Demixing of Polypropylene/Polystyrene Blends by Near-Critical Selective Solubilization

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Blend phase characterization is a fundamental step in a polymer blend study. To analyze the blend composition and morphology, the separation of thermoplastic polymer blends into its components is the method used. This separation by traditional techniques, such as Soxhlet, is very difficult because of the high molecular weight molecules of the polymer blend components. The use of a high-temperature−high-pressure near-critical solvent is an interesting alternative that results in a complete and fast separation. In this work, a systematic study of the demixing of polypropylene (PP)/polystyrene (PS) blends is presented. First, the selectivity of *n*-alkanes was explored at high pressure and over a wide range of temperatures on pure polymers. From this study the processing window for blend separation was obtained. Second, the influence of the blend morphology and composition on the separation efficiency was analyzed. The method was applied to analyze and quantify the copolymer formed in a PP/PS in situ compatibilized blend. It is concluded that the method proposed for blend separation is simple, fast, and accurate for the systems analyzed.

Introduction

The use of commodity thermoplastics in engineering applications has continuously grown during the last several years. Polymeric materials based on commodity thermoplastics are attractive not only for their low cost but also for their technical performance, versatility of processing, and simplicity of recycling. Increasing attention has been directed toward polymer−polymer blending. The principal advantages of these blends are the synergetic combinations of resin−resin properties generally obtained from commodities. One of the principal applications of these materials is in the automotive industry, where the blends rapidly replace engineering materials.[1−3]

Most frequently used commodity thermoplastics [polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), and polystyrene (PS)] exhibit very low entropy of mixing. Therefore, phase segregation will result when they are blended in significant proportions. In addition, formation and coalescence of sizable dispersed phase domains, low adhesion between phases, and poor final properties can be expected from direct blending of thermoplastic commodities.[1−6] To address these problems, an adequate compatibilization is needed to enhance the final properties by reduction of interfacial tension and increase of adhesion between phases.[6−8]

There are two main ways to compatibilize polymer blends: addition compatibilization, in which the compatibilizing agent is added to the blend, and reactive compatibilization, which involves an in situ chemical reaction. Reactive compatibilizers are often preferred because the products appear to be more stable than those obtained from a previously synthesized copolymer.[9,10] The use of the Friedel−Crafts alkylation reaction in melt is a convenient route to compatibilize polystyrene−polypropylene (PS/PP) blends.[11] The reaction products are brush copolymers (PP-*g*-PS) with PP hairs. To optimize the amount of catalyst used and the reaction conditions as a function of the compatibilization efficiency, an accurate analysis of the graft-copolymer obtained is necessary. Next, the separation of thermoplastic

polymer blend into its components must be obtained. Usually this is done by selective solvent extraction in a Soxhlet apparatus. But when the blend components are high molecular weight polymers the complete separation is very difficult, requiring long extraction times and a large solvent/solute ratio.

The use of supercritical fluids (SCF) extraction is an interesting alternative to improve the separation of thermoplastic polymer blends. Some authors have studied the phase equilibria for polypropylene−hydrocarbon in terms of the effects of polymer solubility, solvent quality, and polymer molecular weight.[12] Also, the study of binary fluid mixtures (system type polymer−solvent A−solvent B) was carried out.[13,14] They conclude that binary fluid mixtures can be used to modify selectivity toward a polymer or introduce a greater sensitivity of the system to changes in external parameters such as temperature or pressure.

In a previous paper of our group,[15] the demixing of PE/PS blends was studied. A polymer blend separation by use of high-pressure−high-temperature *n*-alkanes was proposed, and it was concluded that the approach seems to be a promising tool for blend demixing. The use of adequate process conditions and solvent combinations allows for a rapid and complete separation of blend components.

In the present work, a similar method that uses high-pressure−high-temperature *n*-alkanes to obtain the separation of PP/PS blends is applied. A systematic study of the demixing of polymer blends was carried out. The selectivity of two solvents (*n*-pentane and *n*-heptane) on pure polymers, at high pressure and over a wide range of temperatures, was evaluated. From this study, a solvent was selected and the processing window for the physical blend separation was obtained. The influence of the blend morphology and composition on the separation efficiency was analyzed for the physical blend (PS/PP).

In a second step, the separation was applied on reactive blends (PP/PS/PP-*g*-PS). The influence of the components' relative composition on the blend separation efficiency is discussed.

Experimental Section

Materials. Polystyrene Lustrex HH-103 (M_w 256 000 g/mol, M_n 136 000 g/mol) and polypropylene Cuyolen 1102 HX (M_w

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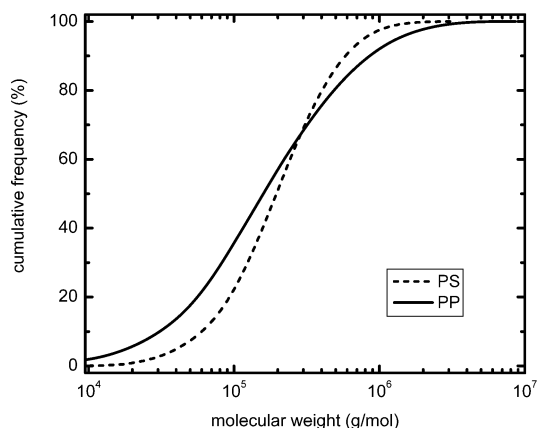
Figure 1. Cumulative molecular weight distributions of PP (—) and PS (---).

Table 1. Composition and Nomenclature of Physical PP/PS Blends

blend	PP (wt %)
PB 05/95	5
PB 15/85	15
PB 25/75	25
PB 40/60	40
PB 50/50	50
PB 65/35	65
PB 80/20	80
PB 95/05	95

303 000 g/mol, M_n 68 000 g/mol) were used as base commodities materials for blending. Figure 1 shows the cumulative molecular weight distributions of the PP and PS used in this study. n-Pentane (T_c 196.5 °C, P_c 33.7 bar) and n-heptane (T_c 267.2 °C, P_c 27 bar) were the solvents. Both solvents had purity higher than 99 wt %.

Blending. Blending was performed under a nitrogen atmosphere, in a polymer batch mixer (Brabender Plastograph W50) at 190 °C and 60 rpm for 24 min. The mixing procedure includes the initial melting of PS and subsequent incorporation of PP.

(A) Physical Blends. PP/PS physical blends were prepared by varying the relative content of each polymer as shown in Table 1.

(B) Reactive Blends. PP/PS reactive blends were prepared on 80 wt % PP and 20 wt % PS. The catalyst for the Friedel–Crafts reaction was added to the already melted and mixed homopolymers. The content of the catalyst ($AlCl_3$) was varied from 0.1 to 1.0 wt %. Styrene (0.3 wt %) was used as cocatalyst. The reactive blends prepared are shown in Table 2.

(C) Reactive Pure Homopolymers. Friedel–Crafts reactions were carried out on pure PP and PS to check for possible secondary reactions. All the samples were prepared under the same process conditions used for reactive blends. The corresponding blend denominations are summarized in Table 2.

Extraction Procedure. A polymer sample, of about 30 mg, is confined in a holder with Teflon microporous filter (porous diameter <0.2 μm) and introduced into a stainless steel 316 cylinder of about 10 cm^3 (full volume). The cylinder was pressurized up to 300 bar and heated to the desired temperature (T_f). The extraction time was 3 h, and the soluble fractions were collected by rapid expansion of the superheated n-alkane. Both samples of soluble (SF) and insoluble fractions (IF) were collected and analyzed. The mass solubilized was determined by weight difference. The experimental extraction cell is shown in Figure 2.

(A) Pure Polymer Solubility. The solvent selectivity was experimentally studied on a wide range of temperatures to obtain
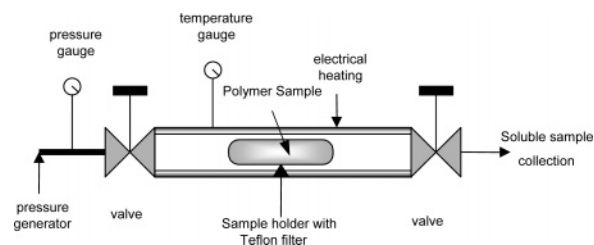
Figure 2. Schematic diagram of the experimental equipment used to perform high-pressure–high-temperature solvent extractions.

Table 2. Nomenclature of Reactive Polymers and Blends Prepared

blend (80/20 PP/PS)	reactive PP	reactive PS	$AlCl_3$ (wt %)
RB 0	PP (pure)	PS (pure)	0
RB 01	RPP 01	RPS 01	0.1
RB 03	RPP 03	RPS 03	0.3
RB 05	RPP 05	RPS 05	0.5
RB 07	RPP 07	RPS 07	0.7
RB 10	RPP 10	RPS 10	1.0

the processing windows for the blend separation. The high-pressure, high-temperature extraction was carried out over samples of pure PP and PS following the procedure explained above but with T_f changed from 120 to 220 °C in increments of 20 °C. The solubility of pure polymers was studied in n-pentane and n-heptane. For PS, a final experiment was carried out at 250 °C.

(B) Separation of Blends. Physical and reactive blend separations were performed with n-pentane at T_f = 180 °C. In the case of reactive blend separations, all extractions were carried out simultaneously with a physical blend, PB 80/20, to allow for comparison of results under the same conditions.

Characterization: (A) Size-Exclusion Chromatography. SEC chromatograms of PP, PS, blends, and all the extracted fractions and residues were obtained in a Waters gel-permeation chromatograph, model 150-CV. The different samples were dissolved in 1,2,4-trichlorobenzene with 0.0125 wt % butylhydroxytoluene (BHT) as antioxidant, at the same initial concentration, and then injected at 135 °C.

(B) Scanning Electron Microscopy. Micrographs on reactive and physical blends, fractured under liquid nitrogen, were obtained. The electron microscope used was a JEOL JSM-35 CF equipped with secondary electron detection. The samples were coated with Au in a sputter coater Pelco 91000. Analysis Pro software was used for processing the particle size data. Approximately 300 particles were considered to calculate the average particle diameter of the minor phase (D_p) and its dispersion $\sigma(D_p)$.

(C) Fourier Transform Infrared Spectroscopy. FTIR spectroscopy was used to analyze the possible oxidative degradation and to quantify the relative polymer contents in blends as well as in soluble and insoluble fractions. The typical carbonyl region oxidative absorption peak, at about 1700 cm^{-1}, was checked in all samples.

The PS concentration was estimated by comparing the ratio of infrared absorption peaks on film samples. Peaks at 2723 cm^{-1} (PP) and 700 cm^{-1} (PS) were used for samples with content up to 50 wt % PS. When the content of PS was higher than 50 wt %, the 2723 cm^{-1} (PP) and 1600 cm^{-1} (PS) peaks were used. Two calibration curves were obtained from PP and PS physical blends of known concentrations.

Results and Discussion

Processing Windows Determination. The old rule, "like dissolves like", can be applied to polymer solubilization.
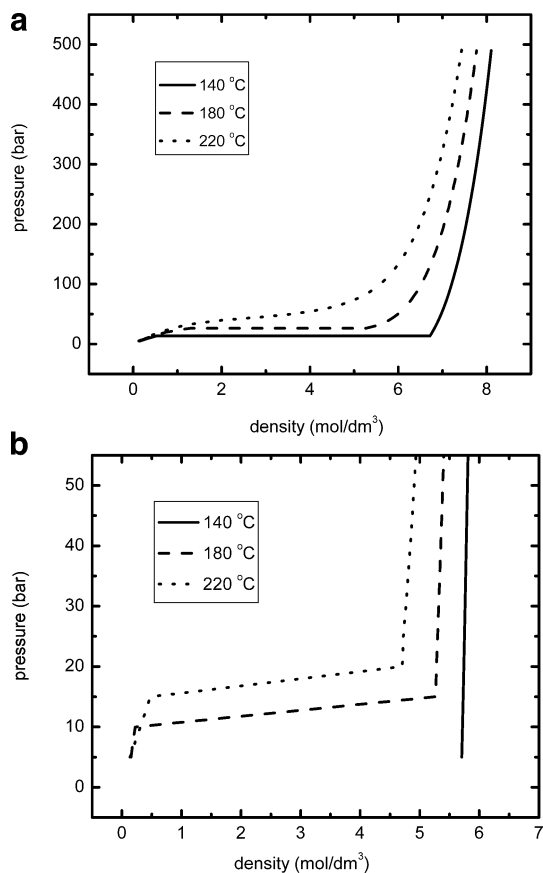
Figure 3. Effect of the pressure on solvent density at different temperatures for (a) *n*-pentane and (b) *n*-heptane.

Therefore, the *n*-alkanes were selected as solvent for PP. However, the rule that solvents composed of certain chemical groups will dissolve those substances containing chemically similar groups applies to polyolefins only to a certain degree. The dispersive forces of these nonpolar solvents are so weak that dissolution can be obtained only at high temperature and high pressure.

Besides the chemical structure, the physical state of a polymer is also important for its solubility properties. Polymers dissolve only at temperatures slightly below or above their melting points (T_m). Except for polymers with strong hydrogen-bonding groups that can be dissolved at room temperature, the polymers are soluble at $T \geq 0.9T_m$.[16] At higher temperatures, the chains acquire mobility and can disentangle and diffuse to the solvent phase.

The effect of high pressure and high temperature on the solubilization will be discussed in detail next. Density is one of the variables that determine the solvent strength of super-critical fluids. In general, solubility increases with increasing solvent density. An approach to solubility in supercritical fluids was derived from the association concept and is directly related to the fluids density.[17] This model is based on the postulate that, at equilibrium, a solute molecule is associated with a fixed number of solvent molecules to form a solvato complex. Although simple, this model depends on the density behavior of the supercritical solvent and is mostly capable of correlating, rather than predicting, the solubility. The relationship between solubility and density of the solvent is

$$C_2 = \rho^k \exp[(a/T) + b] \tag{1}$$

where C_2 is the concentration of a solute in a solvent in grams
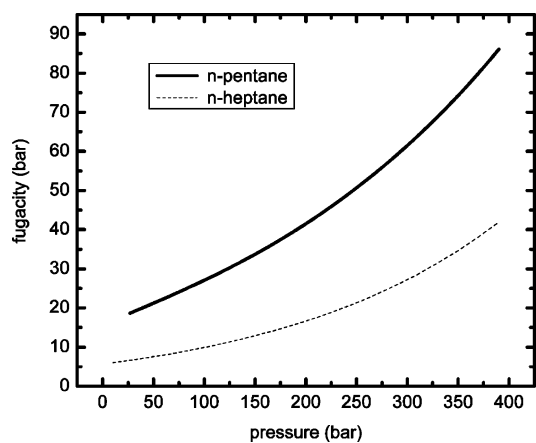
Figure 4. Variation of the fugacity with the pressure at 180 °C for *n*-pentane (—) and *n*-heptane (---).

per liter, ρ is the density of the fluid in grams per liter, k is an association number, and a and b are constants for each combination of solvent and solute.[17]

Figure 3 shows the density of *n*-pentane and *n*-heptane, calculated by use of the ALLPROPS package,[18] as a function of pressure at different temperatures. A sharp increment of solvent density with pressure, which enhances the solubility of the polymer, can be observed. The working pressure was selected in the range where the solvent density change with pressure was less significant. This value was around 300 bar.

The dissolution of a polymer into a solvent mainly involves two transport processes, solvent diffusion and polymer chain disentanglement. When a polymer is in contact with a thermo-dynamically compatible solvent, the solvent will diffuse into the polymer. Subsequently, polymer chains will disentangle from the swollen matrix and dissolve.

From a fundamental point of view, the driving force for the diffusion of the solvent into the polymer is the solvent fugacity gradient. At the beginning, there are two pure phases, polymer and solvent. The fugacity of a pure condensed component at T and P was calculated by use of the Soave-modified Redlich–Kwong (SRK)[19] equation of state. In Figure 4 the fugacities of *n*-pentane and *n*-heptane at 180 °C are shown as a function of pressure. As can be observed, the pressure increases the fugacity substantially. Higher pressure and fugacity values notably increase the penetration of the solvent in the polymer phase.

During the process of chain disentanglement, the self-diffusion of the polymer is an important factor. It has a direct bearing on tackiness, which depends on interpenetration by diffusion of polymer molecules at the interface.[16] The coefficient of self-diffusion of polymers is inversely proportional to the bulk viscosity of this polymer. The following expression, derived by Bueche et al.,[20] may be used as a good approximation:

$$D\eta \approx CkT \tag{2}$$

where D is the coefficient of self-diffusion, k is the Boltzman constant, C is a constant, and T is the temperature. The effect of a high-pressure, high-temperature solvent on the viscosity of the polymer[21] is well-known, and it produces an important viscosity decrease. Therefore, the use of near-critical *n*-alkanes reduces the polymer's viscosity and enhances the chain disen-tanglement, and consequently the dissolution of the polymer.

The combination of the aforementioned effects should achieve a sharp separation of PP and PS in a short time. Therefore, a systematic study of mass solubilized at different temperatures in both solvents was carried out for pure polymers. In all cases,

a

b
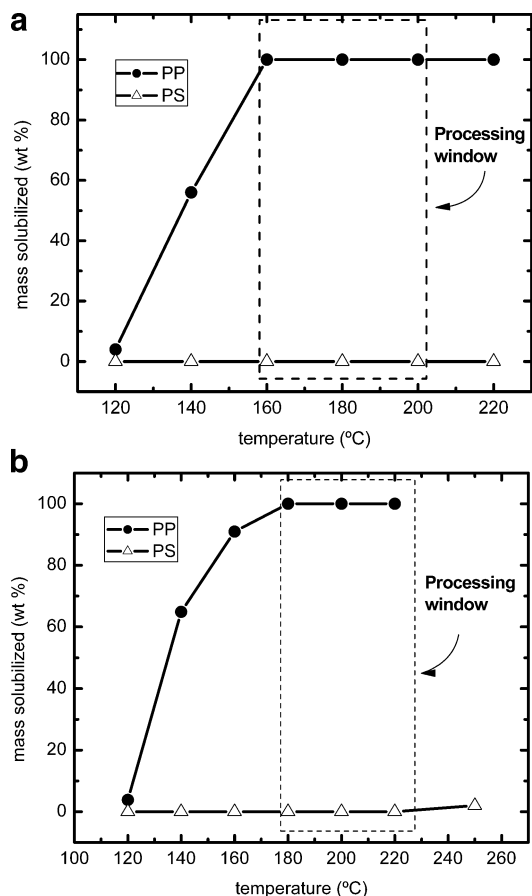
Figure 5. Processing windows determination for PP/PS blend demixing from the curves of the mass solubilized with the temperature at 300 bar by use of (a) *n*-pentane and (b) *n*-heptane.

a

b

Figure 6. DSC thermograms for (a) PP and (b) PS.

Figure 7. SEC chromatogram of the soluble fraction of pure PP extraction at 180 °C compared with the SEC chromatogram of pure PP.

the other processing parameters were kept constant (solvent, pressure, extraction time, solvent/solute ratio, and procedure). The results, shown in Figure 5, demonstrate that both *n*-pentane and *n*-heptane are good solvents for PP under these conditions. The PP used in this work exhibits wide molecular weight distributions (M_w/M_n 4.45); there are molecules from 10 000 up to 9 000 000 g/mol. Therefore, the high molecular weight PP molecules are unaffected and insoluble in common solvents. In addition, the influence of the chain mobility in the solubilization was corroborated from PP thermograms (Figure 6a). When the temperature is lower than 120 °C, only a small fraction of PP short chain can be melted, so that the solvent only swells the polymer. At 140 °C, a greater fraction of PP chains melts and the solubility of PP increases. The large molecules remain in the sample holder. However, complete solubility is observed at 160 °C, when all of the PP chains are melted.

The FTIR analysis on soluble fraction shows the nonexistence of oxidation because the typical carbonyl peak does not appear. The SEC chromatograms of soluble fractions of extractions done for temperatures less than 160 °C (when *n*-pentane was used) and 180 °C (when *n*-heptane was used) show that the molecular weight of molecules solubilized increases with extraction temperature, as expected due to the influence of temperature in chain mobility explained above. However, at the temperatures where the total mass of PP was extracted, the soluble fraction SEC chromatogram is shifted to higher retention times associated with lower molecular weight molecules, as shown in Figure 7. Also, the polydispersion is reduced. These facts are similar for both solvents used and for all temperatures. These results indicate a chain scission of PP molecules. As oxidation is not
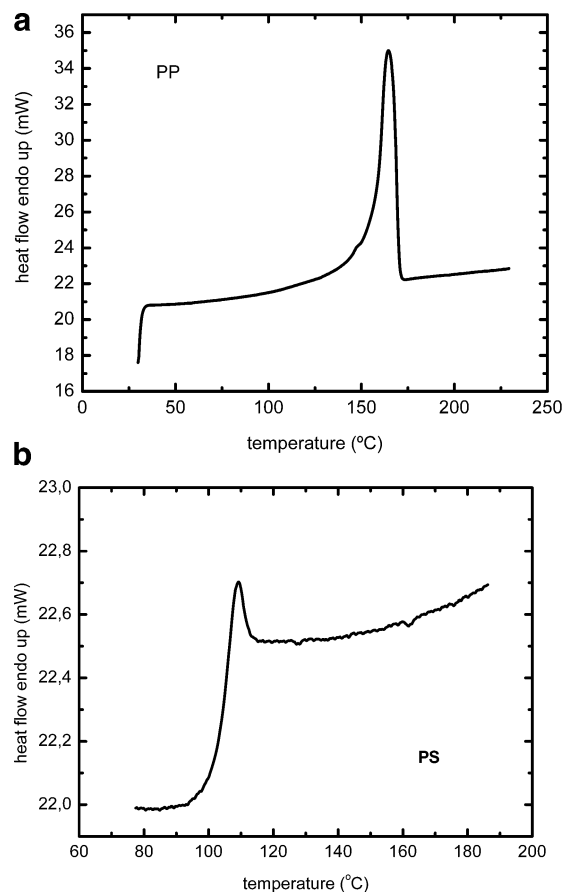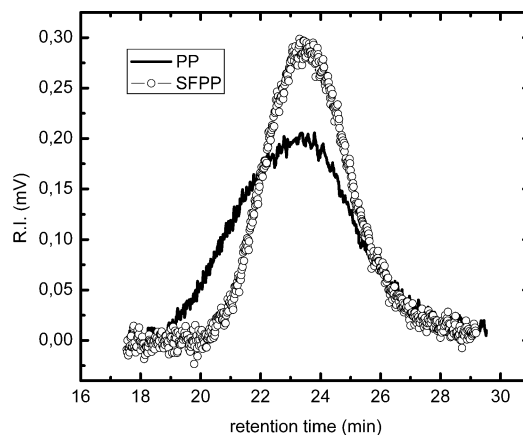
present, a possibility is mechanical degradation during the polymer discharge. In this procedure, strong thermal and mechanical stresses are generated when the polymer solution is discharged. The polymer flows through a 0.25 mm diameter capillary with a pressure drop of 300 bar. The high molecular weight macromolecules degrade under this high stress field,[22] in agreement with the Bueche theory.[23] This theory assumes that the molecules exist in the rubbery or liquid state and shows that the entanglements along the chains play a major role in the rupture process, and the chain rupture depends on the viscosity, shear rate and molecular weight.

The very low solubility of PS is evident in Figure 5. Only 2 wt % of the PS mass was solubilized at the highest temperature studied (250 °C) with *n*-heptane. Furthermore, PS was completely insoluble in *n*-pentane under all conditions studied in
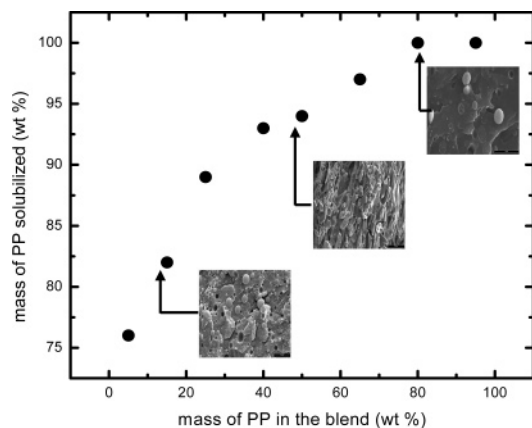
Figure 8. Mass of PP solubilized as a function of the blend composition related with the morphology of each blend.

Figure 9. SEC chromatogram of the insoluble fraction of PB 80/20 PP/PS compared with the SEC chromatogram of original pure PS.

Figure 10. FTIR spectrum of the soluble fraction of PB 80/20 PP/PS (dashed line) compared with the FTIR spectrum of pure PP (straight line).

this work. It should be noted that at 180 °C the PS chains have sufficient mobility because their glass transition temperature is close to 100 °C, as shown in Figure 6b. In the case of PS, the absence of chemical affinity with the solvent results in complete immiscibility despite the use of a near-critical solvent.

From these results, we can say that *n*-pentane is more selective and has higher solvent power (the entire PP phase was solubilized at lower temperature) than *n*-heptane. For this reason, *n*-pentane was the selected solvent to obtain the physical and reactive blend separation.

From 160 to 200 °C under the same conditions, it is possible to dissolve completely the PP without the solubilization of PS. In Figure 5a the processing window for physical blend demixing by use of *n*-pentane is shown.

Physical Blend Separation. Following the procedure explained in the Experimental Section, the PP phase was extracted from PP/PS blends. The working temperature was 180 °C, an intermediate temperature of the processing window. When the PS is dispersed in the PP phase, its particles have a diameter of about 2 μm, so they could be retained by the 0.2 μm grid filter. The mechanical barrier selected was a Teflon microporous filter, a material that is not affected during the extraction.

The extraction was performed on PP/PS blends with different compositions and very different phase morphologies. When PP is the major phase, very small particles of PS are dispersed in the PP matrix. Most of the particles are spherical and homogeneously dispersed in the matrix, as can be observed by SEM. When the content of PS is greater than 50 wt %, the blend has a similar morphology but the particles are of PP and the matrix is PS. But in the blends with around 50 wt % PP the morphology is very different. They show cocontinuity of phases. Only a few very small particles of one phase are dispersed in the other but, in general, there are zones of one polymer and zones of the other. These differences in morphology influence the PP extraction and the blend separation. Figure 8 shows the PP mass solubilized as a function of the blend composition. In this figure, SEM microphotographs are included to show the phase morphology differences in each blend.

The entire phase of PP, when dissolved in hydrocarbon solvents, was extracted in 80/20 and 95/05 blends. Figure 9 shows the SEC chromatograms of the insoluble fraction of PB 80/20. The chromatograms match very well, verifying that only the PS phase remains in the insoluble phase. The verification that the soluble fraction is only PP is shown in Figure 10, where the FTIR spectrum of the soluble fraction is compared with pure PP. There are no typical peaks of PS present.
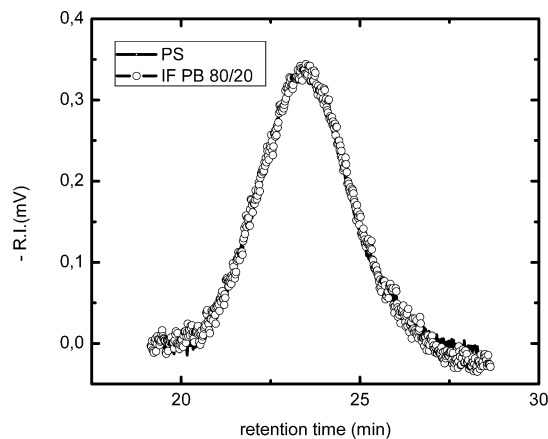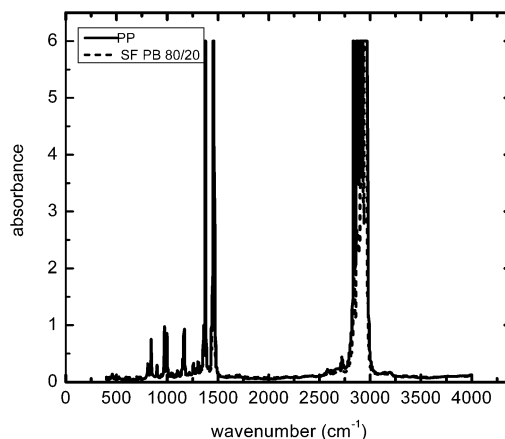
As the fraction of PS in the blend increases, it is not possible to extract completely the PP fraction, because there is a high mass transfer resistance to PP diffusion, and this polymer cannot diffuse totally throughout the PS phase. At the extraction temperature of 180 °C, PS molecules are well above its T_g value (104 °C), and they are only softened and swelled (not dissolved) by the hydrocarbon solvent. Therefore, when the PS is the continuous phase, the PS matrix hinders the diffusion of the PP molecules. However, at the same conditions, when PP is the continuous phase, the diffusion of the PP molecules is enhanced, because the system PP + *n*-pentane is in a single homogeneous phase.

The soluble fractions of PB were also analyzed by FTIR and SEC. The results of this analysis are similar to the results obtained for the soluble fraction of pure PP. The nonexistence of oxidation was verified because the typical carbonyl peak does not appear. Figure 11 shows that the SEC chromatogram of soluble fraction of PB 80/20 is shifted to lower molecular weight regions. These results indicate a chain scission of PP molecules similar to that suggested by pure PP extraction.

Demixing of Reactive Blends. The reactive blending involves a Friedel−Crafts reaction. A product of this reaction is a graft copolymer (PP-*g*-PS) formed at the interface between the PS disperse phase and the PP continuous phase. When the concentration of copolymer is above the critical micelle concentration (cmc), the copolymer migrates from the interface to form micelles into the homopolymer phases. At this concentration the copolymer saturates the interface and the minimum of interfacial tension, and consequently the minimum
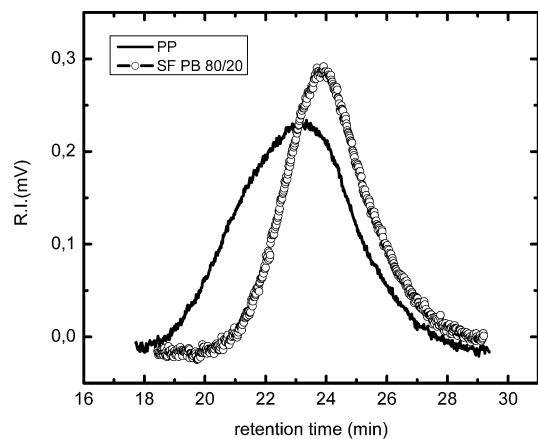
Figure 11. SEC chromatogram of the soluble fraction of PB 80/20 compared with pure PP.
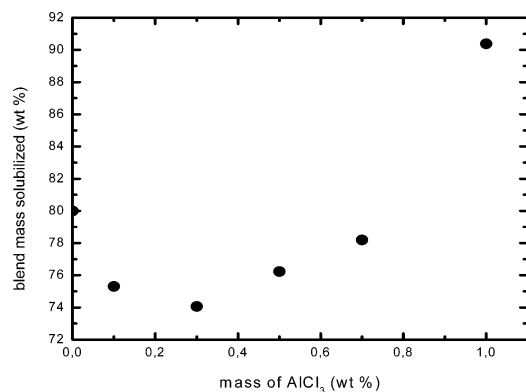

Figure 12. Reactive blend mass solubilized as a function of the amount of AlCl₃.

average-particle diameter is reached.[8,24−25] It was experimentally determined from the emulsification curve that the cmc condition was reached when 0.7 wt % of catalyst was added.[11]

In reactive blends there are "three" phases: PP/PP-*g*-PS/PS, whose relative amount and morphologies depend on the catalyst content. To quantify the amount of copolymer formed and to characterize the phases, blend demixing is necessary. By use of the results of physical blend separation as reference, a set of demixing experiments was carried out.

The mass solubilized as a function of the amount of catalyst is shown in Figure 12. It is worth noting that the entire phase of PP is extracted from PB 80/20. However, when 0.1 wt % AlCl₃ is added, parts of the polyolefin remain in the insoluble fraction, as a consequence of some chains of PP forming high molecular weight copolymer. But also, traces of PS were detected in the soluble fraction by FTIR. Considering that the PS was not solubilized in the other experiments, its presence in the soluble fraction is due to solubilization of a small fraction of copolymer molecules. Owing to the graft-copolymer brush architecture (Figure 13), the solvent cannot see the PS insoluble part of the copolymer molecule. The *n*-pentane drags the PP hairs of the copolymer, as if it were a molecule of pure PP.

The mass solubilized increases with the amount of catalyst due to the increment of copolymer formed. A sharp increment in the mass solubilized between concentrations of 0.7 and 1 wt % can be seen in Figure 12. In this concentration interval two phenomena take place. First, the concentration is over the critical micelle concentration (cmc). The increment of micelles in the PP major phase favors its extraction with the PP phase because there are no diffusion problems.
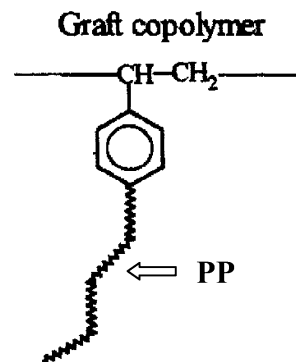
Figure 13. Molecular architecture of the copolymer formed.

Table 3. Average Molecular Weight of the Reactive Polymer Samples

reactive PP		reactive PS	
sample	M_w (g/mol)	sample	M_w (g/mol)
PP (pure)	303 000	PS (pure)	256 000
RPP 01	300 000	RPS 01	257 300
RPP 03	298 000	RPS 03	248 000
RPP 05	240 000	RPS 05	243 000
RPP 07	165 000	RPS 07	194 000
RPP 10	56 000	RPS 10	25 700

The second effect is the chain scission of the PS and PP due to the Friedel−Crafts reaction. The reaction over pure homopolymers was performed and "reactive pure polymers" samples were obtained. The average molecular weights of reactive PP and PS are shown in Table 3. Both, PS and PP present chain scission and molecular weight changes with the amount of catalyst used. The chain scission in PS is higher than in PP, at the same catalyst concentration, because the PS contains tertiary benzylic carbons, more susceptible to be attacked by Lewis acids than PP tertiary alkyl ones.

When the AlCl₃ content is over 0.7 wt %, the scission is so big that the copolymerization is strongly favored (there are more end-chains in the melt) and the amount of copolymer generated increases dramatically. Also, the structure of copolymer molecule changes, the length of PS part in the copolymer at high AlCl₃ concentration is shorter than at lower concentration. Because of that, the copolymer is more soluble in hydrocarbon solvents at high catalyst content.

On the other hand, extraction experiments were performed on reactive PS. When the content of catalyst is over 0.5 wt %, the short chains of PS formed are solubilized. The solubilization is more important in the case of blends with a content of 1 wt % AlCl₃, because very low molecular weight molecules are present. In summary, the chain scission produces higher yield of reaction and higher copolymer and short PS chain solubilization, resulting in a higher amount of mass solubilized.

Conclusions

The thermoplastic blend phase separation, by use of a solvent at high temperatures and pressures, is a fast, noncontaminant and effective procedure. The systematic study presented in this work on PP/PS physical and reactive blends led to the following conclusions:

(1) *n*-Pentane and *n*-heptane are good solvents for PP at supercritical pressures and above the polymer melt temperature. High pressures and high temperatures increase polymer solubility because of the increment in solvent density and the enhancement of the solvent penetration in the polymer (the higher the temperature, the lower the polymer viscosity).

(2) The solubility of PS in these solvents is extremely low. In this case, solute−solvent no-affinity determines the behavior. The decrease in polymer viscosity and the increase in solvent density are not enough to solubilize PS molecules.

(3) It was demonstrated that the *n*-pentane is more selective and has higher solvent power than the *n*-heptane for the separation of this system. The method allows for the complete separation of physical blends of high molecular weight commercial polymers when the PP is the major phase.

(4) The influence of the blend morphology was also analyzed, and it was concluded that the solvent used must be the one that solubilizes the continuous phase in the blend to avoid mass transfer limitations.

(5) The copolymer PP-*g*-PS was solubilized by chemical affinity. The PP hairs drag the copolymer within the "paraffin" phase.

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