

SEPARATION OF PE/PS IN-SITU REACTIVE BLENDS WITH NEAR CRITICAL N-PENTANE

Díaz, Mónica, Mabe Guillermo, Brignole Esteban A.* and Barbosa Silvia
PLAPIQUI (UNS-CONICET) Cno. La Carrindanga Km.7. (8000) Bahía Blanca. Argentina
e-mail: brignole@plapiqui.edu.ar - Fax:#: +59 241 4861600

INTRODUCTION

With the purpose of obtaining new materials with a good compromise of final properties and low cost, great attention has been given to the development of thermoplastic polymer blends. The principal advantages of these blends being the synergetic combinations of resin-resin properties obtained generally from commodities. One of the principal applications of these materials is the automotive industry, where the blends rapidly replace engineering materials [1-3]. Thermoplastic blends consumption was also favored for their ability to be recycled either to the original polymer and then conveniently reused, or transformed into liquid chemicals and fuels [4].

Most frequently used commodity thermoplastics (PE, PP, PVC and PS) exhibit very low entropy of mixing. Therefore, phase segregation will result upon blending them in significant proportions. 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. The key to achieve upgraded properties from immiscible blends is an adequate phase compatibilization implying the reduction of interfacial tension, the increase of adhesion between phases and the dispersion stabilization by inhibiting the coalescence [1,5]. There are two main ways to compatibilize polymer blends, the addition compatibilization, in which the compatibilizing agent is added to the blend, and reactive compatibilization, that involve an in-situ chemical reaction. It can be stated that the main purpose of compatibilization processes is to bring the dispersed phase into intimate contact with the matrix, by maximizing the interfacial area. In this sense, reactive compatibilizers are often preferred because the products appear to be more stable than those obtained by addition of a previously synthesized copolymer [6, 7].

A convenient route to obtain PS/PE compatibilization is the use of the Friedel-Crafts alkylation reaction in melt. In this way, high conversion rates are obtained with low costs and without PE chain scission [8]. The reaction products are brush graft copolymers with PE hairs. The powerful of the copolymer as a compatibilizer depends on its concentration and architecture (length and frequency of the PE hairs, length of PS, etc). To optimize the amount of catalyst used and the reaction conditions as a function of the compatibilization power, an accurate analysis of the graft-copolymer obtained is necessary. Then the separation of a thermoplastic polymer blends into its three components (polymer A-Polymer B – copolymer AB) 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 total separation is lengthy, because of the slow solubilization of large molecules.

The use of supercritical fluid (SCF) extraction of one polymer blend component is an interesting alternative to obtain the total blend separation. There are previous studies that permit understand high-pressure polymer solution. Kirby and McHugh, [9] made a very complete and interesting review. They analyze the homopolymer-SCF phase behavior

regarding the influences on the solubility of SCF, solvent quality, polymer molecular weight, polymer backbone branching and chemical architecture, and end groups interactions. They conclude that the SCF are weak solvents for polymers especially those SCF solvents that are the lowest molecular weight members of a chemical family. The relative improvement in solvent quality diminishes as the molecular weight of the SCF solvent increases as long as the solvents come from the same chemical family. Also the relative polymer-SCF polarity is fundamental in the phase behavior. Also Kiran and Zhuang [10] studied the miscibility and phase separation of polymers in near and supercritical fluids, they had focused the study in diverse ways in which binary fluid mixtures can be used to bring about miscibility (system type: polymer – solvent A – solvent B). They conclude that binary fluid mixtures can be used to modify selectivity towards a polymer, or introduce a greater sensitivity of the system to changes in external parameters such as temperature or pressure.

In a previous work [11], a ternary system including a blend of two commercial high molecular weight homopolymers and one solvent was studied. Three solvents (propene, n-pentane and n-heptane) were explored. The selectivity of the solvents was experimentally analyzed over a wide range of temperatures to obtain the processing windows for the PE/PS blend separation. The principal conclusions of this work were that the thermoplastic blend phase separation using a hot solvent at high pressures is a rapid, non contaminant and effective procedure: This method permits a total separation of high molecular weight commercial polymers that is very difficult to obtain by conventional procedures. The influence of the blend morphology was demonstrated concluding that the solvent to use must be the one that solubilize the matrix or the major component in the blend to avoid diffusion impediments

In this work, an strategy for the separation of the components of the PE/PS reactive compatibilized blend is proposed following the methodology proposed in the previous work. In this case, hot n-pentane at very high pressure was used for the separation of the system PE/PS/PE-g-PS. The methodology used consists in separate the copolymer with the PE phase, by its solubilization in n-pentane, from the insoluble PS phase. The influence of the relative concentration of the components in the blend separation was analyzed..

MATERIALS AND METHODS

Materials: Polystyrene homopolymer Lustrex HH-103 and linear low-density polyethylene Dow-Polisur LLDPE 6200 were used as base materials to blend. The alkylation reaction was catalyzed by a system containing anhydrous Aluminum Chloride (AlCl_3), (>98 % purity) from Merk, and styrene (>99 % purity). The catalyst was immersed in n-hexane to protect it from air moisture. N-pentane (>98 % purity) was used as extraction solvent (T_c : 196.8 °C – P_c : 33 bar).

Blending: PE/PS reactive blends were prepared with 80 wt% of PE and 20 wt% of PS. The blends were prepared, under nitrogen atmosphere, in a polymer batch mixer (Brabender Plastograph W50) at 190°C. The mixing procedure includes the initial melting of PS (powder form), and subsequent incorporation of PE (pellet form) under nitrogen. Mixing was carried out at 30 rpm for 12 min. In all cases the Friedel-Crafts reaction was performed after a complete melting and mixing was reached. A 0.3 % wt. styrene was used, followed by different weight percent of AlCl_3 (0.1, 0.3, 0.5, 0.7, 1.0 and 1.5).

Similar reactions, following the same procedure all the catalyst concentration, were performed on each pure polymer to generate modified PE and PS samples that are called “reactive PE” samples and “reactive PS” samples. These reactions were carried out to check

Table 1. Nomenclature of reactive polymers and blends prepared.

Blend (80/20 - PE/PS)	Reactive PE	Reactive PS	Al Cl 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

the possible chain scission due the Friedel-Craft reaction. Table 1 summarizes all the samples prepared with the correspondent denomination.

High Pressure Solvent Extraction: The polymer extractions were performed into the equipment shown in Figure 1. A polymer sample of approximately 50 mg were confined in a basket with a Teflon microporous filter (porous diameter < 0.3 μm) and introduced into stainless steel 316 cylinder about 10 cm³ (full volume). The cylinder was pressurized to 300 bar and heated to 140 °C. The extraction was done during 1 h (solvent flow rate: 40 cm³/h). The soluble fractions were collected by rapid expansion of the superheated n-pentane. Both samples soluble and insoluble fractions were collect and analyzed. The mass solubilized was determined by weight difference. All of the reactive blend extractions were done in parallel with a physical blend (B0), as indicated in Figure 1. In this way, all the extractions of reactive blends could be compared with the results of the physical blend under the same conditions.

Characterization by Size Exclusion Chromatography (SEC): SEC chromatograms of all samples collected from raw materials and blends were obtained in a Waters Sci. Chromatograph model 150 – CV. The samples were dissolved in 1,2,4 trichlorobenzene (0.0125 % BHT) at the same initial concentration, and then injected at 135 °C.

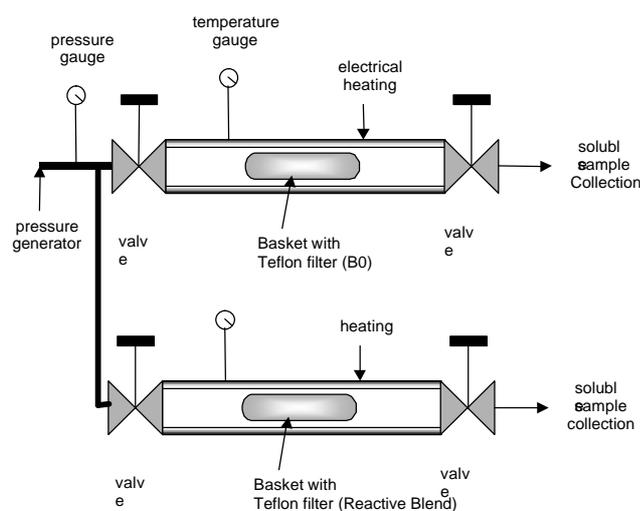


Figure. 1: Schematic diagram of the experimental equipment used to perform the SCE.

RESULTS AND DISCUSSION

Figure 2 shows the mass solubilized (percentage of the original sample mass) during the extractions as a function of the amount of catalyst. The PE-phase extraction is complete (80 % for B0) then, the excess extracted (from 80%) is copolymer. The mass of copolymer increases as the amount of catalyst increases as expected. Due to the graft-copolymer brush-architecture, the solvent cannot “see” the PS insoluble part of the copolymer molecule. The PE hairs drag the entire molecules in n-pentane as it be a molecule of pure PE.

A sharp increment in the mass solubilized between concentrations of 0.7% and 1 % is also observed in Fig. 2. This concentration interval contains the critical micelle concentration (CMC). At the CMC the interface becomes saturated with copolymer and the lowest particle size results. When the concentration is above the CMC or the compatibilization on the blend was performed under high shear stresses, the copolymer escapes from the interface to form micelles into the homopolymers phases. The increment of micelles in the PE major phase favors its extraction with the PE phase because there are not diffusion problems.

To analyze if all of the copolymer generated was extracted, SEC chromatograms of the insoluble phase of reactive blends were performed. Figure 3 shows this curves compared with the chromatogram of pure PS. The difference between the reactive residue's chromatograms with those from pure PS is evident. The size of the residues molecules decrease with the amount of catalyst used. This fact derives from the comparison of the curves minimum shift and is shown through the molecular weight in Table 2. For reaction with catalyst content below 0.7%, the molecular weight and the chromatograms do not change dramatically. The great change is between the molecular weight of R07 and R10. This drastic variation suggests the possibility of PS chain scission during Friedel-Craft reaction. In this order the “reactive pure polymers” samples were extracted and the products evaluated by SEC. Table 2 shows the average molecular weight of “reactive PE” and “reactive PS”. In the case of “reactive PE” all of the chromatograms perfectly match with the pure PE, demonstrating that there is not PE chain scission even for the highest AlCl_3 concentration. This means that for all of the catalyst content, the length of the PE hairs is analogous, then the dragged of the PE-g-PS could be similar in all the samples and only its concentration varies.

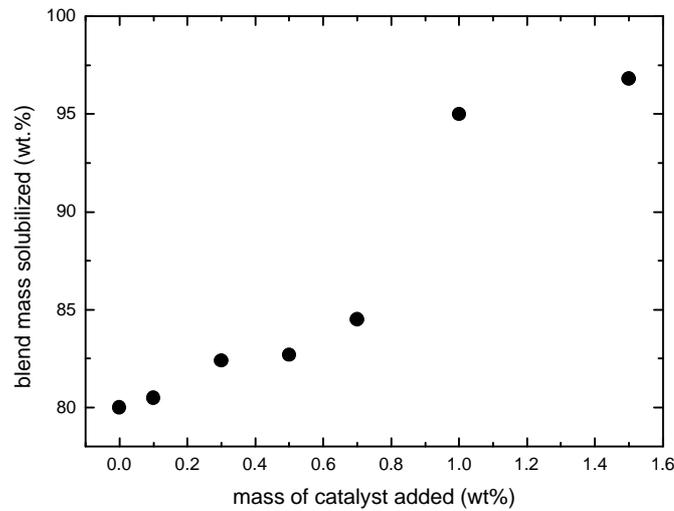


Figure 2: Reactive blends mass solubilized as a function of the amount of AlCl_3 .

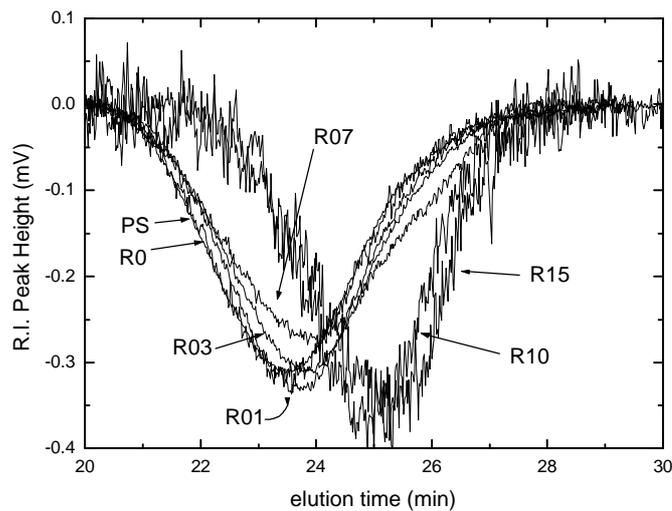


Figure 3: SEC Chromatograms of the insoluble phase of the reactive blends extractions compared with neat PS.

On the other side, “reactive PS” presents chain scission and the molecular weight change with the amount of catalyst used. This change becomes dramatic between R07 and R10. The average molecular weights of values of reactive PS are very similar to those of residues for catalyst content below 0.7% suggesting us that the residue is only PS but with short chains. Over 1%, the PS chain scission is so big, then the copolymerization reaction is favored (there are more end-chains in the melt) and the amount of copolymer generated increases dramatically as shown in Fig. 1. Taking into account the brush copolymer structure, if the length of PS part of the copolymer is short, the copolymer generated at high AlCl_3 concentration is solubilized easier than those for minor concentrations.

The molecular weight of R10 and R15, from table 2, differs from those of RPS10 and RPS15 because the chain scission reaction competes with copolymer reaction and the shorter PS chains copolymerize more rapidly than shorter ones, then the insoluble phases, R10 and R15 are shorter chains of PS.

Table 2. Average molecular weight of the extraction residues and reactive polymer samples

Extraction Residues		Reactive PE		Reactive PS	
	M_w (g/mol)		M_w (g/mol)		M_w (g/mol)
R0	257000	PE (neat)	50700	PS (neat)	256000
R01	260000	RPE01	50200	RPS01	257300
R03	250400	RPE03	50800	RPS03	248000
R05	245000	RPE05	49900	RPS05	243000
R07	200000	RPE07	50000	RPS07	194000
R10	95700	RPE10	49400	RPS10	25700
R15	90000	RPE15	50500	RPS15	< 20000*

* Out of the limit of detection of the SEC columns used.

CONCLUSION

The reactive blend phase separation using a hot solvent at high pressures is a rapid, non-contaminant and effective procedure: This method permits a total separation of high molecular weight commercial polymers physical blends and the separation of the copolymers in reactive ones. This is very difficult to obtain the separation by conventional procedures.

The copolymer PE-g-PS was solubilized by chemical affinity. The PE hairs drag the copolymer with the "paraffin" phase. This dragging was incremented with catalyst concentration because the relative length of the PE/PS chains in the copolymer increased (due PS chain scission).

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