

Thermoplastic Blend Demixing by a High-Pressure, High-Temperature Process

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ABSTRACT: The analysis of a thermoplastic polymer blend requires a precise separation of the blend components, which is usually performed by selective solvent extraction. However, when the components are high-molecular-weight polymers, a complete separation is very difficult. The use of fluids in near critical and supercritical conditions becomes a promising alternative to reach a much more precise separation. In this work, a method to separate reactive and physical blends from high-molecular-weight commercial polymers is proposed. Polyethylene (PE)/polystyrene (PS) blends were separated into their components with *n*-propane, *n*-pentane, and *n*-heptane at near critical and supercritical conditions. The selectivity of each solvent was experimentally studied over a wide range of temperatures for assessing the processing windows for the separation of pure components. The entire PE phase was solubilized by *n*-pentane and *n*-heptane at similar temperatures, whereas propane at supercritical conditions could not dissolve the fraction of high-molecular-weight PE. The influence of the blend morphology and composition on the efficiency of the polymer separation was studied. In reactive blends, the *in situ* copolymer formed was solubilized with the PE phase by chemical affinity. The method proposed for blend separation is easy, rapid, and selective and seems to be a promising tool for blend separation, particularly for reactive blends, for which the isolation of the copolymer is essential for characterization ©2005 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 43: 2361–2369, 2005

Keywords: blends; blend extraction; graft copolymers; high-pressure polymer extraction; separation techniques; thermoplastic blend separation

INTRODUCTION

Thermoplastic polymer blends are attracting attention because of their potential to reach a good balance between final properties and low cost. These materials find applications in several industrial fields. Particularly in the automotive industry, blends are rapidly replacing engineering materials.^{1–3} Thermoplastic blends are also favored for their ability to be recycled or reused.⁴

The most frequently used commodity thermoplastics [polyethylene (PE), polypropylene, poly(vinyl chloride), and polystyrene (PS)] exhibit very low entropy of mixing. Therefore, phase segregation will result when they are blended in significant proportions, leading to the formation and coalescence of sizable dispersed phase domains. Consequently, low adhesion between phases and poor final properties can be expected from the direct blending of thermoplastic commodities. The key to achieving upgraded properties from immiscible blends is phase compatibilization.^{5,7}

A convenient route to compatibilize PS/PE blends is the use of the Friedel–Crafts alkylation reaction in the melt.^{8,9} The reaction products are

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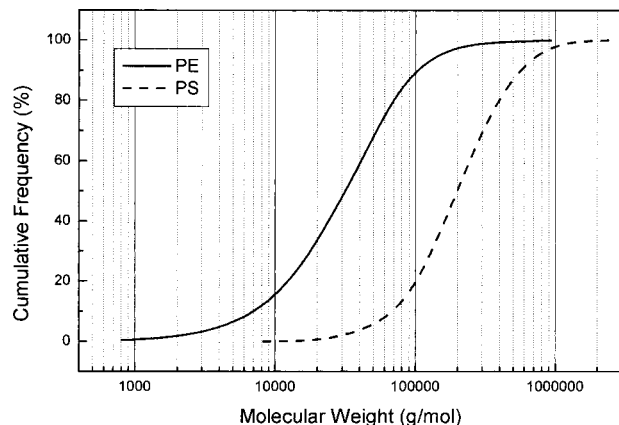


Figure 1. Cumulative molecular weight distributions of PE and PS.

brush graft copolymers (PE-*g*-PS) with PE hairs. The performance of the formed copolymer as a compatibilizer depends on its concentration and architecture (length and frequency of the PE hairs and length of PS). To optimize the amount of catalyst used and the reaction conditions, copolymer characterization is necessary. Therefore, the separation of the blend into its three components (polymer A, polymer B, and copolymer AB) must be carried out. Usually, this is performed by selective solvent extraction in a Soxhlet apparatus. However, when the blend components are high-molecular-weight polymers, the complete separation is time-consuming, if feasible at all, because of the low solubilization rate of large molecules.

The use of supercritical fluid (SCF) extraction is a promising alternative to improve the separation of thermoplastic polymer blends. Kirby and McHugh¹⁰ performed a very complete review of high-pressure polymer solutions. These authors discussed homopolymer-SCF phase behavior with respect to the effects of polymer solubility, solvent quality, polymer molecular weight, polymer backbone branching and chemical architecture, and end-group interactions. Kirán and Zhuand¹¹ studied the miscibility and phase separation of polymers in near critical fluids and SCFs. They studied different configurations of binary fluid mixtures to bring about complete miscibility for systems as polymer-solvent A-solvent B type. They concluded that binary fluid mixtures could be used to modify selectivity toward a polymer or to introduce a greater sensitivity of the system to changes in external parameters such as the temperature or pressure.

In this work, a systematic study of polymer blend demixing is presented. An experimental

program is set up to explore the selectivity of three solvents (propane, *n*-pentane, and *n*-heptane) at high pressures and over a wide range of temperatures on pure polymers. The processing window for the separation of pure components of physical PE/PS blends is assessed. Also, the influence of the blend morphology and composition on the separation efficiency is analyzed.

In a second step, a procedure for the separation of PE/PS reactive blend components is proposed. In this case, hot *n*-pentane at a high pressure is used for the separation of the system PE/PS/PE-*g*-PS. The copolymer and PE phase are dissolved and can be neatly separated from the PS-insoluble phase. The influence of the relative concentration of the components on the blend separation effectiveness is discussed.

EXPERIMENTAL

Materials

PS homopolymer Lustrex HH-103 [weight-average molecular weight (M_w) = 256,000, number-average molecular weight (M_n) = 136,000] and linear low-density polyethylene (LLDPE) Dow-Polipur LLDPE 6200 (M_w = 50,700, M_n = 17,000) were used as base commodity materials for blending. Figure 1 shows the cumulative molecular weight distributions of the PE and PS samples used. The high-pressure, high-temperature extractions were done with propane, *n*-pentane, and *n*-heptane from Aldrich. The solvent purities and critical temperature and pressure (T_c , P_c) are given in Table 1.

Blending

Physical Blends

PE/PS physical blends were prepared with variations in the relative content of each polymer, as shown in Table 2. The blends were carried out, under a nitrogen atmosphere, in a polymer batch mixer (W50 plastograph, Brabender) at 463 K. The mixing procedure included the initial melting of PS (powder form) and subsequent

Table 1. Extraction Solvent Characteristics

Solvent	Denomination	Purity	T_c (K)	P_c (bar)
Propane	C ₃	>99%	373	42.4
<i>n</i> -Pentane	C ₅	>98%	467	33.7
<i>n</i> -Heptane	C ₇	>98%	540	27.4

Table 2. Composition, Minor Phase Average Diameter (D_p), and Standard Deviation of the Average Diameter [$\sigma(D_p)$] of Physical PE/PS Blends

Blend	PE (wt %)	D_p (μm)	$\sigma(D_p)$
B80/20 (B0)	80	3.8	1.95
B50/50	50	Cocontinuity, not major phase	
B20/80	20	6.3	1.04

incorporation of PE (pellet form). Mixing was carried out at 30 rpm for 12 min. The mixer conditions were adjusted to reach the same PE/PS viscosity ratio in each blend.

Reactive Blends

PE/PS reactive blends were prepared with 80 wt % PE and 20 wt % PS. The processing conditions were the same as those applied for the physical blends. In all cases, the Friedel–Crafts reaction was performed after complete melting and mixing were obtained. Styrene (0.3 wt %) was used as the cocatalyst and was followed by different weight percentages of AlCl_3 (0.1, 0.3, 0.5, 0.7, 1.0, and 1.5). More details about the blend preparation can be found in refs. 8 and 9.

Reactive Pure Homopolymers

To check for the occurrence of possible secondary reactions, Friedel–Crafts reactions on pure PE and PS were prepared with the same procedure and conditions used for the reactive blends. Modified PE and PS samples were then obtained, and they are named *reactive PE* and *reactive PS*, respectively. Table 3 summarizes all the samples prepared with the corresponding denomination.

High-Pressure, High-Temperature Solvent Extractions (HPHTSEs)

Solvent extractions of pure polymers and blend samples were performed in high-pressure stainless steel cells working in parallel, as indicated in Figure 2. About 50 mg of a polymer sample was confined in the sample holder with a Teflon microporous filter (pore diameter $< 0.3 \mu\text{m}$) and added to a 10-cm³ cylindrical cell. The cylinder was pressurized to 300 bar, and the temperature was increased to the final temperature (T_f). The extraction time was 1 h, with the sol-

vent flow rate kept at 40 cm³/h. The blend components were separated by sudden solvent expansions and subsequent collection of the soluble fraction.

Pure Polymer Solubility

HPHTSEs were performed on pure PE and PS samples with the procedure described previously. For PE, T_f was varied, for all solvents, from 353 to 473 K with steps of 10 K, with C3, C5, and C7 as solvents. The difference in the masses solubilized between C5 and C7 was analyzed in detail at $T_f = 363$ K. The highest temperature used for PE extraction was 473 K. At higher temperatures, PE chains could degrade, and their solubility changed. For PS, T_f was varied from 393 to 473 K with steps of 10 K. As no solubilization was observed in this temperature range, a final experiment was carried out at 523 K.

Blend Component Separation

The HPHTSEs were performed for the physical blends (B0) with *n*-pentane at $T_f = 413$ K. To compare results under the same conditions, the reactive blend extractions were carried out simultaneously with a physical blend.

Characterization

Size Exclusion Chromatography (SEC)

SEC chromatograms of the collected pure polymer samples, as well as soluble and insoluble blend phases, were obtained with a Waters Sci model 150-CV chromatograph. The samples were dissolved in 1,2,4-trichlorobenzene (TCB) with 0.0125% of butylhydroxytoluene (BHT) and injected at 408 K. The molecular weight of the pure polymers was also calculated.

Table 3. Nomenclature of the Prepared Reactive Polymers and Blends

Blend (80/20 PE/PS)	Reactive PE	Reactive PS	AlCl_3 (wt %)
B0	PE (pure)	PS (pure)	0
B01	RPE01	RPS01	0.1
B03	RPE03	RPS03	0.3
B05	RPE05	RPS05	0.5
B07	RPE07	RPS07	0.7
B10	RPE10	RPS10	1.0
B15	RPE15	RPS15	1.5

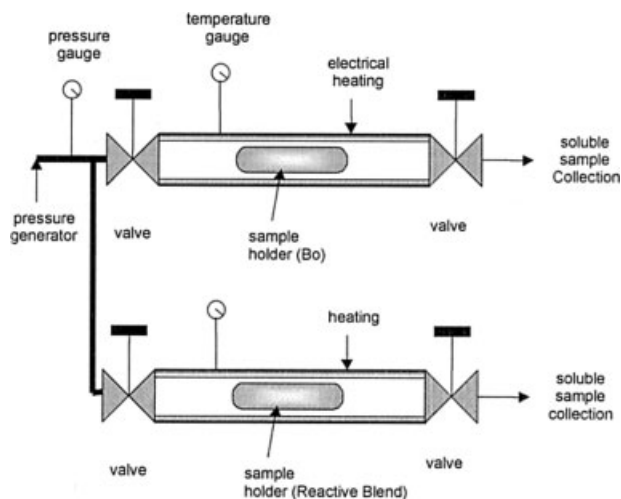


Figure 2. Schematic diagram of the experimental equipment used to perform HPHTSEs of reactive and physical blends.

Scanning Electron Microscopy (SEM)

The blend morphology was analyzed with a JEOL 35 CF scanning electron microscope equipped with secondary electron detection. The samples were fractured under liquid nitrogen, and the fracture surfaces were coated with Au in a vacuum chamber. Analysis PRO software was used for processing the particle size data. About 300 particles were considered to calculate the average particle diameter of the minor phase and its dispersion. These parameters are listed in Table 2.

RESULTS AND DISCUSSION

Processing Window Determination

A systematic study of the PE and PS masses dissolved at different temperatures in three paraffinic solvents was performed at a high pressure (300 bar). The same procedure, extraction time, and solute/solvent ratio were used throughout. The results are shown in Figure 3. The influence of the temperature as well as the solvent chain length on the PE solubilization is evident. At 373 K, 78% of PE was dissolved in C7, and about 50% of PE in C5, but C3 did not dissolve. *n*-Heptane dissolved 99% of PE at 393 K, whereas C5 only dissolved 84%, and propane could not dissolve PE at this temperature [Fig. 3(a)].

The solvents used, C3, C5, and C7, have a chemical affinity to PE chains because of their nonpolar molecules. However, the rule that a

solvent composed of certain chemical groups will dissolve those substances containing the same or chemically similar groups applies to polyolefins only to a certain degree. The dispersive forces of these nonpolar molecules are so weak that dissolution can be obtained only at a high temperature.¹² Also, for semicrystalline polymers such as PE, considerable proportions of the polymer chains lie within the rigid lattice of crystallites precluding solubility. In particular, the PE used in this work exhibits wide molecular weight distributions ($M_w/M_n = 3$). Figure 1 shows that there are molecules from 800 to 920,000 g/mol. Therefore, most of them are unaffected and insoluble in common solvents unless the secondary bonds acting between polymer chains are weakened by an increase in the temperature (increment in the chain mobility).

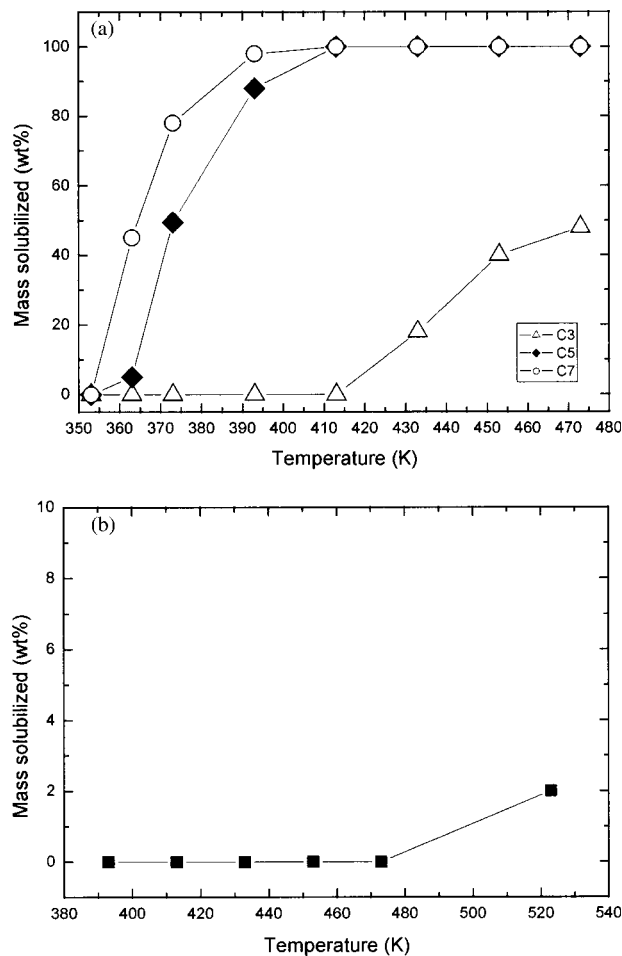


Figure 3. Variation of the mass solubilized with the temperature and solvent (C3 = propane, C5 = *n*-pentane, and C7 = *n*-heptane) at a constant pressure (300 bar) for (a) PE and (b) PS.

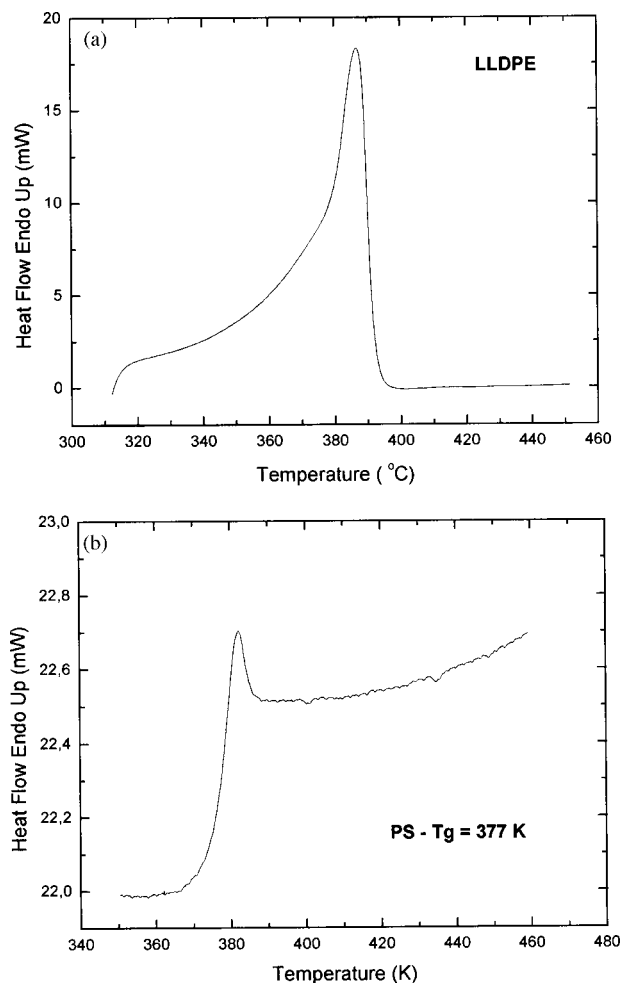


Figure 4. DSC thermograms for (a) PE and (b) PS.

The influence of the chain mobility on the solubilization is corroborated by the PE thermograms shown in Figure 4(a). When T_f is above 393 K, the polymer is in a molten state, and the solubilization in C7 is complete after 1 h at 300 bar. When the temperature is 353 K, only a small fraction of PE short chains can be melted, and consequently the solvent only swells the polymer. At 373 K, the fraction of PE chains melted increases and then is solubilized. The large molecules of PE remain in the sample holder. This observation is in agreement with SEC results. M_w of the soluble fraction is 21,000 g/mol. However, a dramatic increment in the solubility can be observed at 393 K, when all PE chains are melted.

The insolubility of PS in C3, C5, and C7 is clear from Figure 3(b). Only 2% of the PS mass was solubilized at the highest temperature studied (523 K) with C7. Furthermore, PS was

completely insoluble in C3 and C5 solvents. The SEC chromatogram of the insoluble fraction of PS at temperatures different than 523 K matches the SEC chromatogram of pure PS. At 453 K, the PS chains have sufficient mobility because the glass-transition temperature (T_g) is close to 373 K, as shown in Figure 4(b). From these experiments, it is clear that, from 413 to 473 K under the same conditions and without polymer phase interactions, it is possible to obtain the complete and selective extraction of PE from the physical blend with PS. In Figure 5, the processing window for physical blend demixing with C5 or C7 is shown.

Physical Blend Separations

The PE phase was extracted from PE/PS blends with the procedure described in the Experimental section with C5. The working temperature was 413 K because at this temperature PE could be solubilized without being degraded. The PS particles dispersed in PE had diameters of about 3 μm (Table 2), so they could be retained by the 0.3- μm -grid Teflon microporous filter.

Extractions were performed on blends with different compositions, as shown in Table 2, and consequently with different phase morphologies. For B80/20, very small particles of PS are dispersed in the PE matrix. The majority of the particles are spherical and homogeneously dispersed in the matrix, as can be observed by SEM. B20/80 has a similar morphology but greater particles of PE in a matrix of PS. However, in B50/50, the morphology is very different, showing a cocontinuity of phases. Only a

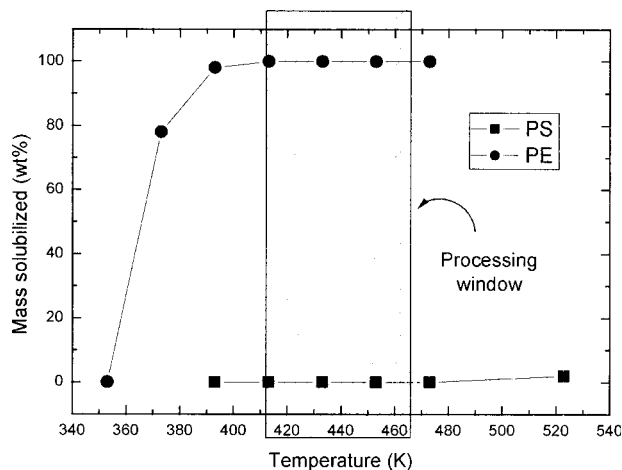


Figure 5. Determination of the processing windows from physical blend demixing with C5 and C7.

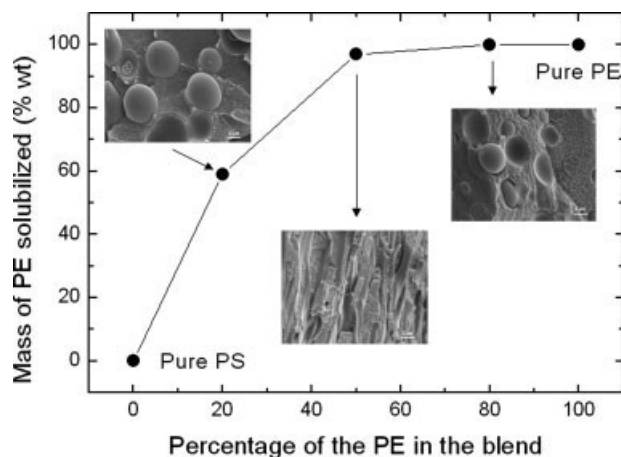


Figure 6. Mass of PE solubilized as a function of the blend composition related with the morphology of each blend. The microphotographs have a magnification of 6000 \times .

few small particles of one phase are dispersed in the other. These differences in the morphology influence the PE extraction and consequently the blend separation. Figure 6 shows the PE mass solubilized as a function of the blend composition. In the same figure, SEM microphotographs are included to show the phase morphology of each blend.

The entire PE phase was extracted from B80/20. Figure 7 shows the SEC chromatograms of the insoluble fraction of the B80/20 blend and pure PS. The chromatograms match very well, and this shows that only the PS phase remains at the insoluble phase. These results were expected because PE is the matrix, and so there is no diffusion control that could disturb the PE solubilization. For B50/50, the PE phase is solubilized up to 97%. The extraction is not complete because part of the PE, in the form of small particles dispersed within the PS phase, cannot diffuse totally out of the PS phase to be dissolved. This diffusional control throughout the PS phase is more evident in the B20/80 blend, in which the matrix is PS and the whole PE phase must diffuse to be extracted. In this case, only 59% of PE was extracted.

Reactive Blend Demixing

In the reactive blends used in this work, the brushlike graft copolymer (PE-*g*-PS) was mainly generated at the PE/PS interface via Friedel-Crafts alkylation reaction. This copolymer remains in it for a concentration below the critical

micelle concentration (cmc). At this concentration, the copolymer saturates the interface, and the minimum of interfacial tension and, consequently, the minimum average particle diameter are reached.^{13,14} Above this concentration, all of the copolymer generated remains in the homopolymeric phases as micelles. In a previous work,⁹ cmc was determined from data of the particle average diameter reduction as a function of the catalyst concentration. The cmc was obtained with 0.3–0.5 wt % catalyst (AlCl_3) and 0.3 wt % cocatalyst (styrene). The average particle diameter suffers an exponential decay from 3.8 (physical blend) up to 0.4 μm at the cmc.

In reactive blends, three phases are present—PE, PE-*g*-PS, and PS—whose relative amounts and morphologies depend on the catalyst content. To characterize these blends, a net separation is required. A set of demixing experiments was carried out on these reactive blends, with the results of physical blend separation used as a reference test. Reactive and corresponding physical blend extractions were performed in parallel and simultaneously (for the experimental equipment, see Fig. 2).

The mass solubilized during the extractions, expressed as percentage of the original sample mass, as a function of the amount of catalyst is shown in Figure 8. PE is completely solubilized and extracted from the 80/20 physical blend (B0). Therefore, the amount extracted in excess of 80% must be copolymer because PS is not dissolved under these conditions.

The copolymer mass increases steadily, as expected, up to a catalyst content of 0.7%. Then,

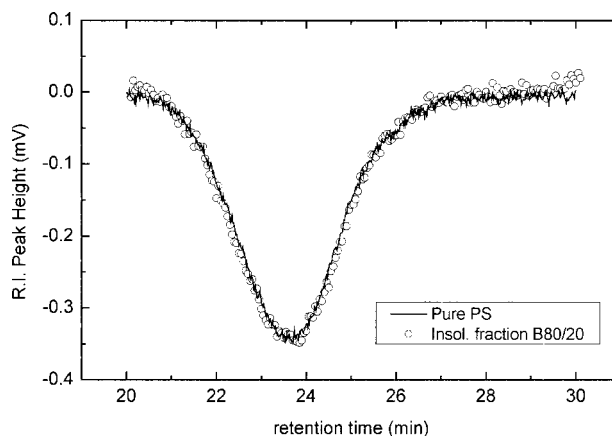


Figure 7. SEC chromatogram of the insoluble fraction of the B80/20 PE/PS blend compared with the SEC chromatogram of pure PS. (R.I.: refractive index).

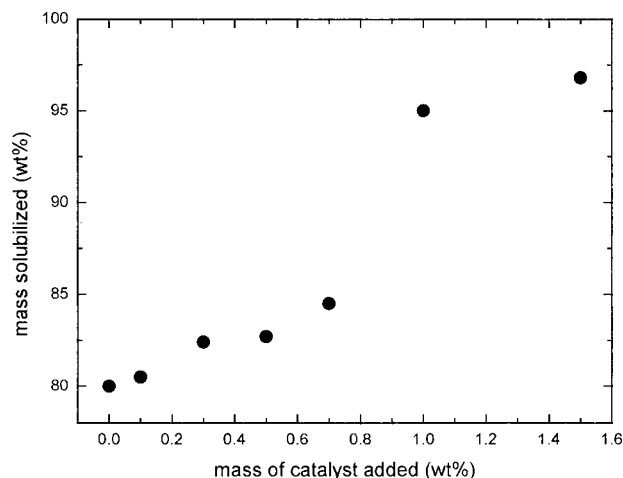


Figure 8. Reactive blends mass solubilized as a function of the amount of AlCl_3 (proportional to the copolymer generated).

an abrupt jump can be observed followed by a moderate growth region beyond 1.0% catalyst. This behavior is related to the copolymer brush-like architecture and can be explained by the dragging action of the PE side of the copolymer molecules. When the copolymer is surrounded by a solvent that exhibits high affinity for PE, the molecules tend to be sterically arranged as a PS core covered by hairs of PE. This configuration is similar to that of copolymer micelles in the PE phase. Then, driven by the solvent affinity for PE, copolymer molecules can be dragged (solubilized) from the PE hairs, as if these were actual PE molecules. As a result, with adequate solvent and operating conditions, the insoluble PS phase could be, in principle, separated from a mixture of a PE phase and copolymer molecules. Nevertheless, the question of whether the copolymer will be completely or partially solubilized by this mechanism remains to be answered.

To assess the solvent efficiency for copolymer solubilization, the composition of the insoluble phase was characterized by SEC chromatography. These results are shown in Figure 9. The SEC chromatograms of pure PS and the insoluble phase of a physical blend (R0) are included. The SEC responses of PE and PS (peaks) are inverse. This comes out from the opposite signs of their TCB solution refractive indices. Therefore, for any blend, the PE contribution will increase the peak height, whereas PS will reduce it. In any case, the blend refractive indices are additive, as verified in a previous work.^{8,9} In particular, the certainly that the

insoluble phase contains only PS comes from the absence of positive peak contributions in the SEC signal. On the basis of this behavior, a qualitative analysis of PE and PS contributions can be depicted by the consideration of the relative positive and negative peak height variations.

SEC chromatograms from the insoluble phases of reactive blends show that the molecular size decreases as the amount of the catalyst increases. This fact derives from a comparison of the minimum shifting to a higher retention time (from R0 to R15). As the insoluble phases contain only PS, the average molecular weights can be calculated, and these values are listed in the second column of Table 4. For reactions with a catalyst content below 0.7%, the molecular weight and the chromatograms do not change dramatically. However, a sudden change can be observed between the molecular weights of R07 and R10. This drastic variation suggests the possibility of PS chain scission during the Friedel-Crafts reaction. In this way, the reactions over pure homopolymers were performed, and reactive pure polymer samples were obtained. The third and fourth columns of Table 4 show the average molecular weights of reactive PE and reactive PS. In the case of reactive PE, all the chromatograms perfectly match that of pure PE, and this demonstrates that there is not PE chain scission even for the highest AlCl_3 concentration.

On the other side, reactive PS presents chain scission and a molecular weight change with the amount of catalyst used. This change becomes

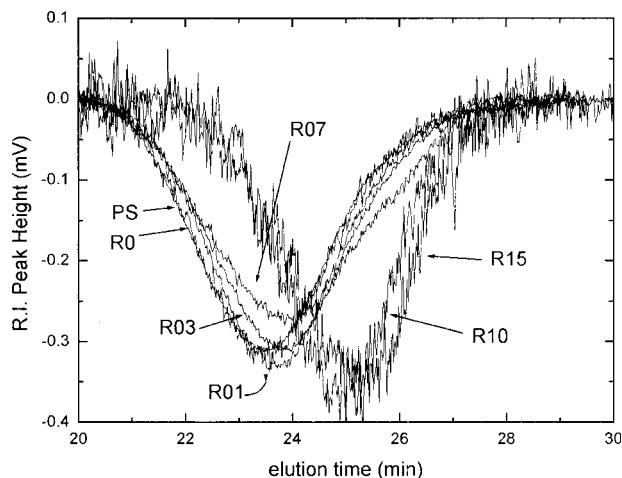


Figure 9. SEC chromatograms of the insoluble phase of the reactive blend extractions compared with that of pure PS. (R.I.: refractive index).

Table 4. Average Molecular Weights of the Extraction Residues and Reactive Polymer Samples

Extraction Residue	M_w (g/mol)	Reactive PE	M_w (g/mol)	Reactive PS	M_w (g/mol)
R0	257,000	PE (neat)	50,700	PS (neat)	256,000
R01	260,000	RPE01	50,200	RPS01	257,300
R03	250,400	RPE03	50,800	RPS03	248,000
R05	245,000	RPE05	49,900	RPS05	243,000
R07	200,000	RPE07	50,000	RPS07	194,000
R10	95,700	RPE10	49,400	RPS10	257,000
R15	90,000	RPE15	50,500	RPS15	<20,000 ^a

^a Out of the limit of detection of the SEC columns used.

drastic between R07 and R10. The average molecular weights of reactive PS are very similar to those of residues for catalyst contents below 0.7%, and this suggests that the residue is only PS but with short chains. When the catalyst content is over 1%, the PS chain scission is so great that the copolymerization reaction is favored (there are more end chains in the melt) and the amount of copolymer generated increases dramatically, as shown in Figure 8. Taking into account the brush copolymer structure, if the length of the PS part of the copolymer is short, the copolymer generated at a high AlCl_3 concentration is more soluble than the copolymer obtained at minor concentrations.

The molecular weights of R10 and R15, from Table 4, differ from those of RPS10 and RPS15 because the chain scission reaction competes with the copolymerization reaction. Therefore, the shorter PS chains copolymerize more rapidly than longer ones, and the insoluble phases, R10 and R15, correspond to shorter PS chains.

The sharp increment in the mass solubilized between concentrations of 0.7 and 1% can be understood from the previous discussions and if we take into account that this concentration interval is over the cmc. This means that interface is saturated with copolymer and the copolymer in excess migrates from the interface to form micelles in the homopolymer phases. The increment of micelles in the PE major phase favors its extraction together with the PE phase because the diffusion problems are minimized.

CONCLUSIONS

Blend phase separation using a hot solvent at high pressures is a rapid, noncontaminant, and effective procedure. From the systematic study presented in this work on PE/PS physical and

reactive blends, the following conclusions can be drawn:

- Hydrocarbon solvents are very selective for PE under the studied conditions. The PE solubility increases as the temperature and solvent length increase under the same procedural conditions. The same solvents are bad for PS, and the processing conditions for blend separation have been assessed.
- The method allows the complete separation of high-molecular-weight commercial polymer physical blends.
- The influence of the blend morphology on the effectiveness of the separation has been studied, and we have concluded that the solvent to be used must be one that dissolves the matrix or the major component in the blend to avoid diffusion impediments.
- The separation of the *in situ* formed copolymers in reactive blends has been achieved. The copolymer PE-*g*-PS is solubilized by chemical affinity. The PE hairs drag the copolymer to the paraffin phase. This dragging is increased with the catalyst concentration because the relative length of the PE/PS chains in the copolymer increases because of PS chain scission at a higher catalyst concentration.

The method proposed in this work seems to be a promising tool for blend separation, particularly for reactive blends, for which the isolation of the formed copolymer is essential for its characterization. The use of an adequate solvent combination and conditions permits a rapid and complete blend component separation.

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