Coarsening of Immiscible Co-Continuous Blends During Quiescent Annealing

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DOI 10.1002/aic.10281
Published online in Wiley InterScience (www.interscience.wiley.com).

The quiescent annealing of four different co-continuous polystyrene/high-density polyethylene blends of widely different viscosity ratios were examined at three different temperatures. In addition, the coarsening of a co-continuous poly(methyl-methacrylate)/high-density polyethylene blend was also studied. Since the morphology of co-continuous systems is very difficult to accurately analyze using microscopic techniques, the pore dimensions of the PS and PMMA phase are characterized, after solvent extraction, using mercury porosimetry. The volume average pore diameter is used in order to track the large pores in the system. A significant coarsening effect, as evidenced by the growth of pore size, is observed. For these uncompatibilized systems a direct relationship between pore size R and annealing time t ($R \sim kt$) is observed. Using a conceptual model of co-continuity, based on thin and thick rods, it is proposed that the driving force for the coarsening process is a capillary pressure effect. The differences in capillary pressure throughout the co-continuous structure result in the continuous merging of thin parts toward the thick ones. This process is confirmed through the presence of a large number of extremely thin threads in contact with very thick ones after annealing. In order to understand the factors influencing the coarsening rate we have adapted an approach used for phase separation. The thick rod is treated as a cylindrical thread which cannot breakup via a capillary instability due to the numerous branches which continuously feed it. In such a case it is proposed that the rate of growth of the distortion amplitude, $d\alpha/dt$, taken from Tomotika's analysis for capillary instabilities, can be directly related to the coarsening rate, dR/dt. Since α_0/R_0 (the ratio of the initial distortion amplitude to the initial thread radius) is found to be constant for all of the co-continuous systems studied, all of the coarsening rates for the various systems are controlled by the interfacial tension, the zero shear viscosity of the surrounding medium and Ω from Tomotika theory. An excellent correlation of this model is demonstrated for all of the systems studied. These results and the proposed mechanism also indicate that the quiescent coarsening of immiscible co-continuous blends can continue over long time periods while still maintaining co-continuity and, hence, can provide an important route toward morphology control in percolated systems. © 2004 American Institute of Chemical Engineers *AIChE J,* 51: 271–280, 2005

Introduction

The properties of an immiscible polymer blend are highly dependent on its morphology and interfacial properties (Polizu et al., 1999), which in turn is particularly sensitive to coalescence phenomena. Coalescence phenomena can be divided into two broad categories: dynamic and static processes. In the former, it is a flow-induced process, in which the dispersed phase experiences a combination of both particle breakup and coalescence (Fortelný and Kovar, 1989; Fortelný and Zivny, 1995b; Fortelný and Kovar, 1996; Schoolenberg et al., 1998; Chesters, 1991; Elemendorp and Van Der Vegt, 1986). In the

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Table 1. Material Characteristics

	$M_w \times 10^{-3}$ (g/mol)	$M_n \times 10^{-3}$ (g/mol)	Density (g/cm^3)		$\eta_0 \times 10^{-3}$ (Pa · s)		
			20°C	200°C	200°C	190°C	180°C
PS1	192000		1.04	0.974	4.5	9.5	21.0
PS2	308000		1.04	0.974	23.0	49.9	105.6
PE1	79000	24000	0.962	0.754	1.8	2.2	2.5
PE2	194000		0.962	0.754	60.0	71.6	85.0
PMMA	76500		1.19	1.00	35.7		

latter, it refers to a quiescent process, in which the dispersed phase/matrix structure is coarsened by coalescence through which the free energy of the system is minimized by reducing the interfacial area between the components (Fortelný and Kovar, 1988; Fortelný and Zivny, 1995a; Fortelný and Zivny, 1998; Fortelný and Zivny, 1999; Yu et al., 2000; Wallheinke and Pötschke, 1999).

Static coalescence for dispersed phase/matrix systems (Fortelný and Zivny, 1995a; Yu et al., 2000; Van Gisbergen and Meijer, 1991) has been studied by a number of laboratories. Fortelný and Zivny (1995a) proposed a theory to describe coalescence in polymer blends with a high content of the dispersed phase. The coalescence process was divided into four stages: particle approaching, film draining, film rupture and particle merging. They took the film drainage time as the coalescence time between two particles. Time dependencies for the mean particle size were achieved by considering different interfacial mobilities (mobile, immobile and partially mobile) and different driving forces (gravitational force, Brownian motion, van der Waals force). Another coalescence model developed by Yu et al. (2000) also suggests a similar four-step coalescence process. Unlike other mechanisms that took the film draining time as the coalescence time (Fortelný and Zivny, 1995a; Van Gisbergen and Meijer, 1991), Yu et al. (2000) also took the merging time into account and considers it as the dominant process for a high viscosity system. They obtained a relation of particle size growth as $R \sim kt^{\alpha}$, where the constant k is related to the volume fraction, interfacial tension, and the zero-shear viscosity of dispersed and matrix phase. The growth exponent α is related to the probability that the surface of a given particle is between the suitable range from the surface of any other particle.

In addition to the coalescence phenomena demonstrated for dispersed phase/matrix structures, significantly coarsened morphologies have also been observed under quiescent annealing conditions at very short times for blends with dual-phase continuity, where both phases are completely continuous (Favis, 1990; Mekhilef et al., 1997; Willemse et al., 1999; Lee and Han, 1999; Quintens et al., 1990; Veenstra et al., 1999a; 1999b; 2000). However, the coarsening of a co-continuous morphology during quiescent annealing has not been as extensively studied as that of the dispersed phase/matrix structure. Lee and Han (1999) regarded the time evolution of the rapidly precipitated co-continuous blend morphology of PMMA/PS during isothermal annealing as being equivalent to the late stages of spinodal decomposition, which is controlled by diffusion and coalescence. Willemse et al. (1999) found that in a melt-blended co-continuous structure, where the volume fraction of one of the phases is much lower than the other, coarsening is observed, and they attributed this to a restructuring process involving fiber retraction and breakup. At higher volume fractions (>30 vol %), coarsening in co-continuous structures is found to take place by retraction only. In the latter case, no coalescence takes place because all the material already belongs to an interconnected phase. Veenstra et al. (1999a,b; 2000) studied blends with thermoplastic elastomers including poly(ether-ester) block copolymer and styrene/(ethylene-butylene) based block copolymer (SEBS). They found that during annealing when the block copolymers are phase-separated into micro-domains that act as physical crosslinks, the phase sizes and composition range hardly changes. Veenstra et al. (2000) also demonstrated a linear relationship for the coarsening of a variety of co-continuous systems under quiescent annealing. This coarsening was shown to be dependent on the interfacial tension and the zero-shear viscosity of the blend materials.

Some articles have studied the composition range of co-continuity before and after annealing. It is well known that under conditions of dynamic flow, the concentration for dual-phase continuity can be shifted depending on viscoelastic parameters (Paul and Barlow, 1980; Utracki, 1991; Andradi and Hellmann, 1995). A number of articles have demonstrated that the concentration range for co-continuity moves into the center region (around 50%) after annealing (Mekhilef et al., 1997; Quintens et al., 1990; Andradi and Hellmann, 1995). Under static conditions, the concentration dominates the morphology and the major phase always forms the matrix.

The objective of this article is to study the quiescent annealing of co-continuous PS/HDPE blends as well as a binary PMMA/HDPE blend. A highly detailed morphological analysis and the influence of temperature, viscosity and interfacial tension will be examined in an effort to determine the principal underlying mechanisms related to the coarsening of immiscible co-continuous blends.

Experimental Procedures

Materials

The materials used in this study were two types of polystyrene (PS), Styron 612 and Styron 663, referred to as PS1 and PS2, respectively, and two types of high density polyethylene (HDPE), HDPE4352 and HDPE58A, referred to as PE1 and PE2, respectively. HDPE58A was obtained from Nova Chemicals and the other three materials were obtained from Dow. The poly(methyl-methacrylate) (PMMA) pellets were IRD-2 obtained from Rohm & Haas. A small amount (0.2 wt %) Irganox 1010 antioxidant was added to the mixture to reduce the thermal oxidation of polyethylene. Some of the characteristics of the materials are summarized in Table 1.

Blend preparation

Five co-continuous binary blends with different viscosity ratios were prepared (PS1/PE1, PS1/PE2, PS2/PE1, PS2/PE2

and PMMA/PE1). The melt blending was carried out in a Haake Rheomix 600 batch mixer under a constant flow of dry nitrogen. The full capacity of this mixer is 69 cm^3. The volume of material used in the batch mixer was maintained at 70% of the capacity (48 cm^3), which is standard practice in order to promote efficient blending. Blending conditions were maintained at 200°C and 50 RPM for 7 min. After mixing, the blends were rapidly quenched in liquid nitrogen to freeze-in the morphology. It should be noted that all concentrations are reported as volume fraction.

Rheological analysis

The polymers were pressed at 200°C in order to obtain the disks used for the rheological measurement. Rheological characterization was carried out using a Bohlin constant-stress rheometer (CSM) for PS and HDPE and a Rheometric Scientific constant stress rheometer (SR5000) for PMMA in the dynamic mode under nitrogen. A parallel-plate configuration was used with a gap of about 1.4 mm. Time sweeps were performed to study the stability of the polymers. Stress sweeps were also carried out to define the region of linear viscoelasticity. The Cox-Merz rule is applicable to the materials measured. The zero-shear viscosity obtained for the pure homopolymer was determined using a Carreau-Yasuda model.

Interfacial tension measurements

The breaking thread method was used to measure the interfacial tension. A Mettler hot-stage model FP 82 HT connected to a FP 90 central processor and to a Nikon transmission optical microscope was used. The approach consists of inserting a thread of one polymer between two films of the second polymer. The sandwich is then placed in a hot stage under an optical microscope. Once the thread and the films have melted, a sinusoidal distortion starts to grow and the growth of the distortion amplitude is observed with time. This can be related to the interfacial tension according to Tomotika theory (Tomotika, 1935). Details concerning the theoretical procedure for the measurements are reported elsewhere (Mekhilef et al., 1997; Elemans et al., 1990). In the current study, the measured interfacial tension for PS2/PE1, PS1/PE1 and PMMA/PE1, carried out in-house with the breaking thread technique at 200°C is 4.5, 4.7 and 6.9 mN/m, respectively. The interfacial tension for PS/HDPE has been reported on several occasions in the literature, and the earlier values compare well with those data (Elemans et al., 1990; Chen and White, 1993; Wu, 1982; Mekhilef et al., 2000). The interfacial tension for all PS/PE blends used in this study was taken as 4.7 mN/m since at these high molecular weights there is very little effect of M_w on interfacial tension.

Annealing

Annealing tests were carried out in a compression molding press. Small pieces of samples were cut from the blend which were then sandwiched between two aluminum foil sheets and subsequently transferred into the cavity of a frame. The frame, together with the material, were then placed between two metal plates on the compression molding press. While annealing, the upper heating plate of the compression press just touched the metal plate on the sample without imposing any pressure in order to minimize any deformation or flow of the sample. The annealing was carried out under nitrogen. The binary blends PS1/PE1 were annealed at five different temperatures: 180°C, 185°C, 190°C, 195°C and 200°C, while other PS/PE blends were annealed at 180°C, 190°C and 200°C. The binary PMMA/PE1 blend was annealed at 200°C only. After annealing, the samples were quenched immediately in liquid nitrogen to freeze-in the morphology.

Solvent extraction

After annealing, selective solvent extractions of PS and PMMA in cyclohexane and acetic acid were performed in a Soxhlet extraction apparatus for one week. The weight loss measurements were carried out to calculate the extent of PS or PMMA continuity using the following equation

$$\% \text{ continuity} = \frac{(\text{wt of PS or PMMA})_{\text{initial}} - (\text{wt of PS or PMMA})_{\text{final}}}{(\text{wt of PS or PMMA})_{\text{initial}}} \times 100$$

Scanning electron microscopy

Using a microtome (Leica-Jung RM 2165) equipped with a glass knife, the samples were microtomed under liquid nitrogen. After solvent extraction and coating with a gold-palladium alloy, the morphology of the samples was examined by a Jeol JSM 840 scanning electron microscope at 10 kV.

Mercury intrusion porosimetry

The porosity of the extracted samples was examined by mercury intrusion porosimetry (MIP) (Poresizer 9320), which provides the volume average pore diameter (d_v) and pore-size distribution. The experimental data treatment is based on the Washburn equation (Washburn, 1921)

$$Pr = -2\sigma \cos \theta$$

where, P is the applied pressure, r is the radius of the pore, σ is the surface tension and θ is the contact angle. In the experiments, a value of 140° for θ and 0.485 N/m for σ were used for all measurements. More details concerning the experimental and theoretical procedures for the measurements are reported elsewhere (Lowell and Shields, 1991; Gregg and Sing, 1982).

In a previous article from this group (Li and Favis, 2001), mercury intrusion porosimetry techniques were used to characterize the microstructure of a co-continuous blend of PS/HDPE after solvent extraction of the PS phase. It was found that mercury porosimetry could lead to erroneous results due to the creation of tiny pores in the blend resulting from the uneven distribution of the high operating pressure. In that work, the blend was pressed into a very thin film with a thickness no larger than 100μm. In this experiment the samples were much thicker (about 2mm thick), and for this reason it was decided to reconsider MIP as a potential characterization technique. In the current study, the pore dimensions measured by MIP were found to be consistent with the pore size range estimated from

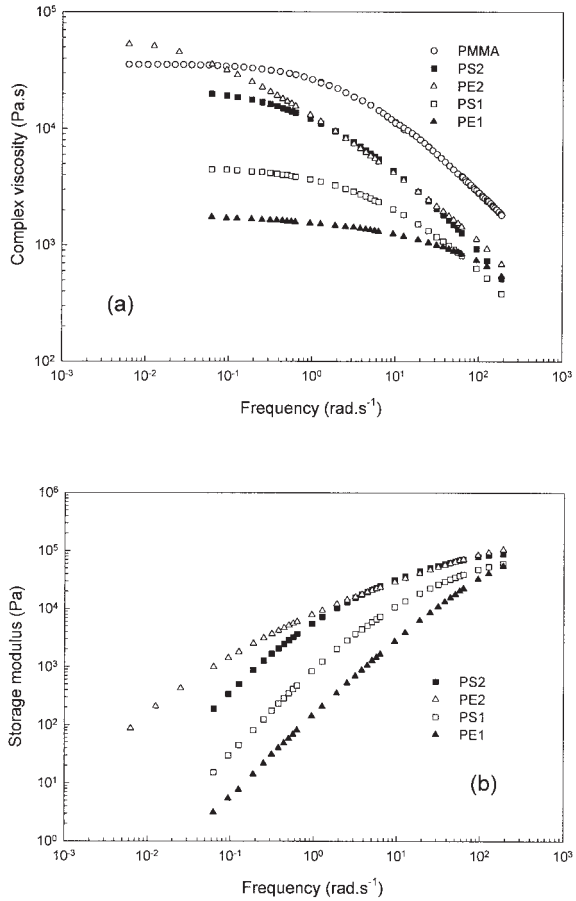


Figure 1. Rheology curves of the materials used at 200°C.

(a) Complex viscosity; and (b) Storage modulus.

the SEM results. It appears that a thin polyethylene sample is much more likely to result in uneven operating pressures within the sample and this leads to the discrepancies noted earlier. Thicker polyethylene samples were able to yield reliable results from MIP.

Results

Rheology

Figure 1a shows the complex viscosity as a function of frequency for the raw materials used. The viscosities of both PS2 and PE2 are higher than those of both PS1 and PE1 in the whole frequency region. The zero-shear viscosities (η_0) of the materials (see Table 1) were determined using a Carreau-Yasuda model. The viscosity ratios (viscosity of PS/viscosity of HDPE) at 200°C of these four PS/HDPE blends at zero and 50 rad/s are listed in Table 2.

Figure 1b shows the storage modulus (G′) vs. frequency for the blend components. As earlier, PS2 and PE2 demonstrate a higher elasticity for the whole range of frequencies compared to PS1 and PE1.

Phase inversion

The continuity/composition dependences of PS1 in PS1/PE1 and PS1/PE2 blends, and PS2 in PS2/PE1 and PS2/PE2 blends

Table 2. Initial Pore Radius R_0 After Blending and Viscosity Ratios p (Viscosity of PS/Viscosity of HDPE) at 200°C

	PS1/PE1 50/50 (a)	PS2/PE1 50/50 (b)	PS1/PE2 50/50 (c)	PS2/PE2 50/50 (d)
R_0 (μm)	5.0	2.0	3.5	1.5
p at 50 rad/s	1.1	1.7	0.58	0.90
p at 0 rad/s	2.5	13	0.075	0.38

are shown in Figure 2. It can be clearly seen that for PS2 in PS2/PE1 and PS2/PE2, the regions of phase inversion are between compositions of 0.50–0.60 and 0.30–0.60, respectively. The blends containing 70% and higher PS2 were not self supporting after extraction. For PS1 in PS1/PE1 and PS1/PE2, the apparent co-continuous structures are observed to be in the ranges of 0.50–0.55 and 0.40–0.50 PS1 compositions, respectively. The blends collapse after extraction when its PS1 composition reaches 60% and higher. For blend PMMA/PE1, 100% continuity is achieved at composition of 0.50. In this article, all the co-continuous blends were prepared with composition ratios of 50/50.

Morphological analysis and pore size measurement

(1) Initial pore dimensions of different co-continuous PS/HDPE blend systems. The initial pore-size data (before annealing) characterized using mercury intrusion porosimetry are listed in Table 2. It is evident that the largest pore size is found for the co-continuous blend with lower viscosities of both phases (PS1/PE1). An increase in the viscosity of either phase results in a decrease in the pore dimensions. It appears that the viscosity ratio of the co-continuous system at the blending condition (50 s^{-1}) does not have much influence on the final morphology (see Table 2): both the blends PS1/PE1 and PS2/PE2 have a similar viscosity ratio around 1, but their phase dimensions are quite different. This is not the case in dispersed phase/matrix structures. In a dispersed phase/matrix structure, it is generally accepted that increasing the viscosity of the minor phase (or the viscosity ratio) will lead to the increase of

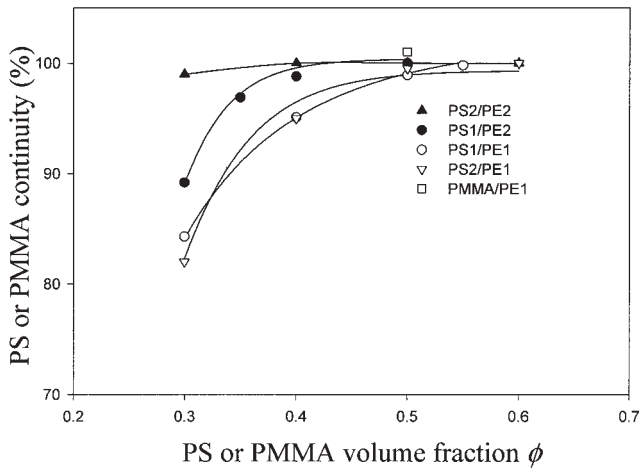


Figure 2. Continuity of PS or PMMA as a function of the composition.

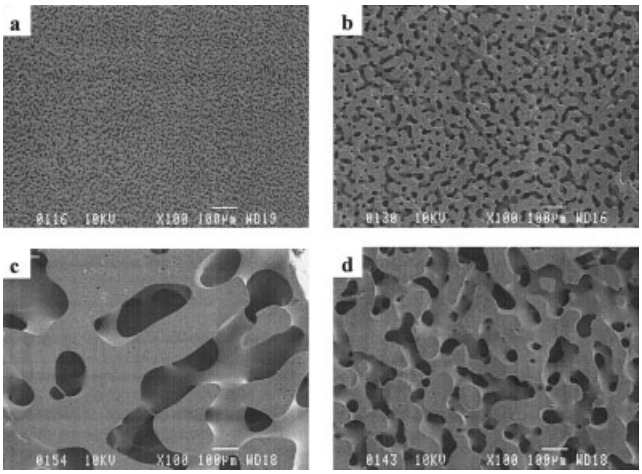


Figure 3. SEM micrographs for PS1/PE1 50/50.

(a) nonannealed sample; (b) annealed at 180°C for 10 min; (c) annealed at 200°C for 30 min; and (d) annealed at 180°C for 30 min. (The white bars denote 100 μm).

the particle size, and a fine dispersion of particle size could be achieved when the viscosity ratio is approximately unity (Favis and Chalifoux, 1987; Karger-Kocsis et al., 1984; Wu, 1987). The reason that the phase size of a co-continuous structure is independent of the viscosity ratio but dependent on the component viscosities is an indication of the dominant role of dynamic coalescence in controlling the morphology of such systems during melt blending. Thus, the increase of any phase viscosity will suppress the coalescence, and, hence, leads to a smaller phase size during mixing.

(2) Coarsening of the morphology of the co-continuous blend upon annealing. Figure 3 shows the morphology of the 50/50 PS1/PE1 blend annealed at the indicated temperatures. The initial morphology observed in Figure 3a (0 min) shows a continuous structure for both the PS and HDPE. As the blend is annealed, pore sizes grow with increasing annealing time and annealing temperature indicating that significant coarsening effects are taking place. However, the original co-continuous morphology is maintained and both phases form a continuum. This is also confirmed by the solvent extraction result which shows that for all the samples before and after annealing, 100% of the PS phase can be extracted out while the remaining HDPE phase is still self-supported.

The morphologies of the PS2/PE1 blend with and without annealing are presented in Figure 4. A similar coarsening phenomenon upon annealing, as in Figure 3, was also found, that is, more pronounced coarsening was observed for the blends annealed at higher temperature and with longer annealing time. From Figures 3 and 4, it is clear that although the pore size coarsening rates are very different for the systems investigated, the basic features of the coarsening phenomena are the same for all the blends, that is, the pore sizes of all samples grow with annealing time and are clearly dependent on annealing temperature.

The pore size data obtained using the mercury intrusion porosimetry characterization technique were drawn as a function of annealing time, and are shown in Figures 5a and 5b. Figure 5a shows the pore sizes of 50/50 PS1/PE1 annealed at different annealing temperatures, while Figure 5b shows the pore sizes of the four PS/PE blends annealed at 200°C. It is quite clear that the pore diameter increases linearly with annealing time at all annealing temperatures and for all the co-continuous PS/PE blends which supports previous work (Veenstra et al., 2000; Andradi and Hellmann, 1995). This relationship can be described as

$$D/2 = R \sim kt \tag{1}$$

where D is the volume average pore diameter, R is the average pore radius, t is the annealing time, and k refers to the pore size growth rate (coarsening rate). All the coarsening rates, k, of the four PS/PE blends annealed at 180°C, 190°C and 200°C are summarized in Table 3 (here the experimental k value is referred to as k_e). It is evident that k_e increases with increasing annealing temperature. In addition, comparing the k_e of the blend PS1/PE1 with those of three other blends, we found that an increase of the viscosity of either phase results in a decrease of the experimental coarsening rate.

Discussion

In a co-continuous morphology, each phase is fully interconnected throughout the blend system. In such a case, one can regard each phase as being composed of a large number of randomly oriented rods with various lengths and thicknesses that "touch" each other. A similar description has been used by Willemse et al. (1999) in a study related to the detection of the region of dual-phase continuity. The rods can be considered to vary in thickness because there is always a phase-size distribution in an immiscible blend (see Figure 6). On the basis of such a treatment, a capillary pressure effect should be present in such a system. It is well known that capillary pressure is proportional to the interfacial tension and inversely proportional to the rod thickness (Siggia, 1979). A thick part of the structure having a large cross section generates a capillary force lower than a thin part having a smaller cross section. This imparts a force gradient which results in flow from the thin part toward the thick part. A capillary pressure driving force for coalescence related phenomenon has been reported by Nakai et

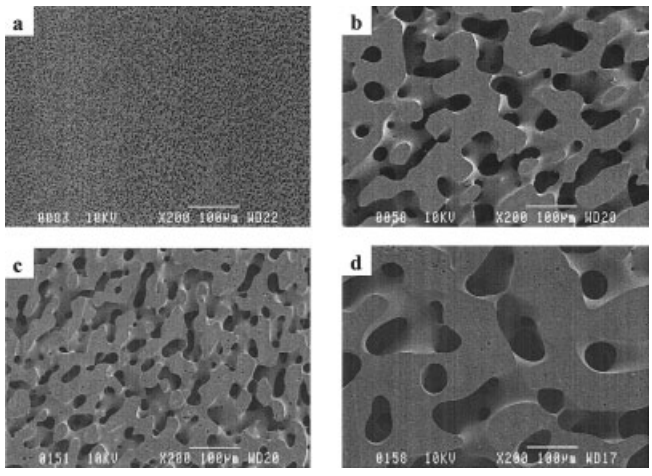
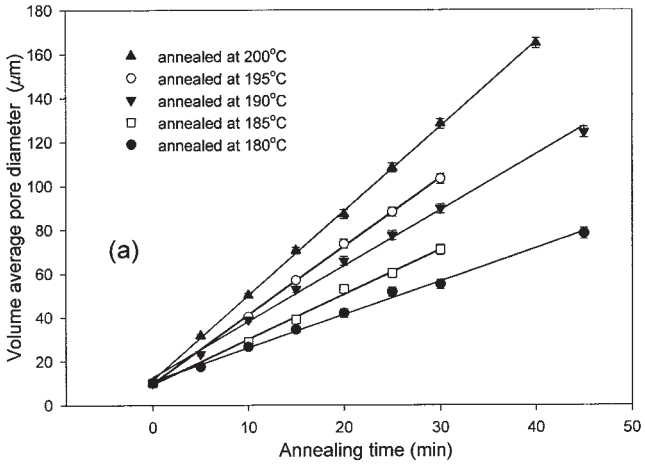


Figure 4. SEM micrographs for PS2/PE1 50/50.

(a) nonannealed sample; (b) annealed at 200°C for 25 min; (c) annealed at 180°C for 25 min; and (d) annealed at 200°C for 35 min. (The white bars denote 100 μm).



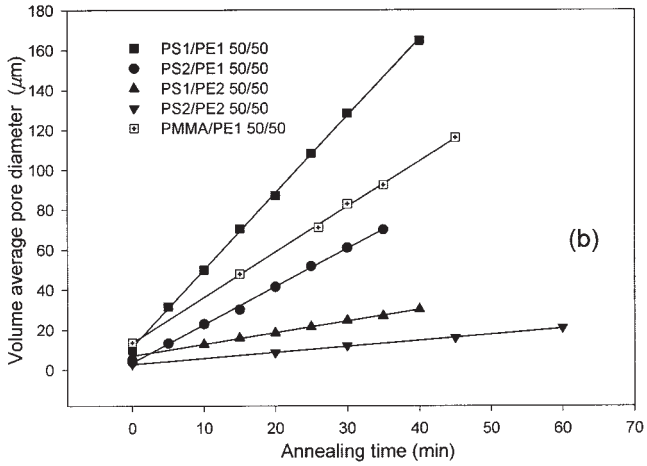


Figure 5. Experimental pore size growth of: (a) 50/50 PS1/PE1 annealed at different temperatures; and (b) various blends annealed at 200°C for different times.

The straight line here is added as a guide for the eye.

al. (1996) to describe a liquid-liquid phase separation process from solution cast polymer mixtures.

The support for a capillary pressure effect can be seen directly by SEM results. One can see in Figure 7 that after annealing there are many very thin rods, which are nearly broken, but are still connected with the trunks (thick rods) as a bridge. The thin rods do not break during coarsening until most of the material in the thin rod has been transferred (merged) into the thick rod. Once the rod has become very thin, one or several breaks/splits will take place at the thinnest part and the residual parts that connected with the thick rod will shrink/

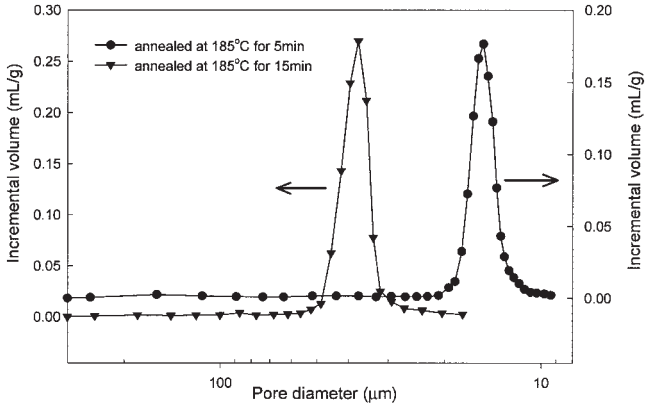


Figure 6. Pore-size distribution of different 50/50 PS1/PE1 samples.

retract and merge into the thick rod very quickly through rapid relaxation of the local curvature of the interface. This breakup at the end of the merging process results in very small dispersed particles throughout the blend system. These particles make up very little of the overall volume of the blend and, hence, do not effect the volume average pore diameter as derived from mercury porosimetry. The coarsening process is shown in Figure 8.

Other supporting evidence of the proposed driving force for coarsening is the shift of the pore-size distribution curves obtained from the mercury porosimetry study (see Figure 6). Upon increasing the annealing time, the distribution curve of volume average pore size shifts to a higher value without significantly changing the shape of the distribution. (The difference of the incremental volume peak value is due to the difference of the average pore sizes of these two samples). This supports the concept of a continuous merging process of the polymer material from thin parts into thick parts during annealing where the thin parts disappear while the thick parts in turn become thicker.

In another study, Veenstra et al. (2000) speculated that the coarsening of co-continuous morphologies was related to a fiber retraction process. Fiber retraction is a well-known viscoelastic response (Cohen and Carriere, 1989; Stone et al., 1986), where a polymer rod dispersed in the matrix of another polymer evolves to a sphere without breakup. Such a mechanism is unable to explain a number of experimental features. First, it cannot explain the observed presence of very thin rods that still connect with the thick rods as bridges after annealing (see Figure 7). Finally and perhaps most convincingly, equations related to fiber retraction (Carriere et al., 1989)

$$t_r = \frac{3D(\eta_m + \eta_d)}{\sigma} \ln\left[\frac{(L')^3 - 1}{6L' - 5}\right]^3$$

Table 3. Experimental Coarsening Rates k_e for Different Blends at Different Annealing Temperatures

	Experimental Coarsening Rates k_e (μm/min)				
	PS1/PE1 50/50 (a)	PS2/PE1 50/50 (b)	PS1/PE2 50/50 (c)	PS2/PE2 50/50 (d)	PMMA/PE1 50/50 (e)
200°C	1.9	0.95	0.29	0.15	1.2
190°C	1.3	0.60	0.19	0.095	
180°C	0.76	0.36	0.12	0.055	

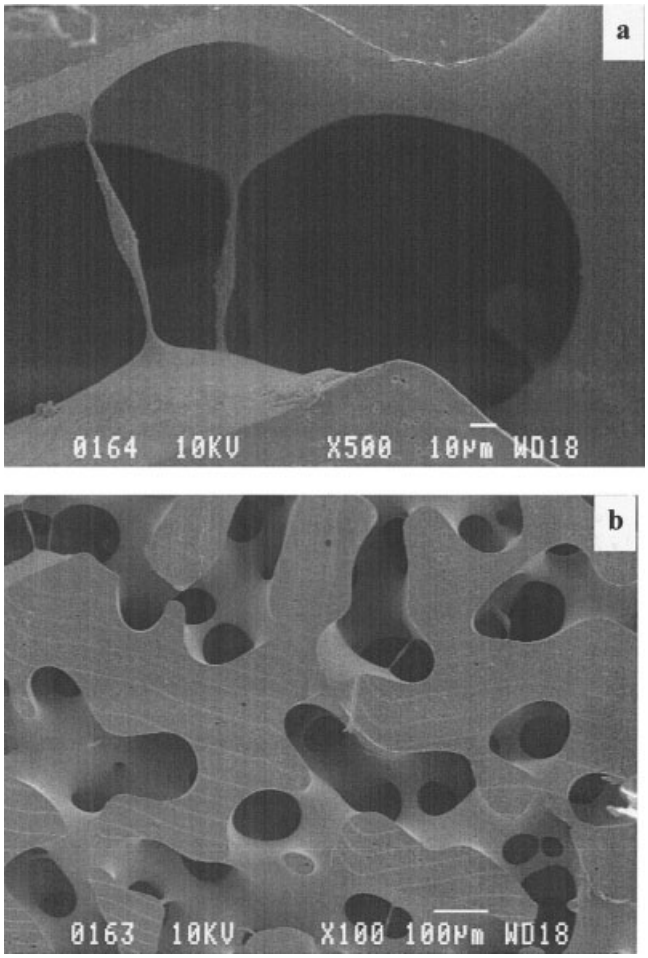


Figure 7. Presence of thin rods/threads in SEM micrographs of PS1/PE1 50/50 annealed at 190°C for 45 min.

The white bar in a denotes 10 μm, in b denotes 100 μm.

for a system similar to the one shown in this study would predict a time for complete retraction for a rod of 10 microns of 6.5 minutes (where $L' = 2\ L/D$, L/D is the aspect ratio of the fiber length and diameter, taken here as 6. η_d and η_m are the viscosity of the dispersed phase and matrix phase, respectively, σ is the interfacial tension). Shorter rods would retract even more quickly. Clearly in this work, coarsening progresses well beyond this timescale.

Therefore, it appears likely that the coarsening of a co-continuous immiscible blend structure upon annealing can be considered accordingly as a process of continuously merging thin rods into thick ones via capillary forces. Once a thin rod has been essentially emptied, it breaks up into small droplets. We will assume for the purposes of this study that all trunks (thicker rods) do not shift during the quiescent melt annealing process.

What are the physical phenomena controlling the rate of rod size growth? In this part of the analysis we will consider only those thick rods (backbones) that are growing all the time and which do not merge into other rods during annealing. Every such thick rod can be considered as a "cylindrical thread" with an initial average radius R_0 and infinite length encapsulated in another phase. These threads would typically be expected to demonstrate capillary instability effects and generate sinusoidal distortions during annealing. The theory of capillary instabilities is well known and the basic equations governing their formation have been developed by Tomotika (1935). Capillary instabilities are an interfacial tension driven process and are a consequence of the decrease of the total interfacial area with increasing amplitude. Only distortions with a wavelength larger than the original circumference of the cylinder grow. Tomotika (1935) found that the dominant wave number X_m ($=2\pi R_0/\lambda_m$) has a maximum value of 0.6 depending on the viscosity ratio of the two phases, which means the dominant wavelength λ_m should be at least 10 times larger than the initial radius R_0. As mentioned previously, a system with a co-continuous structure contains a large number of interconnected rods with various lengths and thicknesses, which provide numerous branch points along the "cylindrical thread" (see Figure 9). Under this condition, the average distance L between two adjacent branch points is generally smaller than the dominant wavelength λ_m.

McMaster (1975) studied the mechanisms of liquid-liquid phase separation of a binary system. For an interconnected binary system, under the condition where the average distance L between two adjacent branch points is smaller than the dominant wavelength λ_m, he found that the breakdown of the "cylindrical thread" is inhibited during the annealing process. In his study, McMaster found that for a phase-separated highly interconnected SAN/PMMA two-phase structure, the coarsening rate k can be estimated by recognizing that the dominant wavelength is continuously changing as the diameter of a growing thread is fed by other threads which are decreasing in size. From the Tomotika analysis, the distortion amplitude α grows exponentially with time t

$$\alpha = \alpha_0 e^{qt} \tag{2}$$

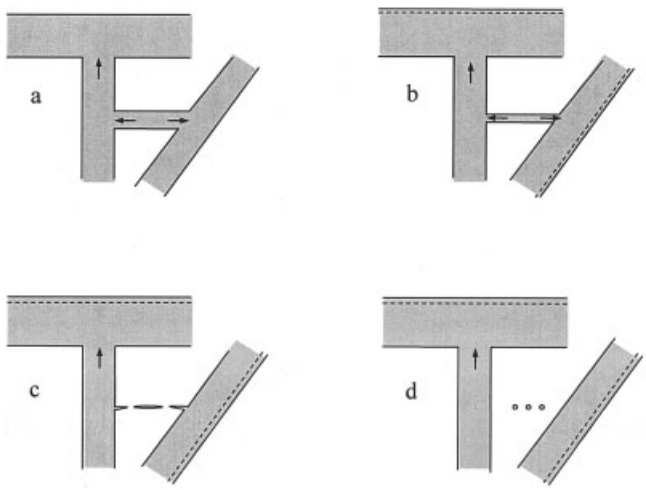


Figure 8. Coarsening process in co-continuous structure upon annealing.

(a) the thin rod merges/flows into thick ones at both sides, the thick rod merges into a much thicker one at the same time; (b) the thin rod becomes thinner during the merging process; (c) the thin rod breaks/splits; and (d) the residual parts retract/shrink to the thick rods.

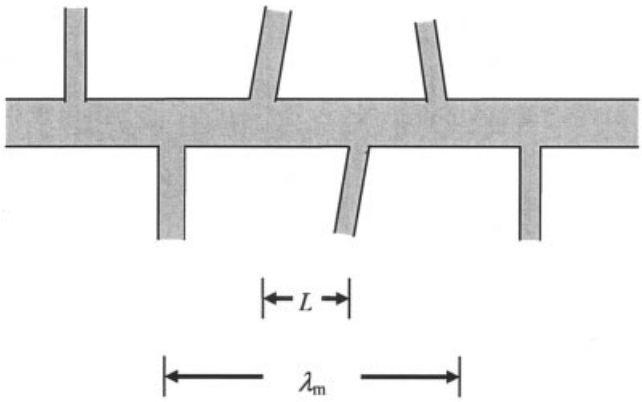


Figure 9. Cylindrical thread with interconnected rods where the distance between branches *L*, is less than the dominant wavelength λ_m.

Differentiating this equation, the initial growth rate of the amplitude at zero time is

$$\frac{d\alpha}{dt} = \alpha_0 q \tag{3}$$

where the growth rate q of the thread is given by

$$q = \frac{\sigma\Omega(\lambda, p)}{2\eta_c R_0} \tag{4}$$

with α_0 the original distortion amplitude, σ the interfacial tension, η_c the viscosity of the continuous phase, and $\Omega(\lambda, p)$ the Tomotika function related to the dominant wavelength λ and the viscosity ratio p ($p=\eta_d/\eta_c$, η_d the viscosity of the dispersed phase). Combining Eq. 3 and 4 yields

$$\frac{d\alpha}{dt} = (\alpha_0/R_0)\,\frac{\sigma\Omega(\lambda, p)}{2\eta_c} \tag{5}$$

where α_0/R_0 is the ratio of the original amplitude to the thread radius. Under the above conditions, McMaster (1975) proposes that the phase size growth can be directly related to $d\alpha/dt$, based on which a long linear growth behavior was explained. In McMaster's work, long linear growth periods are shown for interconnected structures comparable to the timescales in our work. Long linear growth behavior has also been reported in a number of other articles on immiscible blends (Veenstra et al., 2000; Andradi and Hellmann, 1995). McMaster shows that the linear growth period terminates at some point and transits to an exponential one. As for the exponential growth behavior observed by McMaster, he suggested that it is "associated with a gradual breakdown in interconnectivity so that the dominant wavelength and the scale of interconnectivity become comparable". In our study, complete co-continuity is maintained throughout the experiment- an indication that complete interconnectivity is also maintained- thus Eq. 5 and linear growth should be applicable over the timescale of our experiments.

Another question to consider in comparing McMaster's work to ours is the significant difference in interfacial tension between the systems. Tomotika's theory applies to polymer blend systems over a wide range of interfacial tensions. The interfacial tension is incorporated directly in the theory (see Eq. 4), and a number of experimental studies have shown that Tomotika theory applies to both very low and very high interfacial tension systems (Elemans et al., 1990; Mekhilef et al., 1997). Hence, although McMaster's work is applied to partially miscible systems with low interfacial tension, it should be possible to apply McMaster's approach to immiscible polymer blends.

Applying McMaster's work to the current system, the pore size growth, dR/dt in the immiscible co-continuous blend, should also be directly related to $d\alpha/dt$. Hence, Eq. 5 can be described as

$$\frac{dR}{dt} = (\alpha_0/R_0)\,\frac{\sigma\Omega(\lambda, p)}{2\eta_c} \tag{6}$$

Since it has been shown earlier that the coarsening of co-continuous blends progresses linearly in time it follows that

$$R \sim kt \tag{7}$$

and, hence

$$k = \alpha_0 q = (\alpha_0/R_0)\,\frac{\sigma\Omega(\lambda, p)}{2\eta_c} \tag{8}$$

Since, the coarsening rate, σ, Ω and the zero shear viscosity are known, α_0/R_0 can be estimated for each annealed system shown in Table 3. The calculated values demonstrated in Table 4 are shown to be constant with an average value of 0.49. The only possible exception is for PS2/PE1 at 180°C. At that temperature PS2/PE1 has a very large viscosity ratio ($p=42.2$) which makes the estimation of Ω, and, hence, α_0/R_0 difficult. McMaster (1975) also considered α_0/R_0 as a constant in his work. He estimated the value to be 0.5 for his highly interconnected SAN/PMMA system undergoing phase separation. In order to test the concept that the pore size growth is determined

Table 4. Ratios of α_0/R_0 Calculated from Equation 8 for Different Blends at Different Annealing Temperatures

	α_0/R_0^*				
	PS1/PE1 50/50 (a)	PS2/PE1 50/50 (b)	PS1/PE2 50/50 (c)	PS2/PE2 50/50 (d)	PMMA/PE1 50/50 (e)
200°C	0.50	0.48	0.47	0.52	0.46
190°C	0.54	0.43	0.48	0.53	
180°C	0.47	0.31	0.48	0.49	

*$\alpha_0/R_0 = k_e/[\sigma\Omega(\lambda, p)/2\eta_{pe}]$

by the distortion amplitude growth, a theoretical curve based on Eqs 7 and 8 and applied to the initial pore size prior to annealing is compared to the experimental data. This is shown in Figure 10 for all the systems at 200°C, and it can be seen that the correlation is excellent. Note that an average value of α_0/R_0 of 0.49 was used in that figure for all the blend systems.

Equation 8 indicates that the ratio of experimental coarsening rates k between different co-continuous PS/HDPE blends during annealing is actually related to distortion amplitude growth rates. In other words, the more easily a thread of one phase can breakup according to Tomotika theory, the more readily a thread of that phase can grow, the faster this phase can coarsen upon annealing. The correlation between the ratios of the experimental coarsening rates k_e, with the theoretical coarsening rates k_t generated from Eq. 8 is shown in Table 5. An excellent correlation is demonstrated for all blend system pairs at all temperatures. The only possible exception is for system pair PS1/PE1 (a) and PS2/PE1 (b) at 180°C. As discussed earlier, at that temperature PS2/PE1 has very large viscosity ratio (p=42.2 at 180°C), which makes an estimation of the Ω value difficult (Elemans et al., 1990).

In order to verify the validity of Eqs. 7 and 8 even further, a blend system of different interfacial tension, 50/50 PMMA/PE1, was also prepared and annealed at 200°C. The linear time dependence of pore size growth, and the coarsening rate is shown in Figure 5b and Table 3, respectively. The experimental and theoretical coarsening rate ratios between the blend systems PS1/PE1 (a) and PMMA/PE1 (e) correlate closely as shown in Table 5. Also, the theoretical curve for PMMA/PE1 shown in Figure 10 correlates very well with the experimental data. All of the earlier results taken together indicate that Eq. 7 and 8 can be used to quantitatively predict the coarsening of co-continuous immiscible blend systems during quiescent annealing.

This model explains all of the principal features observed in the coarsening of immiscible co-continuous blends: (a) the linear time dependence, (b) the continuous coarsening over long timescales, (c) the influence of the interfacial tension and zero shear viscosity, and (d) the actual coarsening rate itself.

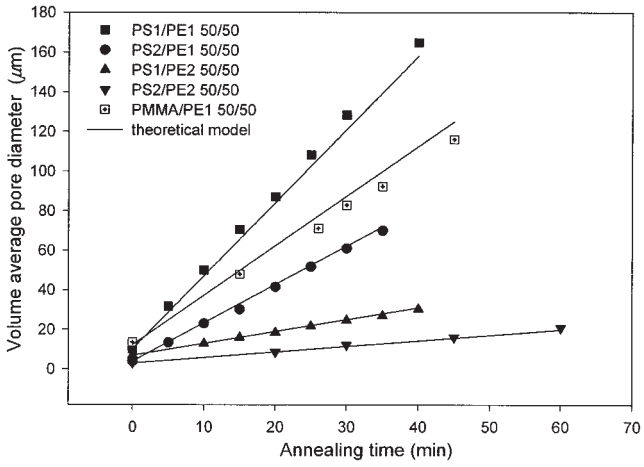


Figure 10. Experimental pore size growth (points) with the theoretical model (solid lines) for different blends annealed at 200°C.

A value of (α_0/R_0)=0.49 is used in all cases above.

Table 5. Ratios of Experimental Coarsening Rates, k_e, and Ratios of Theoretical Coarsening Rates, k_t, Derived from Tomotika Theory Between Different Blends

		(a)/(b)	(a)/(c)	(a)/(d)	(a)/(e)
k_{ex}/k_{ey}	200°C	2.0	6.6	13	1.6
	190°C	2.2	6.8	14	
	180°C	2.1	6.3	14	
k_{tx}/k^*_{ty}	200°C	1.9	6.2	13	1.5
	190°C	1.7	6.1	14	
	180°C	1.4	6.5	15	

*$k_t = (\alpha_0/R_0)(\sigma\Omega(\lambda, p)/2\eta_c)$, therefore, $k_{tx}/k_{ty} = \sigma_x\Omega_x\eta_{cy}/\sigma_y\Omega_y\eta_{cx}$

Conclusions

Using a conceptual model of co-continuity based on thin and thick rods it is proposed that the driving force for the coarsening process during static annealing is a capillary pressure effect. The differences in capillary pressure throughout the co-continuous structure result in the continuous merging of thin parts toward the thick ones. This process is confirmed through the presence of a large number of extremely thin threads in contact with very thick ones after annealing. In order to understand the factors influencing the coarsening rate we have adapted an approach used by McMaster for phase separation. The thick rod is treated as a cylindrical thread which cannot breakup via a capillary instability due to the numerous branches which continuously feed it. In such a case it is proposed that the rate of growth of the distortion amplitude, $d\alpha/dt$, taken from Tomotika's analysis for capillary instabilities, can be directly related to the coarsening rate, dR/dt. Since α_0/R_0 (the ratio of the initial distortion amplitude to the initial thread radius) is found to be constant for all of the co-continuous systems studied here, all of the coarsening rates for the various systems are controlled by the interfacial tension, the zero shear viscosity of the surrounding medium and Ω from Tomotika theory. In other words, the more easily a thread of one phase can breakup according to Tomotika theory, the more readily a thread of that phase can grow, the faster this phase can coarsen upon annealing. An excellent correlation of this model is demonstrated for all of the systems studied.

This model explains all of the principal features observed in the coarsening of immiscible co-continuous blends: (a) the linear time dependence, (b) the continuous coarsening over long timescales, (c) the influence of the interfacial tension and zero shear viscosity, and (d) the actual coarsening rate itself.

Acknowledgments

Financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Strategic Grant is gratefully acknowledged.

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Manuscript received Nov. 5, 2003 and revision received Apr. 21, 2004.