Polypropylene/Polystyrene Blends: *In Situ* Compatibilization by Friedel-Crafts Alkylation Reaction

MÓNICA F. DÍAZ, SILVIA E. BARBOSA, NUMA J. CAPIATI

Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Cno. La Carrindanga Km. 7, (8000) Bahía Blanca, Argentina

Received 27 March 2003; revised 30 August 2003; accepted 6 September 2003

ABSTRACT: The application of Friedel-Crafts alkylation reaction to the compatibilization of polypropylene (PP)/polystyrene (PS) blends was assessed. A PP macrocarbocation is chemically bonded to the PS benzene ring by aromatic electrophilic substitution. The graft copolymer formed at the interphase (PP-g-PS) showed relatively high emulsification strength, suggesting an effective behavior as in situ compatibilizer. The critical micelle concentration (CMC) was related to Friedel-Crafts catalyst concentration. The amount of PS grafting and possible appearance of crosslinking and chain scission side reactions were also analyzed. The reaction products were characterized by a combination of size exclusion chromatography and Fourier transform infrared techniques applied after a careful solvent extraction separation. It was found, from the emulsification curve, that CMC was achieved when 0.7 wt % AlCl₃ was added. This value was confirmed by scanning electron microscopy observation of phase adhesion on fractured sample surfaces. Mass balances of extracted PS showed that at least 15 wt % of the initial PS resulted grafted at the CMC condition. Chain scission reactions, in parallel with grafting, were verified to occur for PP as well as for PS. Instead, crosslinking reactions were not detected. © 2003 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 452-462, 2004

Keywords: PP/PS compatibilization; PP/PS grafting reaction; reactive blending; poly(propylene) (PP); polystyrene; compatibilization

INTRODUCTION

The use of commodity thermoplastics in engineering applications has continuously grown during the last years. Positive features for their success include good cost-performance balance, wide range of processing-transformation possibilities, and recycling simplicity. Either thermoplastic blends or thermoplastic—matrix polymer composites have been reported to achieve competitive properties as engineering plastics in many applications. 1–3 Particularly, various processes and ap-

The largest tonnage thermoplastics, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinylchloride (PVC), are mutually immiscible. It is well known that the direct blending of two or more of them, in appreciable proportion, causes phase segregation, low interfacial adhesion, and poor mechanical properties.^{2–6} Therefore, a compatibilization treatment to im-

plications involving multicomponent thermoplastic blends are currently appearing; for example, the development of complex blends and composites aiming to balance stiffness/toughness properties in automotive applications, the design of novel printable materials for packaging, and the recycling of commingled municipal or industrial plastics residues.¹

 $^{{\}it Correspondence~to:~S.~E.~Barbosa~(E-mail:~sbarbosa@plapiqui.edu.ar)}$

Journal of Polymer Science: Part B: Polymer Physics, Vol. 42, 452–462 (2004) © 2003 Wiley Periodicals, Inc.

prove the phase adhesion, the reduction of interfacial tension, and the phase stabilization by the inhibition of droplet coalescence, is needed. ^{6–8} In particular, multiple phase blend compatibilization poses a quite complex problem particularly in controlling the different interphases involved.

Low-cost Friedel-Crafts (FC) alkylation is an attractive reaction to be applied to compatibilize thermoplastic blends containing PS. By this reaction, a hydrocarbon chain can be chemically bonded to the PS benzene ring through an aromatic electrophilic substitution. The graft copolymer formed (polyolefin-g-PS), situated at the interphase, will behave as an *in situ* compatibilizer for the specific polyolefin and PS blend. In the case of multicomponent blends, an addition compatibilization is pertinent. It can be accomplished by mixing a masterbatch containing the different polyolefin-g-PS copolymers together with the blend components.

These compatibilization procedures require a fine control of the copolymer concentration. As is well known, the *in situ* compatibilization effect is improved while the modifier concentration at the interphase approaches the saturation. At this point, the critical micelle concentration (CMC) condition is reached. ^{3,8} Instead, the addition compatibilization requires an excess of copolymer migrating from the phase to the interphase. Hence, the masterbatch must contain a copolymer concentration greater than CMC to allow micelles in excess to be able to conduct the compatibilization step.

The grafting performance of PE onto PS by FC reaction was studied in a previous work. The extent of reaction, as well as the length of grafted PE chains, showed to be dependent on the PE molecular weight. The *in situ* and addition compatibilization efficiency of PE/PS blends was also discussed in terms of copolymer concentration and molecular architecture. To

Although PE/PS blends compatibilization has been given considerable attention, the literature review reveals a notable lack of research results published on compatibilization of PP/PS systems. Only a few articles regarding virtually addition compatibilization aspects were published. D'Orazio et al. 11,12 added a graft copolymer of unsaturated propylene and styrene (uPP-g-PS) to PP/PS blends. They assessed the morphology of PP/PS blends, compatibilized by grafting of an unsaturated propylene—styrene copolymer. These authors found more uniform particle size distribution as well as greater crystalline lamellar

thickness and lamellar amorphous layer thickness as the copolymer concentration increased. Their results are consistent with a better degree of compatibilization. Syed Mustafa et al. 13 investigated the use of an (aromatic vinyl monomer)g-PP copolymer as a possible addition compatibilizer for PP/PS systems. They observed some evidence of compatibilization from mechanical properties and morphology data obtained at different grafted aromatic vinyl monomer concentrations. Several authors studied the potential of block copolymers as addition compatibilizers for PP/PS systems. Macaúbas and Demarquette¹⁴ observed the emulsification effect of triblock styrene/butadiene copolymer addition. They inferred the interfacial tension and compatibilization behavior of the resulting blends by using rheological and morphological determinations. Hlavatá et al. 15 used styrene-butadiene copolymers containing different numbers of blocks. A key factor is the PS block molecular weight, which has to exceed a critical value to allow the PS entanglements formation. In subsequent works, 16 these authors analyzed the compatibilizing effect of a series of block copolymers ranging from diblock to heptablock, and having PS block masses greater than critical. It was found, from mechanical tests and small-angle X-ray scattering, that triblock (S-B-S) and pentablock (S-B-S-B-S) behaved as better compatibilizers than diblock and both heptablock (S-B-S-B-S-B-S, B-S-B-S-B) copolymers.

Sun et al.¹⁷ and Sun and Baker¹⁸ incipiently investigated the application of the FC reaction to PP/PS *in situ* compatibilization. Their results from mechanical tests evidenced that some compatibilization had taken place, but no further analysis was reported on reaction performance and product morphology.

In this work, the FC alkylation reaction, performed in molten state, is proposed to graft PP chains onto PS to achieve the *in situ* compatibilization of PP/PS blends. AlCl₃ is used as Lewis acid and styrene as cocatalyst. It is postulated that the aromatic electrophilic substitution occurs by attacking the PS benzene ring with a PP macrocarbocation. This reaction would yield a graft copolymer family (PP-g-PS) having a distribution of chain lengths in both components. The emulsification strength of the graft copolymers formed was assessed and the CMC condition determined. The copolymers formed at concentrations up to CMC would behave as in situ compatibilizing agents for the blend. Above CMC, the copolymer in excess, that is located within the

homopolymer phases, may act as addition compatibilizer. 19-21

As reaction byproducts, very low- and high-molecular-weight polymer fractions can be expected to appear, coming from chain scission and crosslinking reactions, respectively. The possible thermal and oxidative degradation were previously checked in order to discard the chain scission owing to these causes. Gel permeation chromatography and Fourier transform infrared (FTIR) analyses were performed on homopolymers and physical blends (PBs) after processing to assess a possible molecular weight decrement and the presence of typical oxidation peaks, respectively. The absence of oxidation was also verified for all of the reactive blends (RBs).

These side reactions may affect the blend viscosity and consequently the processing conditions. The addition compatibilization performance will be particularly sensitive to them, because viscosity has an important role in dispersing and mixing the copolymer within the blend. A crosslinking reaction, even in a small proportion, will greatly increase the melt viscosity, perturbing the masterbatch incorporation to the blend. Conversely, a moderate chain scission will probably not produce a great effect on the compatibilizer addition.

The grafting, chain scission, and crosslinking processes involve considerable changes in molecular weight. Therefore, an analytical routine based on molecular size assessment was designed to characterize the reaction products. The amount of grafted PS, as well as the possible PP and PS chain scission and crosslinking side reactions, was worked out. A careful solvent extraction followed by a comparative size exclusion chromatography (SEC) was applied to pure polymers and blends. In addition, FTIR was used to determine the remaining PS content in soluble and insoluble fractions. All the samples for characterization were prepared at the CMC condition, which was determined from the corresponding emulsification curve.

EXPERIMENTAL

Materials

PS Lustrex HH-103, supplied by UNISTAR SA, and PP from Petroquímica Cuyo SA, were used as basic materials. The alkylation reaction was catalyzed by a system containing Merk anhydrous

Table 1. Designation and Description of the Reacted Polymers and 80:20 PP/PS Blends

Sample	Description	Catalyst Content (wt %)
PB	Physical blend	0
RB01	Reactive blend	0.1
RB03	Reactive blend	0.3
RB05	Reactive blend	0.5
RB07	Reactive blend	0.7
RB10	Reactive blend	1.0
RPP	Pure PP upon FC reaction	0.7
RPS	Pure PS upon FC reaction	0.7

aluminum chloride, AlCl₃ (>98% purity) and styrene (>99% purity).

Blending

PB

PP (80 wt %)/PS (20 wt %) blends were prepared. Blending was performed, under nitrogen atmosphere, in a batch mixer (Brabender Plastograph W50) at 200 °C. The mixing procedure includes the initial melting of PS, and subsequent incorporation of PP. Mixing was performed at 60 rpm for 24 min.

Homopolymers (PP, PS)

The blending routine was performed on the pure homopolymers to check possible degradation due to processing. PP and PS were melted at 200 °C in a batch mixer under nitrogen atmosphere at 60 rpm during 24 min. Samples, called PPp and PSp, were collected and characterized.

RBs

The reaction was performed in the same batch mixer and at the same conditions as used for PBs. The catalyst was added to the already melted and mixed homopolymers. A set of RBs was prepared using 0.3 wt %. styrene and different concentrations of AlCl₃.

Reacted Homopolymers

Pure PP and PS were reacted at the same conditions as used for RBs. The reacted PP and PS are named RPP and RPS, respectively. Table 1 sum-

 $\begin{tabular}{ll} \textbf{Table 2.} & PS \ wt \% \ Content \ in \ Soluble \ and \ Insoluble \\ Extracted \ Fractions \end{tabular}$

Sample	Description	PS Content ^a (wt %)
SFPB SFRB IFPB	Soluble fraction of PB Soluble fraction of RB07 Insoluble fraction of PB	90 84 3.5
IFRB	Insoluble fraction of RB07	6.6

^a Determined by FTIR.

marizes the description of all the samples prepared.

Solvent Extraction

A careful phase separation was performed by selective Soxhlet solvent extraction from PB and RB07. The samples were prepared in film form (80 μm). PS was extracted using tetrahydrofuran (THF) for 48 h. The PB was used as a control to check the error of the method. The PS, when it is included in a PP matrix, is dissolved in a slightly less amount than at pure PS condition. As shown in Table 2, approximately 90 wt % of the PS content was extracted from the control, although PS is completely soluble in THF. This error will be considered in the reaction product analysis. Also, pure PP and PS were subjected to extraction at the same conditions in order to check the solvent selectivity. Complete extraction was achieved for PS, whereas <1 wt % of PP appeared in the soluble fraction.

Characterization

SEC

SEC chromatograms of PP, PS, PPp, PSp, RPP, RPS, PB, RB07, and all the extracted fractions and residues were obtained in a Waters Scientific Chromatograph model 150-CV. The different samples were dissolved in 1,2,4 trichlorobenzene (0.0125 wt % 2,6-Di-tert-butyl-p-cresol) at the same initial concentration, and then injected at 135 °C. Molecular weight distributions were also calculated for PP, PS, PPp, PSp, RPP, RPS, as well as soluble fractions from PB and RB07 after 48 h in THF.

FTIR Spectroscopy

FTIR spectroscopy was used to analyze the possible oxidative degradation and to quantify the PS

in the copolymers. In the first case, the typical carbonyl oxidative absorption peak, at about 1700 cm⁻¹, was looked for in all of the samples. The general shape of the spectra from PPp and PSp was compared with those from the starting materials PP and PS.

The PS concentration was estimated by comparing the ratio of infrared absorption peaks on film samples (70 μm). Peaks at 2723 cm $^{-1}$ (PP) and 700 cm $^{-1}$ (PS) were used for samples containing 0–50 wt % PS. For samples containing 50–100 wt % PS, the 2723 cm $^{-1}$ (PP) and 1600 cm $^{-1}$ (PS) peaks were used. Two calibration curves were traced from PP and PS PBs of known concentrations. The data summarized in Table 2 show average values from 10 film measurements.

Scanning Electron Microscopy

Micrographs on RB and PB, fractured at cryogenic temperature, were obtained from samples with and without superficial extraction of the PS dispersed phase. The extraction was done with THF at room temperature. From nonextracted samples, the increment in particle-matrix adhesion as well as the decrement in particle size can be observed. The particle sizes were measured from the extracted samples. Because the PP continuous phase retains the shape at these extraction conditions, the remaining holes provide a direct measure of PS particle size. The electron microscope used was a JEOL JSM-35 CF with secondary electron detector. The samples were coated with Au in a sputter coater PELCO 91000. Analysis PROTM software was used for processing the particle size data. Approximately 300 particles were considered to calculate these parameters. The average diameters with its dispersion (standard errors) were plotted versus catalyst concentration to build the emulsification curve.

RESULTS AND DISCUSSION

Reaction Mechanism

The general scheme of FC alkylation reactions is ²²:

$$C_6H_6 \, + \, \xrightarrow{AlCl_3} C_6H_5R \, + \, HX$$

Benzene ring is susceptible to electrophilic attack primarily because of its exposed π electrons. The

reaction occurs in three steps: 1) a carbocation is formed by reaction of an halogenated alkane with aluminum chloride; 2) the carbocation (acting as an electrophile) hits the benzene ring to form an arenium ion; and 3) the arenium ion loses a proton to produce the alkylated benzene.

FC alkylation reactions were previously proposed to compatibilize PS/PE blends. Carrick²³ performed early studies, working with low density PE and PS in a boiling cyclohexane solution with AlCl₃. He observed the formation of copolymer before degradation begins. Approximately 20 wt % of the PS added appeared in the graft copolymer. Sun et al.¹⁷ and Sun and Baker¹⁸ also studied FC compatibilization reactions of PS/PE, performed both in a batch mixer and in a twin screw extruder, using AlCl₃ as catalyst and styrene as cocatalyst.

Although the mechanism of this reaction has not been properly explained yet, previous studies^{17,18,23} proposed a mechanism in which a low-molecular-weight carbocation is first formed from an AlCl₃ ionic complex. Then, the carbocation hits the PE molecule to yield a macrocarbocation. Finally, this one produces, by electrophilic attack on the PS benzene ring, a graft copolymer. The cocatalyst (styrene) could act as initial carbocation as well.

In this work, FC reactions were performed on PP/PS blends to obtain compatibilizing graft copolymers PP-g-PS. A similar general mechanism, as previous authors proposed for PE-g-PS formation, is expected. Furthermore, it is important to consider that PP is more susceptible to suffer chain scission (β -scission) because of the presence of tertiary carbon atoms. ²⁴ As a consequence of this, a high amount of PP chain scission is expected as byproducts. A general scheme of PP-g-PS formation is:

$$R + CH - CH_2 - \frac{AICI_3/St}{\text{(molten state)}} - CH - CH_2$$

$$R: PE: PP$$

CMC Condition

The emulsification effect of an interphase modifier, in immiscible polymer blends, is directly related to the interfacial tension reduction caused by such modifier. Because the interfacial tension is proportional to the particle size of the dispersed phase, ^{20,21} the emulsification behavior can be assessed from particle size variation with the concentration of copolymer formed. Several authors have reported that the emulsification effect (analogous to compatibilization efficiency) reaches a maximum when the interphase is saturated with modifier. At this point, the interfacial tension and particle size are minimum and the CMC condition is reached. ^{3,8} Above CMC, the interfacial tension as well as the particle size remain constant. Any copolymer in excess to CMC will form micelles, which will remain within the homopolymer phases not contributing to the emulsification process.

The CMC condition for our PP/PS blends was determined from particle size versus catalyst concentration (which is proportional to copolymer concentration) curves. ^{20,21} Because all the samples were processed at the same mixing conditions, any decrease in particle size can be attributed to interphase modifications produced by the PP-g-PS formed during the FC reaction.

Figure 1 shows that the emulsification curve follows a typical trace, which was frequently reported for immiscible blend compatibilization. It is clear that after a significant decrease in particle size, an equilibrium value is reached at approximately 0.7 wt % $AlCl_3$. This value has been taken as the CMC condition. It has to be remarked that the particle size decreases to one-third of its initial value, reaching an equilibrium diameter of approximately 0.5 μ m. These figures,

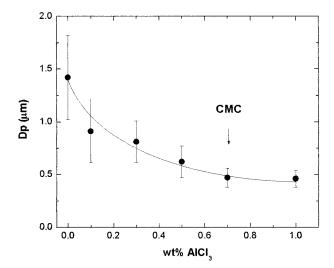
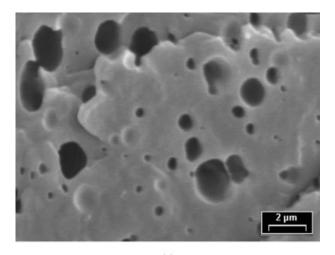


Figure 1. Emulsion curve for PP/PS (80:20). Effect of the catalyst concentration on the average particle diameter (Dp).



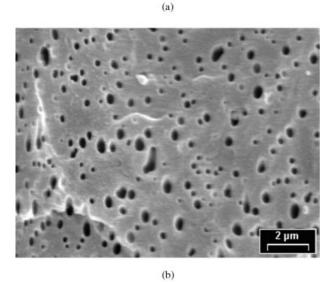


Figure 2. SEM micrographs (original magnification, $6000\times$) of PS extracted fracture surfaces: (a) PB, (b) RB10

in general, agree or are slightly better than those reported in the literature for polyolefin blends compatibilization. Macaúbas and Demarquette to studied the addition compatibilization of PP/PS blends having similar molecular weights and polydispersities to those used in this work. They found particle size reductions to about a half and a final diameter of 1.5 μ m. In regards to these results, it appears that the copolymer formed by the FC reaction behaves as an efficient *in situ* compatibilizer for the PP/PS blend.

Figure 2 shows micrographs of physical and RBs (1 wt % catalyst content) with the PS phase extracted. From it, the particle size data were obtained. The remarkable change in size domains is evident, as well as the increment in size homogeneity for the case of RBs.

The emulsification data closely correlate with the observed adhesion between phases. Figure 3 shows micrographs of the fracture surfaces corresponding to PB, 0.1, 0.3, 0.5, 0.7, and 1.0 wt % catalyst. A consistent improvement in adhesion is clearly observed, along with particle size decreasing, as the copolymer content increases. Particularly, it appears that starting from CMC (0.7 wt % catalyst), the interphase becomes almost indiscernible, indicating a very good adhesion.

The particle size homogeneity, given by the error bars in Figure 1, provides additional evidence of the CMC value for these blends. The particle size homogeneity increases up to 0.7 wt % catalyst remaining quasi-constant afterwards.

Reaction Product Characterization

The reaction product analysis and quantification were done at CMC. Characterization techniques by SEC and FTIR were combined with selective solvent extraction to assess the event of FC alkylation and side reactions. The SEC chromatogram peak polarity depends on the value of the sample refractive index respect to the pure solvent one. Figure 4 shows the chromatograms corresponding to the pure homopolymers (PP, PS). They exhibit opposite peak signs because PP and PS solutions have refractive indices higher and lower than that of the pure solvent. Also, the blend chromatograms should be the result of a balance between negative (PS) and positive (PP) peak contributions.

Chain Scission and Crosslinking Reactions

To learn about the possible event of side reactions that could lead to chain scission and/or crosslinking, a systematic study was performed. First of all, the possible thermal degradation was analyzed on both pure polymers and PBs. The processing routine was applied to starting materials, as explained in the Experimental section, and the products were characterized. In the case of "processed" homopolymers PPp and PSp, the SEC curves matched closely their corresponding starting materials, indicating that homopolymers did not change with the processing (Fig. 5). The molecular weight average values, listed in Table 3, confirm this. The FTIR results are in accordance. The homopolymers spectra before and after processing remain unchanged and the typical oxidation peak ($\approx 1700 \text{ cm}^{-1}$) does not appear.

For the PBs, the SEC chromatograms were compared with the corresponding *simulated* PB

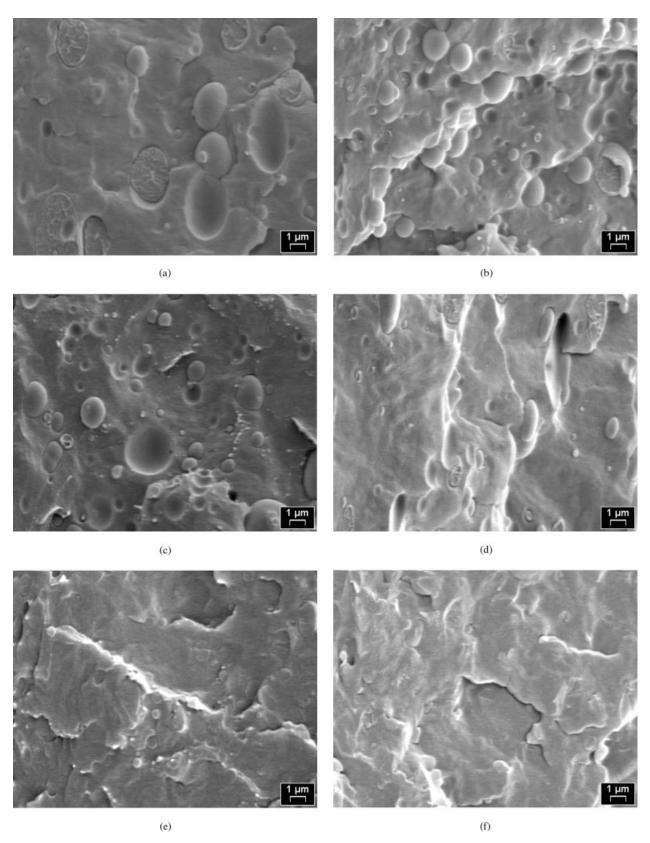


Figure 3. SEM micrographs (original magnification, $6000\times$) of blend fracture surfaces. (a) PB, (b) RB01, (c) RB03, (d) RB05, (e) RB07, and (f) RB10.

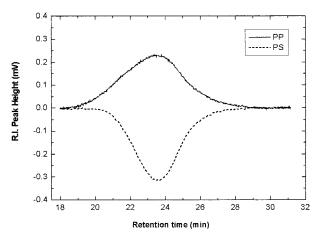


Figure 4. SEC chromatograms for pure PP and PS.

one (simPB). The chromatogram for simPB was obtained from the pure PP and PS SEC chromatograms weighted in the same proportion; following

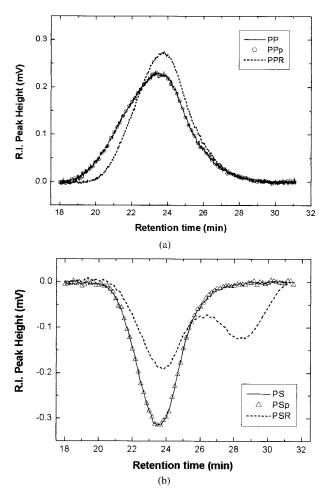


Figure 5. SEC chromatograms for (a) pure, processed, and reacted polypropylene, PP, PPp, and RPP, respectively. (b) Pure, processed, and reacted polystyrene, PS, PSp, and RPS, respectively.

Table 3. Molecular Weight and Polydispersity of PP and PS (Pure, Processed, and Reacted) and Soluble Fraction of PB and RB07

Sample	$M_{ m w}$ (g/gmol)	$M_{ m w}/M_{ m n}$
PP	303,000	4.4
PS	258,000	2.1
PPp	304,000	4.3
PSp	260,000	2.2
RPP	164,000	3.4
RPS	142,000	16.8
SFPB	220,000	1.8
SFRB	51,000	3.96

a method we had previously used.⁹ The close matching observed in Figure 6 confirms that no thermal scission is present. This result also shows the additive character of the blend refractive indexes, indicating the absence of chemical interaction between components in the PBs. The nonexistence of oxidation was verified for the physical as well as the RBs.

Having the certainty that no thermal degradation is present, the homopolymers were reacted at the same conditions as used for RB. Then the reaction products (RPP, RPS) were compared with the pure polymers (PP, PS). Table 3 shows the molecular weights (as $M_{\rm w}$) and polydispersities of the initial and reacted materials. It is apparent that reacted polymers exhibit average molecular weights considerably lower than unreacted ones. On the other side, Figure 5 shows the SEC chromatograms from RPP and RPS samples. It is observed here that RPP has undergone both

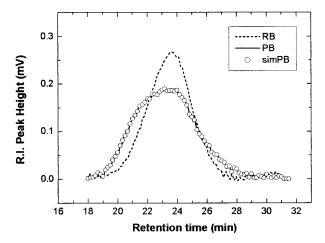


Figure 6. SEC chromatograms for PB, simPB, and RB07.

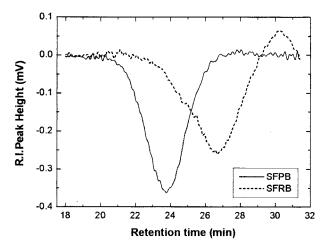


Figure 7. SEC chromatograms for SFPB and SFRB.

a reduction in polydispersion and a trace shift to the lower molecular weight region, upon reaction [Fig. 5(a)]. Also, the RPS sample shows the same general trend [Fig. 5(b)] but two neat peaks appear. One of the peaks is located at the same retention time as unreacted PS and the other one shifted to the low-molecular-weight region (28–30 min). These results clearly indicate that low-molecular-weight fractions of PP and PS that could be assigned to chain scission appeared because of reaction. However, there is no evidence of crosslinking reactions that would be detected by an increase in the high-molecular-weight zone of the chromatogram. Consequently, only low-molecular-weight fractions of PP and PS, along with the graft copolymer, can be expected to appear in RB07.

Amount of PS Grafted

The reaction product assessment would be readily performed if a perfect separation of copolymer from the homopolymers were possible. However, a solvent combination, selective enough to allow such isolation, was not found. Alternative supercritical extraction techniques are being worked out to improve the solvent selectivity. Nonetheless, as it is explained below, the complete separation and analysis of one of the homopolymers would provide a qualitative proof of chain scission and FC reaction progress.

The PB and RB07 were subjected to extraction with a good solvent for PS (THF). Therefore, it is expected that soluble fractions be rich in PS. On the other side, because THF dissolves neither PP nor PP-g-PS, the IFRB should contain the major

part of PP and the copolymer molecules (if the FC reaction has taken place).

The SEC chromatograms from physical and RBs are shown in Figure 6. The curve for RB07 is narrower than PB indicating a decrease at highas well as at low-molecular-weight regions. This behavior suggests the occurrence of reactions such as chain scission and short-length molecule consumption (by grafting), respectively. To determine the event of these reactions, SEC chromatograms from soluble and insoluble fractions of RB07 and PB were assessed. The traces for SFPB and SFRB (Fig. 7) show, as expected, negative peaks corresponding to extracted PS. From the data of Table 3, it is observed that the extracted PS from SFPB exhibits virtually the same molecular weight as the original PS. On the other side, for SFRB, a considerable reduction in PS molecular weight is noted, indicating that chain scission reaction probably has taken place. Also, the SFRB chromatogram shows a low positive peak at a very high retention time. Because PS always gives a negative trace, this signal might correspond, in principle, to low-molecular-weight fractions of **PP**-g-PS or **PP**. These fractions, able to be dissolved by THF, could be originated in chain scission reactions. However, such peak cannot correspond to **PP**-g-PS because a positive signal would require a greater amount of PP than PS, and in this case either the copolymer would be insoluble in THF, or the peak would appear in the high-molecular-weight region. Finally, it can be inferred that side chain scission reactions occur, giving rise to PP fractions of molecular weight low enough to be dissolved by THF.

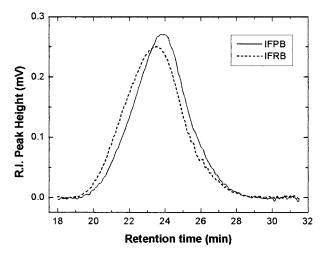


Figure 8. SEC chromatograms for IFPB and IFRB.

Table 4. Weight Percent Decrease after THF Extraction (48 h)

Sample	Weight Decrease (%)
PP	0.6
PS	100
PB	20
RB07	17

Regarding the insoluble fractions, it can be expected that only PP be present in IFPB and PP and PP-g-PS in IFRB. The chromatograms from IFPB and IFRB (Fig. 8) only show PP peaks. The PS peaks, of negative polarity, are not perceptible in the SEC curves, for they are subtracted from the PP positive peaks. Also, it is observed that the IFRB curve is shifted to lower retention times (higher molecular weights) relative to the IFPB curve. In consequence, because no crosslinking reactions appeared, it can be inferred that this high-molecular-weight fraction corresponds to PP-g-PS molecules, which obviously exhibit greater molecular weight than each of its homopolymers does.

The amount of grafted PS can be estimated from extraction data. The key factor considered here is the small amount of PS remaining in the insoluble fractions. Table 2 shows that 3.5 wt % PS remains in IFPB and a greater amount, 6.6 wt % PS, in IFRB. This extra PS should correspond to the graft copolymer as was inferred from SEC results.

Mass balances of insoluble and soluble fractions were calculated from data on Tables 2 and 4. The difference in PS content (between IFRB and IFPB), referred to the total PS in the PB (20 g of PS in 100 g of blend), yielded approximately 15 wt % grafted PS for the reaction at CMC condition. It is worth noting that this value may contain a small defect error caused by the possibility of PS-rich copolymer molecules being present in the soluble fraction.

CONCLUSIONS

The pertinence of FC reactions for *in situ* compatibilization of PP/PS blends was assessed in this work, leading to the following conclusions:

• A detectable (by SEC and FTIR) amount of copolymer (PP-g-PS) was formed upon FC

- reaction from catalyst concentrations starting from 0.1 wt %.
- The CMC could be related to key reaction parameters. It was experimentally determined from the emulsification curve that CMC condition was reached when 0.7 wt % of catalyst was added. This result is in agreement with particle size homogeneity measurements and interfacial adhesion observation (SEM) from sample fractured surfaces. Also, PS mass balances, involving soluble and insoluble fractions, showed that at least 15 wt % of the initial PS was grafted at the CMC condition.
- The copolymer formed upon FC reaction showed an *in situ* compatibilization effect similar to or better than that reported in the literature for the compatibilization of PP/PS blends by copolymer addition.
- Side reactions, leading to chain scission, were proved to occur for PP and PS, in parallel with grafting. Instead, crosslinking reactions, that could cause difficulties in the blending in addition compatibilization applications, were not detected.

The authors gratefully acknowledge the financial support from the following institutions of Argentina: CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), SETCIP (Secretaría de Ciencia, Tecnología e Innovación Productiva), and UNS (Universidad Nacional del Sur).

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