Ultralow Percolation Thresholds in Ternary Cocontinuous Polymer Blends

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Introduction. In binary immiscible polymer blends, as the concentration of the minor component increases, the structure percolates and its continuity also increases.[1,2] At higher concentrations, closely associated with the region of phase inversion, a cocontinuous morphology is obtained and is characterized by two fully continuous phases. By selectively controlling the interface, composition, processing temperature, shear rate and annealing time of the blends, it is possible to control the pore size of the cocontinuous network over 2−3 orders of magnitude.[3,4] Cocontinuous polymer blends have the potential of opening particular application fields where the presence of interconnected structures are a necessary feature (as in separation phenomena, electrical conductivity, tissue engineering scaffolds and drug delivery devices). A significant body of literature has examined factors influencing the percolation threshold in binary cocontinuous polymer blends and also the width and concentration range of the region of dual-phase continuity.[3,4] Most studies on binary systems report percolation thresholds in a range of about 15−20% concentration of minor component. This significant amount of the second phase, necessary to obtain a continuous structure, considerably limits the range of possible applications. However, very few studies have examined continuity phenomena in multiphase (more than two phases) systems. The possibility of dramatically decreasing the percolation threshold of one component in order to achieve cocontinuity at concentration levels of a few percent would be an important achievement. A few studies have contributed toward attaining such a result. Jérôme and co-workers reported on the preparation of a cocontinuous polymer blend with the addition of a solid filler showing a very low percolation threshold for the filler at about 0.2 vol %. Interestingly, this filler was located at the interface in a chain-like structure shape.[5,6] However, the limitation in that case is that the particle is not thermodynamically stable at the interface. It has a particular affinity for one of the phases and is simply transiting from one phase to the other. In a subsequent work from that group, Calberg et al.[7] showed that carbon black could be localized at the interface of a binary polyblend due to the lack of interaction of CB with each polymer phase. Jorgensen and Utracki report very low percolation thresholds for polyethylene in polystyrene binary blends of very high molecular weight.[8] Mezzenga et al.[9] obtained a low percolation threshold for an electrically conductive polymer starting from a colloidal solution. The percolated network of the conducting polymer is a result of polymer demixing during the evaporation of the solvent contained in the continuous minor phase. In other studies, Narkis, Zilberman, and co-workers[10,11] achieved multiple percolation by dispersing a third phase into one of the phases in a cocontinuous binary blend. This ultimately creates a third percolated system, but the percolation thresholds are relatively high at 8−12% composition of this third phase.

A potentially interesting way to achieve low percolation threshold materials is to combine a cocontinuous structure with a composite droplet type of morphology. The composite droplet morphology is a matrix/dispersed phase system in which the dispersed phase has a droplet-in droplet structure. Although little work has been published on polymeric versions of such systems, a number of key papers have appeared.[12−16] The spreading coefficients[17] (eq 1) and variations on that concept have been successfully used[18−20] to predict the thermodynamically stable preferential encapsulation of one polymeric phase by another. Encapsulation is governed by the various interfacial tension pairs within a ternary polymer blend and is related to the minimization of the interfacial free energy. In eq 1

$$\lambda_{ij} = \gamma_{jk} - \gamma_{ik} - \gamma_{ij} \tag{1}$$

λ_{ij} is defined as the spreading coefficient describing the tendency of component *i* to encapsulate or spread around component *j* in a matrix of component *k*. γ_{jk}, γ_{ik}, and γ_{ij} are the interfacial tensions of the different polymer pairs. In blends of one major constituent (polymer A) and two minor ones (polymers B and C, the dispersed phases), four different morphologies are possible (Figure 1): (a) separate dispersions; (b) partial encapsulation; (c, d) two possibilities of complete engulfing (composite droplets). Each morphology has a distinct set of spreading coefficients.

Recently, in our group, studies have been conducted on ternary immiscible polymer blends of high-density polyethylene (HDPE), polystyrene (PS), and poly(methyl methacrylate) (PMMA).[13,14,19] When PS and PMMA are dispersed in a HDPE matrix, composite droplets constituted of a well-segregated PMMA core and PS shell are formed. By controlling the relative amounts of PS and PMMA, it is possible to control the thickness of the PS shell down to 30−40 nm, near the range of a molecular layer of PS. Furthermore, virtually all of the PMMA is present as sub-inclusions within the PS dispersed phase after approximately 2 min of mixing.

This paper reports on the development of ternary percolated cocontinuous systems in HDPE/PS/PMMA blends in which HDPE and PMMA form two continuous networks, while the PS forms a continuous sheath structure at the HDPE/PMMA interface (Figure 2). By controlling the relative amounts of HDPE, PS and PMMA, it will be shown that it is possible to decrease the percolation threshold of the PS layer down to less than 3%, resulting in a PS continuous network of ultralow composition.

Experimental Section. Materials. HDPE 04352N and PS 615APR were both obtained from the Dow Chemical Company. PMMA 200336 was purchased from Sigma-Aldrich. An antioxidant, Irganox B225 from Ciba-Geigy, was added to the mixture to reduce thermal oxidation of polyethylene (0.2 wt %). Physical properties of the materials were measured previously[13] and are given in Table 1.

Measurement of the Interfacial Tensions and Calculation of the Spreading Coefficients. The interfacial tensions were measured using the breaking thread method, as described in an earlier publication.[19] The different interfacial tensions and

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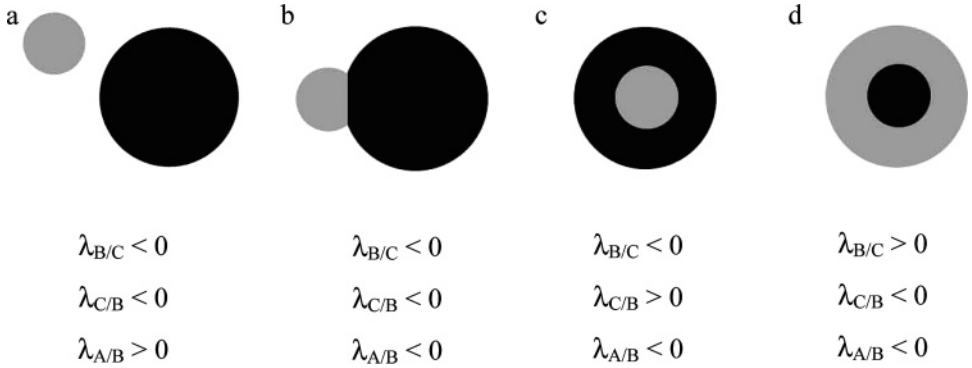

Figure 1. Morphologies of ternary polymer blends containing one major phase (polymer A (white)) and two minor ones (polymers B (gray) and C (black)): (a) separate dispersions; (b) partial encapsulation; (c and d) composite droplets (complete engulfing)

Table 1. Homopolymer Properties

polymers	M_w[a] × 10^{-3} g/mol	M_n[a] × 10^{-3} g/mol	melt index[b] ASTM, g/10 min	density,[b] g/cm^3, at 20 °C	density,[b] g/cm^3, at 200 °C	$\eta^* \times 10^{-3}$,[c] Pa·s at 200 °C, $\dot{\gamma}$[e]	$\eta^* \times 10^{-3}$,[c] Pa·s at 200 °C, τ[f]	$N_1 \times 10^{-4}$,[d] Pa at 200 °C, $\dot{\gamma}$[e]	$N_1 \times 10^{-4}$,[d] Pa at 200 °C, τ[f]
HDPE	79	24	4	0.96	0.75	1.2	1.2	2.2	2.2
PS	290	141	15	1.04	0.97	1.7	2.6	11	5.1
PMMA	11.9	7.8			1	0.04	0.04	0.02	0.6

[a] Measured by GPC. [b] Obtained from supplier. [c] η^* is the complex viscosity. [d] N_1 is the first normal stress difference. [e] At average shear rate during blending: $\dot{\gamma} = 25\ s^{-1}$. [f] At average shear stress during blending: $\tau = 2.7 \times 10^4$ Pa.

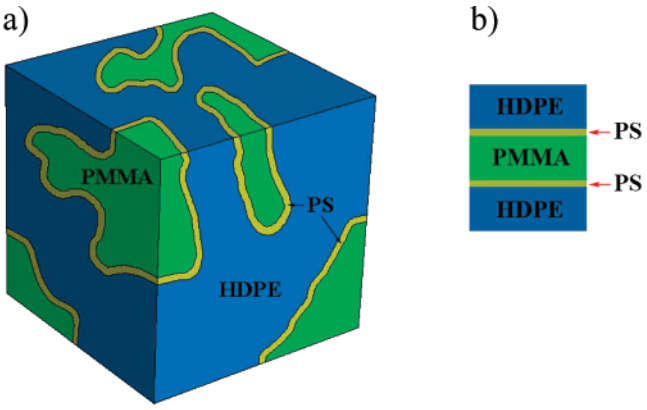

Figure 2. Schematic of the HDPE/PS/PMMA multiple percolated structure: (a) three-dimensional view of the blend structure, showing the thin PS layer at the HDPE/PMMA interface; (b) section showing the relative position of the different phases.

Table 2. Interfacial Tensions and Spreading Coefficients for HDPE/PS/PMMA Blends at 200 °C

polymer pairs	interfacial tension γ (mN/m)	polymer pairs, spreading of i on j (i/j)	spreading coeffs λ (mN/m)
HDPE/PS	5.1	PS/PMMA	1.1
PS/PMMA	2.4	PMMA/PS	−5.9
HDPE/PMMA	8.6	HDPE/PS	−11.3

spreading coefficients for the HDPE/PS/PMMA ternary blends are given in Table 2.

Blend Preparation. Prior to melt mixing, all polymers were predried for 24 h at 80 °C in a vacuum oven to remove any moisture from the pellets or powders. Ternary blends were prepared by melt-mixing in a 50 mL Haake internal mixer with twin cam rotors, with the temperature of the mixing chamber initially set at 200 °C and rotor speed set at 50 rpm. After mixing for 7 min under a constant flow of dry nitrogen, samples were immediately quenched in a bath of liquid nitrogen to freeze-in the morphology.

Continuity Measurement. Solvent extraction has been used to determine the composition region of cocontinuity of the blends. As a primary advantage, solvent extraction is an absolute measurement[21] and is capable of detecting the existence of continuous microstructures when the components are soluble in specific solvents.[2] The level of continuity of a phase in a sample is given by eq 2:

$$\%\ \text{continuity} = \frac{m_{\text{initial}} - m_{\text{final}}}{m_{\text{initial}}(i)} \times 100 \qquad (2)$$

In this equation, m_{initial} is the initial mass of the sample, m_{final} is the final mass of the sample and $m_{\text{initial}}(i)$ is the mass of polymer i contained in the sample before selective extraction, calculated by considering the blend as homogeneous. Selective solvent extraction of the PMMA and PS phases were performed respectively in acetic acid and cyclohexane in a Soxhlet extraction apparatus. Mass loss measurements were carried out for 1 week and were used to calculate the extent of continuity of the PMMA and PS phases using eq 2.

Focused Ion Beam (FIB) Preparation and Atomic Force Microscopy (AFM) Morphology Analysis. The specimens were initially cryomicrotomed to create a plane face using a Leica RM2165 microtome equipped with a cooling chamber. FIB surface etching was performed using a Hitachi 2000A Ga^+ focused ion beam operated at 30 keV and 0.8 nA, with a dwelling time of 3 μs. The etched surface was then analyzed by tapping mode atomic force microscopy (AFM) using a scanning probe microscope Dimension 3100 from Veeco Instruments equipped with a Nanoscope IVa controller. Silicon tips, model PPP-NCH-W from Nanosensors, with a force constant of 10−130 N/m (nominal value of 42 N/m) and resonance frequency of 204−497 kHz (nominal value of 330 kHz), were used. The cantilever was oscillated at approximately 98% of the resonance frequency and topographic (height) images were taken at approximately 95% of the free oscillating amplitude. The samples were fixed on a metallic support using graphite tape. This procedure is thoroughly described in a previous paper.[22]

Results and Discussion. Initially, the continuity development of the PMMA phase in binary HDPE/PMMA blends was

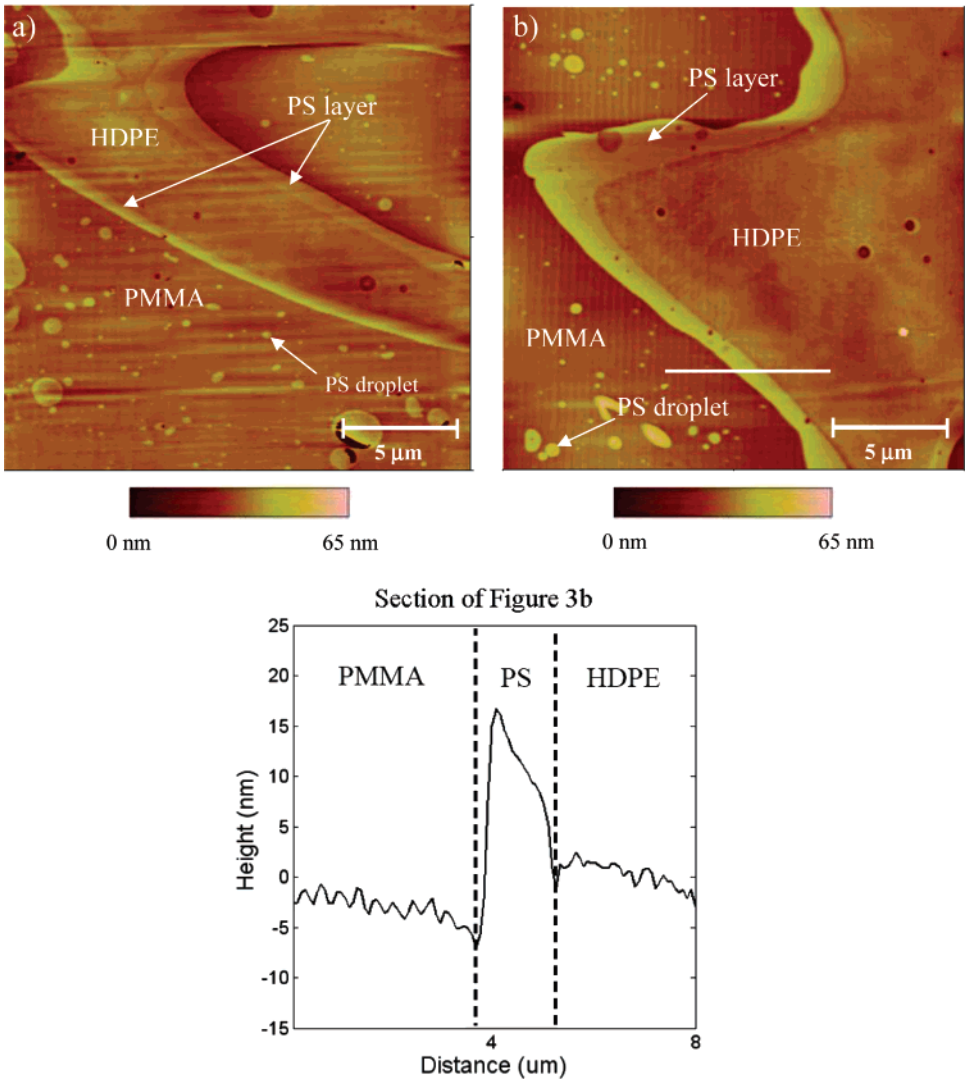

Figure 3. FIB-AFM images of HDPE/PS/PMMA ternary blends: (a) 50/10/40 (% vol.) and (b) 50/12.5/37.5. Images were taken at 95% of the free oscillation amplitude. Scan sizes are 20 μm × 20 μm. The white line in Figure 3b indicates the section analyzed below.

Table 3. Continuity of the PMMA and PS Phases as a Function of Composition Using the Selective Solvent Dissolution Technique

blend no.	vol fractions (%)			extracting PMMA, PMMA continuity (%)	extracting PS, PS continuity (%)
	HDPE	PMMA	PS		
1	50	50	0	103	0
2	50	47	3	103	69
3	50	45	5	102	73
4	50	42.5	7.5	103	74
5	50	40	10	102	76
6	50	37.5	12.5	104	77

examined in order to determine the boundaries required to achieve cocontinuity in HDPE/PMMA. After preparation by melt-mixing, the blends were immediately quenched in liquid nitrogen to freeze-in the morphology. To measure the continuity of the PMMA phase in each blend, a selective solvent extraction of the PMMA phase, using acetic acid, was performed. As the PMMA volume fraction increases from 30% to 40%, the continuity increases very rapidly from 17% to 95%. A further increase of the PMMA volume fraction to 45% yields a 98% continuous PMMA phase and results in a binary cocontinuous polymer blend.

Subsequently, ternary HDPE/PS/PMMA blends were prepared at different compositions (given in Table 3) based on the cocontinuity region found for HDPE/PMMA binary blends. The qualitative microstructural features of the blends were analyzed using a focused ion beam (FIB)− atomic force microscopy (AFM) method described in a previous article.[22] FIB etching involves the interaction of a gallium ion beam with the blend surface and is a surface preparation step prior to the AFM surface analysis. Since the gallium ion beam has significantly different etching rates for each of the individual components, this etching process induces a topological contrast between the different phases, each surface level corresponding to a specific phase. Observation of these surfaces by AFM in the topological mode allows for the acquisition of images with a very high contrast. Since all the three polymers are immiscible, the three different levels observed on the AFM images each correspond to a given polymer. In HDPE/PS/PMMA ternary blends, PS is the less etched material, and thus corresponds to the high-level domains, while HDPE corresponds to the midlevel domains and PMMA to the low-level ones. This method of analysis is particularly useful for multicomponent blends and for fine structure analysis since the etching process is sensitive to the nature of the materials and eliminates some artifacts related to classical microtomy and staining preparation methods.

Figure 3 shows AFM images after FIB treatment for ternary blends nos. 5 and 6, as described in Table 3. The HDPE (midlevel domains, notice the fine texture corresponding to the crystalline structure) and PMMA phases (low-level domains,

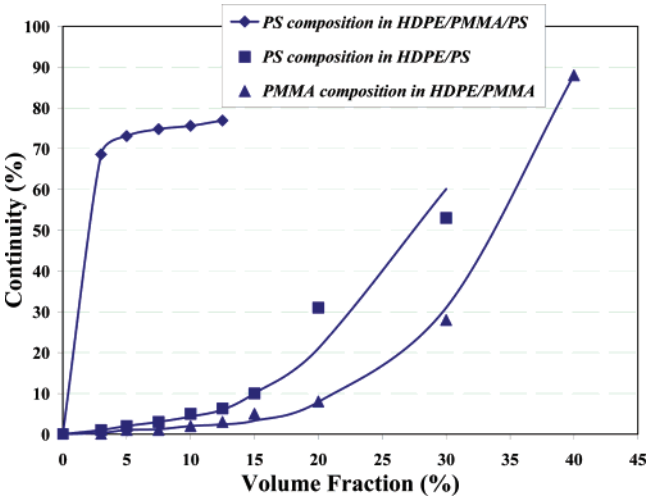

Figure 4. Continuity of PS or PMMA as a function of the composition using the solvent dissolution technique

in dark orange) appear as the main components and are separated by a thin PS layer (high-level domains, in yellow). PS/PMMA and PS/HDPE composite droplets can also be seen in the HDPE and PMMA phases respectively, while some pure dispersed PS is observed in the PMMA. Finally, small quantities of PMMA and HDPE are visible in the PS layer. Even though the segregation is not perfect, it is clear that most of the PS is located at the interface between the PMMA and the HDPE phases. The white bar in Figure 3b corresponds to the section analyzed below the AFM image, quantitatively showing the relative topographical levels of each phase.

The presence of a PS layer at the interface of the cocontinuous HDPE/PMMA blends significantly reduces the PS volume fraction required for its percolation and continuity development as compared to classical binary HDPE/PS and PMMA/PS blends. Continuity data based on gravimetric solvent extraction clearly demonstrate this effect and are shown in Table 3 and Figure 4. Cyclohexane and acetic acid were used to extract PS and PMMA respectively. It can be seen that in this triple percolated system, a PS volume composition as low as 3% results in a PS phase continuity of about 70%, a very high level of continuity for such a small volume fraction of PS. Moreover, the PS layer continuity increases with increasing PS volume content, reaching an apparent maximum value of approximately 80%. Interestingly, it seems impossible to further increase the PS continuity by increasing its relative composition. This upper limit in the apparent continuity of the PS is most probably due to the PS trapped as droplets and composite droplets in the PMMA and HDPE phases as shown in Figure 3. Nevertheless, most of the PS has clearly and spontaneously structured itself at the HDPE/PMMA interface.

Conclusions. Through a combination of composite droplet and cocontinuous blend morphology preparation methodologies, a continuous shell structure of polystyrene has been situated at the interface of a cocontinuous polyethylene/poly(methyl methacrylate) blend. This multiple percolated, interfacial tension driven structure results in a dramatic decrease in the percolation threshold volume fraction of the encapsulating PS component. As little as 3% polystyrene is shown to generate a continuous PS network. The encapsulation effect follows the prediction based on the spreading coefficient theory. This approach could be used as a route to generate novel cocontinuous structures and also as a technique to significantly reduce percolation thresholds in multiphase blends.

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