-morphology relationship, Polystyrene-SAN blends

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INTRODUCTION

Due to the highly curved interface between the two phases in cocontinuous blends, a considerable 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. Neglecting inertial forces, there are only three parameters that determine the blend morphology, i.e., viscosity (η_0), interfacial tension, (Γ), and volume fraction, (ϕ) [1].

Several methods have been used to detect and quantify cocontinuity. These include microscopy with image analysis, and rheology [2, 3]. Both two and three-dimensional imaging has been explored. One difficulty in using two-dimensional techniques is the possibility to misinterpret the blend morphology [2] (e.g. confusing perpendicularly cut fibers with drops) and inaccurate measurements of the real interfacial area per unit volume (Q). Additionally, 2D-images do not contain the interface principal curvatures (κ_1 and κ_2), or alternatively the mean curvature, ($H = 0.5(\kappa_1 + \kappa_2)$), and the Gaussian curvature, ($K = \kappa_1\kappa_2$) which along with the interfacial area completely describes the interface structure [4]. In contrast, 3D-images have the complete microstructure information to accurately calculate interfacial area and local curvatures.

Rheological measurements have been used for detecting the presence of interconnected structures [2, 5, 6]. A power law-like relation of the storage modulus at low frequencies has been observed in cocontinuous blends which is attributed to the presence of domains with different length scales generating different characteristic times [6]. Since the length scales grow during annealing of the blend, the numerical value of G' will decrease accordingly. Vinckier and Laun [5] observed a decrease in the elastic modulus with time of a 40/60 PMMA/P α MSAN blend with cocontinuous morphology. They found that their results were qualitatively predicted by the semiphenomenological Doi-Ohta theory [1]. This model describes the morphology of concentrated mixtures of immiscible fluids using an "interface" vector, \mathbf{q} , which is a function of the interfacial area and the anisotropy of the interface. However it does not consider the local curvature, which is crucial for the dynamics of the surface evolution.

In this paper we present the geometrical parameters (i.e. interfacial area and average curvature) and viscoelastic properties of a 50/50 (w/w) blend of PS/SAN. Experimental relations between the time-evolution of elastic modulus and interface shape are analyzed.

MATERIALS AND METHODS

Experiments were performed on a 50/50 wt% blend of fluorescently-labeled polystyrene (FLPS) and acrylonitrile-styrene copolymer with 20% mol acrylonitrile (SAN20). Both polymers were synthesized by free radical polymerization in toluene at 60°C with AIBN as initiator. The zero shear viscosities of FLPS and SAN20 are 1.5 kPa-s and 2.3 kPa-s, respectively. The polymers were mixed at 180°C using a 4.3 cm³ twin screw microcompounder (Daca Instru-

ments). After 10 min of mixing the blends were extruded out of the mixer and quenched at room temperature. Small pieces of the extrudate were annealed between a microscope glass slide and a cover slip at 200 °C for different periods of time. These samples were observed in a LSCM (Olympus FluoView 1000) at room temperature. About 100 image slices from 20 to 120 μm away from the cover slip were taken with an oil-immersed 40X objective with an incident laser beam of wavelength of 405 nm. The 2D sliced images were deconvoluted, thresholded and reconstructed into three-dimensional images using the software Amira (Visage Imaging). A triangular mesh of the interface is produced in the rendering process and subsequently used to measure the local curvatures and interfacial area per unit volume.

Dynamic viscoelasticity data were obtained using a strain-controlled rheometer (TA Instruments Rheometrics series ARES) with parallel plate geometry (25 mm diameter). Dynamic frequency sweeps at 200 °C were made over a range of 100-0.02 rad/s with strains of 20 %. Dynamic time sweeps were performed at 200 °C at a frequency of 0.1 rad/s with strains of 20 %. All measurements were made under nitrogen purge to minimize sample degradation.

RESULTS AND DISCUSSION

Dynamic frequency sweeps of the components and the blend are shown in Fig. 1a. The typical power law tail in the elastic modulus at low frequencies is observed, indicating the presence a broad distribution of characteristic sizes. Figure 1b shows a fast decay in G' in the early times compared to later times. However the entire time range can be fit with a power law: $G' \propto t^{-0.2}$ which is evident in the log-log plot (Fig.1c).

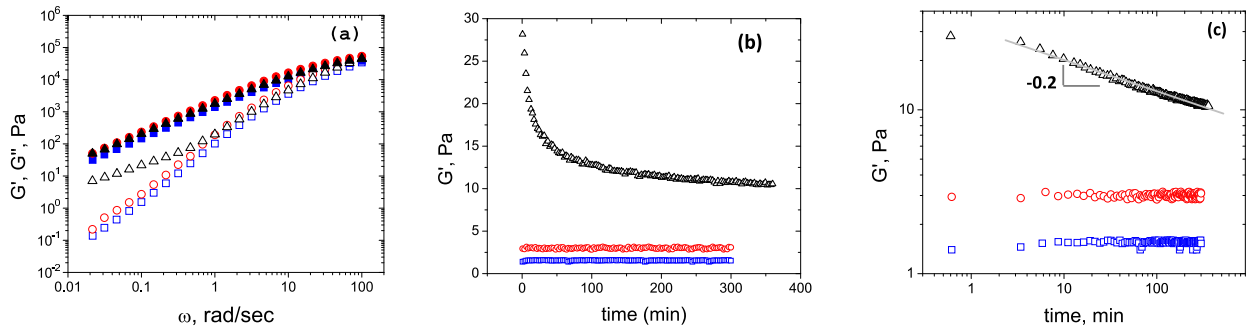


FIGURE 1. Storage (empty symbols) and loss (filled symbols) moduli as a function of (a) frequency and (b,c) annealing time of PS (\square), SAN (\circ) and 50/50 (w/w) PS/SAN blend (\triangle) at $T = 200^\circ\text{C}$

Reconstructed images of the 50/50 blend are shown in Fig. 2. The series of images show the effect of annealing after the blend was mixed. The change in the size scale is evident but the cocontinuous character of the microstructure is retained. The instantaneous curvature was measured using differential geometry on the triangular mesh generated during the 3D image rendering. The calculated specific interfacial area (Q), the area-averaged absolute curvature, $\langle |\kappa| \rangle$ (with $|\kappa| = 0.5(|\kappa_1| + |\kappa_2|)$) and the negative average Gaussian curvature $\langle -K \rangle$ are shown in the log-log plots in Fig. 3. Interestingly, these variables also show a power law decay but with different exponents: $Q \propto t^{-0.73}$, $\langle |\kappa| \rangle \propto t^{-0.52}$, and $\langle -K \rangle \propto t^{-1.3}$.

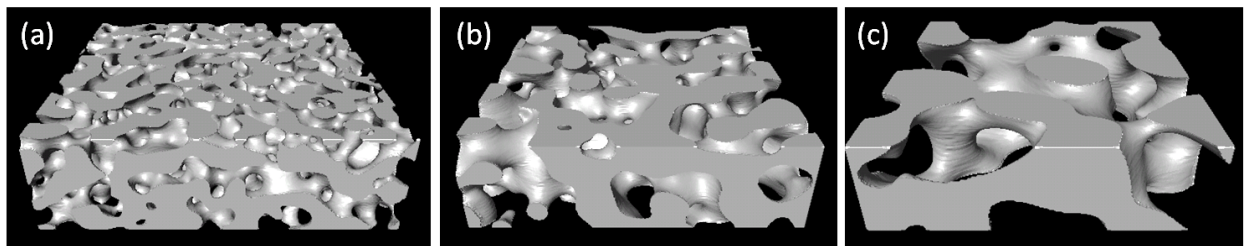


FIGURE 2. 3D reconstruction of cocontinuous structure of PS/SAN blend observed by LSCM corresponding to annealing times of (a) 5, (b) 10, and (c) 20 min. The volume of each image is $150 \times 158 \times 46.5 \mu\text{m}^3$

Using these power laws the interface relaxes slightly faster than the relation proposed by Doi and Ohta [1], $dQ/dt \propto Q^{2.4}$ vs $dQ/dt \propto Q^2$. The Doi-Ohta relation results from the assumption that the morphology is characterized by a single length scale ($1/Q$) which gives rise to the classical result obtained by Siggia [7], i.e. the characteristic

length increases in proportion with time. From our morphology analysis, we observed that the growth of the parameter $1/Q$ is not linear, which could reflect the fact that the coarsening involves two processes, the flow of fluid within the channels forming the interconnected structure (considered in Siggia's analysis[7]) and the breakup of the thin threads formed after the fluid in the threads is exhausted. The latter process is governed by local curvature of the thin threads. Hence, the pattern is characterized by two characteristic lengths: $1/Q$ and $1/|\kappa|$.

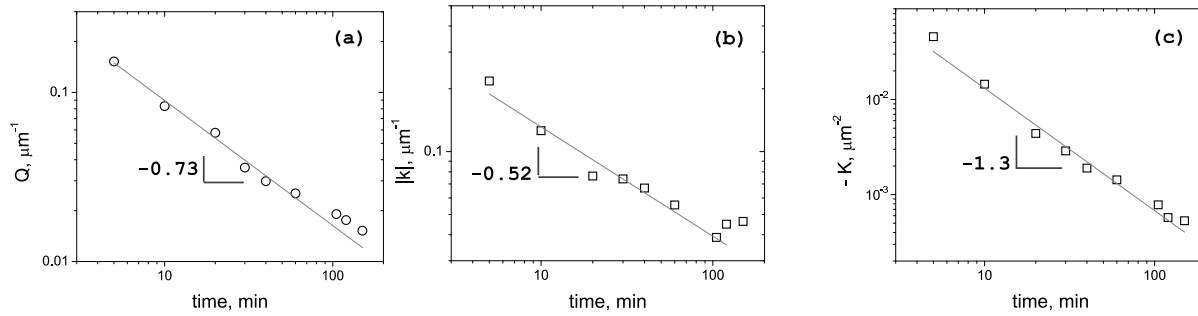


FIGURE 3. Time evolution of (a) interfacial area per unit volume and area average (b) absolute curvature and (c) Gaussian curvature of 50/50 PS/SAN blend annealed at 200°C

According to the theory proposed by Doi and Ohta [1], the stress tensor for a mixture is composed by the component contribution and the interface contribution. The latter is described by the "interface" vector (\mathbf{q}), which describe the extent and anisotropy of the interface. Using the Doi-Ohta theory [1], Vinckier and Laun [5] deduced that G' should be proportional to the vector \mathbf{q} . However the relation between the quantity called "anisotropy" and the curvature of the interface is not clear. Given that the extra contribution to the elastic modulus (Fig 1b) is due to the interface shape relaxation, it should be associated to the amount of interface, local curvature and shape (described by the Gaussian curvature [4]). From the experimental results, the following relations are obtained: $G' \propto Q^{0.3} \propto |\kappa|^{0.38} \propto -K^{0.16}$. The decay of G' , in turn, reflects the interface evolution. From the experiments the rate of G' -decay follows: $dG'/dt \propto (dQ/dt)^{0.7}$, $dG'/dt \propto |\kappa|^{2.3}$, $dG'/dt \propto -K^{0.93}$.

CONCLUSIONS

Monotonic decays of G' , Q , $|\kappa|$, and $-K$ were fitted with simple power laws. The geometrical parameters (Q , $|\kappa|$ and K) show a weak effect on G' but strong effect on the time derivative dG'/dt , indicating that the interface shape has a big effect on the coarsening dynamics. The classic models that describe the morphology evolution of interconnected structures under hydrodynamic interactions ([1, 7]) do not accurately describe the experimental results. The source of that discrepancy could be the fact that those theories do not consider the difference in time scale between the flow and the breakup processes.

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