



# Interfacial coarsening of ternary polymer blends with partial and complete wetting structures



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## ABSTRACT

The coarsening of polymer mixtures is an important route towards major morphology modification in multiphase polymer systems. To date however the coarsening of ternary systems has not been significantly examined. In this study the phase coarsening mechanism via annealing for partial wetting, and complete wetting morphologies in ternary polymer blends is characterized. This is a route towards the examination of interfacial coarsening in polymer blends since ternary partially wet systems involve the presence of interfacial droplets while completely wet ternary systems are comprised of a complete interfacial layer. A partial wetting type of morphology is obtained for polybutylene succinate (PBS)/poly(lactic acid) (PLA)/polycaprolactone (PCL). Three different compositions for that system with composition ratios of  $\phi_{(PBS/PLA)} = 1.5$ ;  $\phi_{(PBS/PLA)} = 3$ ; and  $\phi_{(PBS/PLA)} = 10$  are prepared to show the effect of the concentration of the self-assembled PLA droplets located at the interface of PBS/PCL. As the concentration of PLA decreases, the growth rate of the PLA phase during the annealing process sharply decreases due to a significant increase of the “surface to volume ratio” of the PLA droplets required in order to cover the interface. In this case, due to the short inter-droplet distances between PLA droplets at the interface, coalescence is controlled by the drainage time. This mechanism is confirmed by the observation of a linear relationship between the third power of droplet size and annealing time. For the 37.5%PBS/12.5%PLA/50%PCL blend, the conservation of interfacial-angles confirms that the annealing time has no effect on the angle values between phases, as predicted by Harkins spreading theory.

The annealing process for complete wetting is studied at four compositions for an HDPE/PS/PCL blend where the PS phase is located as a continuous layer at the interface of co-continuous HDPE/PCL. In 33.3% HDPE/33.3%PS/33.3%PCL after 30 min of annealing, the PS phase thickness increases 49 times from 2.3  $\mu\text{m}$  to 112  $\mu\text{m}$ . Even for very low concentrations of 3%PS, a high coarsening rate of 0.0039  $\mu\text{m/s}$  is observed. This sharp linear increase in PS phase size implies a capillary pressure mechanism and an impeded growth of Tomotika-like capillaries for all three phases that cause a confinement effect for coarsening of the middle PS phase.

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## 1. Introduction

One of the pioneering areas in advanced material research is the control of the microstructure in multiphase polymer systems comprising three or more phases [1]. Such complex morphologies are principally self-assembled by interfacial tension driving forces and are controlled by two dominant wetting behaviors, partial and complete wetting [2–4].

A ternary blend can demonstrate one of, or a combination of complete and partial wetting. The equilibrium morphology in both cases can be predicted by Harkins spreading theory [5,6]. Torza and

Mason [2] used the Harkins approach for wetting phenomenon and generalized it for emulsions of three immiscible liquids. According to the generalized Harkins equation, in a ternary  $i/j/k$  blend, the spreading coefficient,  $\lambda_{ij}$ , is defined as the tendency of component ( $i$ ) to encapsulate or spread onto component ( $j$ ) in a matrix of component ( $k$ ) and is related to the interfacial tension of the components in the following manner:

$$\lambda_{ij} = \gamma_{jk} - \gamma_{ik} - \gamma_{ij} \quad (1)$$

where  $\gamma$  represents the interfacial tension for various polymer pairs and sub-indexes  $i, j$ , and  $k$  refer to each component. There are three different spreading coefficients in a particular ternary blend including  $\lambda_{ij} = \lambda_{ik}$ ,  $\lambda_{jk} = \lambda_{ji}$ , and  $\lambda_{ki} = \lambda_{kj}$ . In this analysis, the sign of the spreading coefficients determines the type of wetting in the

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system. A positive value of one of the spreading coefficients such as  $\lambda_{ij}$  demonstrates a complete wetting morphology (two-phase contact) in which phase  $i$  spreads and forms a complete layer at the interface of phases  $j$  and  $k$  [3,7,8]. Three negative spreading coefficients indicate a partial wetting behavior in which none of the three spreads at the interface of other phases and all three meet along a common line of three-phase contact [2,4].

The coarsening of polymer blends via an annealing process involves coalescence phenomena. As the system absorbs energy, phases coarsen in order to reduce the interfacial area between the components thus minimizing the free energy of the system. This effect is particularly pronounced for interconnected co-continuous systems. Studies related to the coarsening of polymer blends can be divided into two types of systems: dispersed phase/matrix and co-continuous systems. The coalescence of two particles in a dispersed phase/matrix system can be divided into four stages including: approach of the particles, drainage of the matrix trapped between the particles, rupture of the film due to instability, and evolution of a dumbbell-shaped particle to a coalesced spherical particle [9,10]. Fortelný and co-workers [11,12] examined the role of these various stages in polymer coarsening and developed the matrix drainage and film rupture stages by defining various mobilities for the interface between droplets and matrix. They described that in annealing, different types of interactions will dominate the different stages of coalescence. These interactions include Brownian motion, intermolecular forces between neighboring particles, capillary forces, buoyancy forces, and friction resulting from viscous flow. Depending on the dominant interaction, the phase size/time relationship can vary from a linear to a cubic dependence. The four stages of coalescence can involve all of these interactions at some point. For example, the first stage of particle approach is governed by Brownian motion. They mentioned that for a viscous system, drainage time could also be important and should be considered.

Brownian motion, intermolecular forces and gravity can generally influence coalescence in quiescent dispersed phase/matrix polymer blends. The contribution of individual steps to the coalescence in quiescent blends depends on the average distance between a droplet and its nearest neighbor at the start of coalescence. For a low concentration of minor phase, droplets are far from each other and coalescence in this case is best described by classic Smoluchowski theory [13] of coalescence induced by Brownian motion. For a higher concentration of droplets where there is a short inter-droplet distance, the approach of droplets is influenced by intermolecular forces and their contribution increases with decreasing inter-droplet distance. Generally, in a dispersed phase/matrix binary mixture with a volume fraction of dispersed phase higher than 0.1, many droplets are in touch with each other since the percolation threshold for a system is reached at 0.16 [14,15]. Fortelný and Živný [12] developed the following equation for polymer systems with high viscosities that are mostly categorized as immobile interfaces:

$$R^n = R_0^n + mt \quad (2)$$

in which  $R$  is the droplet size at time ( $t$ ),  $R_0$  is initial droplet size at zero annealing time, and the values of  $n$  and  $m$  in each system are dependent on the type of driving force required for approaching particles during coarsening. Fortelný and Živný [12] showed that for immobile interfaces,  $n$  equals 5, 2, and 3 for gravitational force, Brownian motion, and intermolecular forces, respectively. The assumption for systems with immobile interfaces is that there is no motion of the interface in the direction perpendicular to the film thinning direction. Several systems including matrix/dispersed phase blends with a high viscosity of dispersed phase, systems with surfactants, and thermodynamically stable systems such as self-assembled partially wet systems can reasonably meet this criterion.

In the case of partial wetting, intact droplets of phase B collect at an A/C interface. These drops, although separated by a thin film of phase A or C, are very close to each other and are almost touching. In such a case, since inter-droplet distances are very short, it is reasonable to assume that the particle approach stage 1 is virtually complete and that film drainage and intermolecular forces can be applied to describe coalescence for such a system. In this sense, the coarsening growth rate of droplets in a ternary blend with a partial wetting morphology can be considered to be comparable to that of a binary blend with a dispersed-matrix morphology at the end of stage 1 (particle approach).

The following equation was developed for coalescence induced by film drainage and intermolecular forces for a binary system with an immobile interface [12,16]:

$$R^3 = R_0^3 + \left(128\pi\sigma^2 h_c^4 t\right) / (3\eta_m A) [1 - \exp\{(-9\phi)/[4(1 - \phi)]\}] t \quad (3)$$

where  $\sigma$  is the interfacial tension,  $h_c$  is the critical distance where coalescence begins,  $\eta_m$  is viscosity of the matrix,  $A$  is Hamaker constant ( $10^{-20}$  J), and  $\phi$  is the volume fraction of the dispersed spheres. Hence, when intermolecular forces apply to a system, the change of droplet size with time follows a 3rd power dependence.

Mekhilef et al. [17] showed that a binary blend of 50%PS/50%PE results in significant coarsening during the annealing process. They also observed that the coarsening of this sample narrows the dual-phase continuity region considerably. Veenstra et al. [18] studied the coarsening of binary blends under quiescent annealing and reported a linear relationship between phase size and annealing time. Yuan et al. [19], in a detailed work, proposed a conceptual model of co-continuous phase coarsening on thin and thick rods and proposed that the driving force for the coarsening process under static annealing is a result of capillary pressure. In this case, the continuous merging of thin parts towards thick ones occurs due to the differences in capillary pressure throughout the co-continuous structure. They found that the linear dependence of phase size with time could be explained based on Tomotika theory [20] and a mechanism of impeded capillary breakup. The more readily a thread of one phase can breakup, the more readily a thread of that phase can grow, the faster this phase can coarsen upon annealing. They demonstrated a very close relationship of experimental data to theoretical prediction. Although linear coarsening was observed for several co-continuous structures, a number of studies [21–23] reported a linear coarsening at early times of growth, followed by a second regime of slower growth at longer annealing times. Lopez-Barron et al. [23,24] suggest that the free energy of the interface is the driving force for coarsening, however this free energy is proportional to the curvature of interface. They found that the continuous reduction of the global curvature of the interface results in the decrease of the coarsening rate during the annealing process. They predicted that at a capillary number of about 0.003, the crossover between two regimes occurs. Sarazin et al. showed that the annealing of a co-continuous PS/PE system could increase the phase size from 0.9  $\mu\text{m}$  to 72  $\mu\text{m}$ . Ravati et al. [25] reported on the annealing of ternary polymer blends with a complete wetting structure. It was shown that the phase diameter of the interconnected co-continuous threads of PMMA and PVDF could be increased from 40  $\mu\text{m}$  to 500  $\mu\text{m}$  for 33.3%HDPE/33.3%PMMA/33.3%PVDF. Moreover, they observed that geometrical restrictions enormously accelerated coalescence effect for multi-percolated structures while still maintaining full continuity for all components.

In this work, the quantitative interfacial coarsening of ternary polymer systems through an annealing process will be studied for

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