

Addition Compatibilization of PP/PS Blends by Tailor-Made Copolymers

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The thermoplastic polymer blends of commercial interest generally need a phase compatibilization to reduce the interfacial tension, to stabilize the morphology, and to increment the interfacial adhesion. This work deals with the compatibilization of PP/PS blends by addition of a tailor-made copolymer, which is prepared from the pure homopolymers by a Friedel-Crafts reaction. This addition compatibilization process comes out as an economic alternative applicable to the recycling of mixed plastics from urban and industrial wastes. The influence of compatibilizer concentration and blending time on the emulsifying effect, morphology, and mechanical properties of the resulting blends are analyzed. The compatibilization process effectiveness is assessed through the improvement in phase adhesion, emulsification and ductility of the compatibilized with respect to the physical blends. An increase of three times in ductility is achieved using very low compatibilizer concentrations (0.5–0.7 wt%). No appreciable detriment in yield strength or modulus is observed in these compatibilized blends. POLYM. ENG. SCI., 46:329–336, 2006. © 2006 Society of Plastics Engineers

INTRODUCTION

The polymer blends of commercial interest are frequently developed starting from incompatible components [1]. Large and nonhomogeneous particulate morphologies result from direct components blending, which exhibit low interfacial adhesion and stability (tendency to coalesce during melt processing), and poor mechanical properties. The phase compatibilization, generally produced by an agent that modifies the interphase, is a well-known technique to mitigate these problems. This process is characterized by reduction of interfacial tension, stabilization of morphology, and increment of interfacial adhesion [2, 3]. In general, the

compatibilizer agent is a copolymer containing chemical structures, which are affine with one or more of the blend components. It is located at the interphase, between the homopolymers, and forms entanglements with each phase, according to its physicochemical compatibility. Blend compatibilization can be performed either by the in situ generation or by the addition of an interfacial agent. In the former case, the compatibilizer is directly made at the interphase by chemical reaction; while in addition to compatibilization the interfacial agent reaches the interphase by migration through the homopolymer phases [4, 5].

In our previous work, in situ compatibilization via Friedel-Crafts alkylation reaction (F-C) was applied to PP (polypropylene)/PS (polystyrene) blends. The graft copolymer produced, PP-*g*-PS, performed as a good compatibilizer for these blends. The catalyst concentration was optimized as a function of the blend morphological aspects and mechanical properties. Also, the range of catalyst concentrations that produce the interphase saturation was determined [6, 7]. Considerable improvement in ductility and toughness was achieved without appreciable loss of yield strength [8]. Also, the low cost F-C reaction proved to be an easy-to-process compatibilizing technique.

In this work, the PP/PS addition compatibilization procedure is carried out using a tailor-made compatibilizer (TMC). The methodology proposed includes two steps. Initially, the TMC is generated and in the second step, the TMC is added to the PP/PS blend in a proportion that can be chosen as a function of the desired blend mechanical properties.

The TMC is obtained in molten state by F-C reaction on PP/PS blend. The catalyst concentration used is higher than the needed to produce enough compatibilizing agent (PP-*g*-PS) to saturate the interphase [6, 7]. The purpose is to obtain an excess of compatibilizer, above the saturation concentration, that is available for the subsequent addition compatibilization process. This TMC was palletized and added to the molten PP/PS blends in a batch mixer.

This addition compatibilization process would appear as an economic alternative applicable to the recycling of mixed

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plastics from urban and industrial wastes [9]. The following advantages can be listed for this application:

1. The compatibilizing agent (PP-*g*-PS) is tailor-made from pure resins and controlled reaction conditions, allowing the optimization of amount and quality of the copolymer formed.
2. The copolymer is prepared from the same homopolymers that constitute the physical blend (PB), thus promoting the greatest affinity between the blend components.
3. The process is economically attractive, since it uses small amounts of low cost reactants.
4. The addition compatibilization, as opposed to the in situ one, is a simple process not affected by secondary reactions, like chain scission and crosslinking, which can degrade or modify the properties of the blend [10 “Chapter 1”].

The results of this work were analyzed in terms of effects of TMC concentration and mixing time on the process efficiency. Particular consideration deserved the blend morphological aspects, including emulsifying effect and interfacial adhesion, as well as the final mechanical properties.

The TMC concentration influence was studied within an appropriate range to the mechanical properties variation. For example, since ductility presents a maximum, the TMC concentration was varied from well below to above that maximum zone. The mixing time limits were established to obtain good homogeneity and to avoid thermal degradation.

EXPERIMENTAL

Materials

Polystyrene Lustrex HH-103 (PS) supplied by UNISTAR, and polypropylene (PP) from Petroquímica Cuyo SA, were used as basic materials. F-C alkylation reaction was catalyzed by Merk anhydrous Aluminum Chloride (AlCl_3), (>98% purity) and Styrene (>99% purity).

Blending

The blending conditions were adjusted to reach a PP/PS viscosity ratio (λ) slightly less than 1. The theory of emulsion microrheology defines a range of viscosity ratios for drop splitting under shear flow as $0.1 \leq \lambda \leq 1$ [2]. Similar viscosities for PP and PS (at same shear stress) were reached in the batch mixer with 60 rpm and 200°C [7]. The mixing times were chosen as a function of the compatibilizer dispersion. Screening experiments to choose the mixing time range were performed. PBs and compatibilized ones (with 1.0 wt% of TMC) were prepared at 12, 24, 36, and 48 min. The results showed that in blends prepared during 12 min, the TMC dispersion was not homogeneous. This fact was determined by several FTIR determinations in different zones of the bulk. On the other side, blends prepared during 48 min presented thermal degradation (evalu-

TABLE 1. Designation and description of PB and CB mixed during 24 and 36 min.

Sample	TMC concentration (wt%)
PB-24	0.0
CB 01-24	0.1
CB 1.0-24	1.0
CB 10-24	10.0
PB-36	0.0
CB 01-36	0.1
CB 03-36	0.3
CB 05-36	0.5
CB 07-36	0.7
CB 1.0-36	1.0
CB 1.3-36	1.3

ated by the presence of FTIR carbonyl peak). Consequently, 24 and 36 min were chosen as mixing times for the blends preparation.

Physical Blends

PP (80 wt%)/PS (20 wt%) blends were prepared. Blending was carried out, under nitrogen atmosphere, in a batch mixer (Brabender Plastograph W50) at 200°C. The mixing procedure included the initial melting of PS, and subsequent incorporation of PP. Mixing was performed at 60 rpm for 24 min and 36 min.

TMC Preparation

The F-C alkylation reaction was performed in the same batch mixer and at the same conditions as used for PB, for 24 min. AlCl_3 (1.0 wt%) and 0.3 wt% of styrene were added to the already melted and mixed homopolymers. Details of preparation method are available in Ref. 6.

Homopolymers (PP, PS)

The blending routine was also 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 for 24 min and 36 min. Samples, called PPp and PSp, were collected and characterized.

Compatibilized Blends

The addition compatibilization was carried out in the same batch mixer and at the same conditions as used for PB. Different TMC concentrations were added to the already melted and mixed homopolymers. Two sets of CB were prepared, one for each time of mixing. The names and concentrations used are summarized in Table 1.

Characterization

Fourier Transform Infrared Spectroscopy. This technique was used to analyze the possible oxidative degradation

TABLE 2. Average disperse phase diameter (D_p), relative diameter decrease (D_p/D_0) and standard deviation ($\sigma(D_p)$) for physical and compatibilized blends mixed during 24 min.

Sample	D_p (μm)	$\sigma(D_p)$ (μm)	D_p/D_0
PB	1.45 (D_0)	0.45	1.00
CB 01	1.28	0.42	0.88
CB 1.0	0.95	0.36	0.66
CB 10	0.76	0.19	0.52

of the materials. The typical carbonyl oxidative absorption peak, at about 1700 cm^{-1} , was looked for in all of the samples. This test was performed on all the blends prepared, as well as on PPp and PSp. Also, the blend concentration homogeneity in the bulk was estimated by comparing the ratio of infrared absorption peaks on 10 film samples ($70\text{ }\mu\text{m}$). Peaks at 2723 cm^{-1} (PP) and 700 cm^{-1} (PS) were used. A detailed description of this technique is reported in Ref. 7.

Scanning Electron Microscopy. Micrographs on PB and CB, 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 variation in particle-matrix adhesion, as well as in particle size, was studied. The particle sizes were measured from the extracted samples. As the PP continuous phase retains the shape, at these extraction conditions, the remaining holes provide a direct measurement 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. About 300 particles were considered to calculate these parameters. The average diameters (D_p) and standard deviation $\sigma(D_p)$ were plotted versus TMC concentration to build the emulsification curve.

Mechanical Properties. Quasi-static tensile tests were carried out at room temperature in an Instron tester at a crosshead speed of 5 mm/min . Flat dog-bone shaped tensile specimens were cut from plates prepared by compression molding. The specimen dimensions were scaled to one-third of ASTM D638M standard (specimen type IV). Ten specimens for each sample were measured. Yield strength and elongation at break were comparatively assessed from stress-strain curves.

RESULTS AND DISCUSSION

Emulsifying Effect

The compatibilization process affects the morphology of the blend phases and their interphases, and particularly the emulsifying effect. As was reported elsewhere [3, 11], the effectiveness of this process is well assessed by the shape and size of phase particles, as well as by interfacial adhesion determinations. Before starting this study all of the blends

prepared were analyzed by FTIR to determine possible thermal degradation. The typical carbonyl peak (1700 cm^{-1}) was not observed in any sample, showing that oxidation was not present.

The emulsifying effect of the compatibilizer on our PP/PS blends was determined by particle size decrease and its dispersion. The evaluation was carried out monitoring the relative change D_c/D_0 as a function of TMC concentration, where D_c and D_0 being the CB and PB particle diameters, respectively.

The particle size variation for the CB samples, prepared by 24-min mixing, is presented in Table 2. The D_p falls to 88% (65%) of D_0 with the TMC addition of 0.1 (1) wt% and to 52% with 10 wt%. Also, a continuous decrease in D_p is observed without reaching a constant value. So, it can be expected that, at this condition, the copolymer cannot saturate the PP/PS interphase, even at TMC concentrations as high as 10 wt%.

At the longer mixing time (36 min), a more typical emulsification curve results, in which the exponential decay is followed by a constant D_p region. The saturation of the interphase is considered to be achieved at the TMC concentration where the particle size becomes constant (Fig. 1). Similar results are frequently reported for immiscible blends compatibilization [2, 11]. The point of D_p stabilization, regarded as the critical micelle concentration (CMC), was reached in this case at about 0.7 wt% of TMC addition. The D_p at this point dropped to 50% of D_0 , while standard deviation (error bars) decreased indicating that the particle size distribution is becoming more uniform on compatibilization. Other authors (see for example Macaubas et al. [12]), compatibilizing PP/PS blends by addition of commercial block copolymers reported a D_p reduction of the same order as in the present work. However, their results were achieved by using a considerably larger amount of compatibilizer (5 wt%). When a TMC (instead of a commercial copolymer) is used for addition compatibilization, the affinity between phases is greatly increased. This effect is due to the close

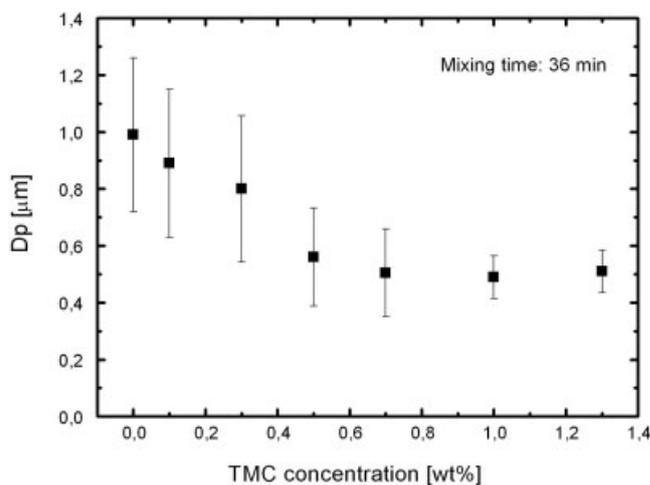


FIG. 1. Emulsification curve for blends mixed during 36 min. Effect of TMC concentration on the average particle diameter (D_p).

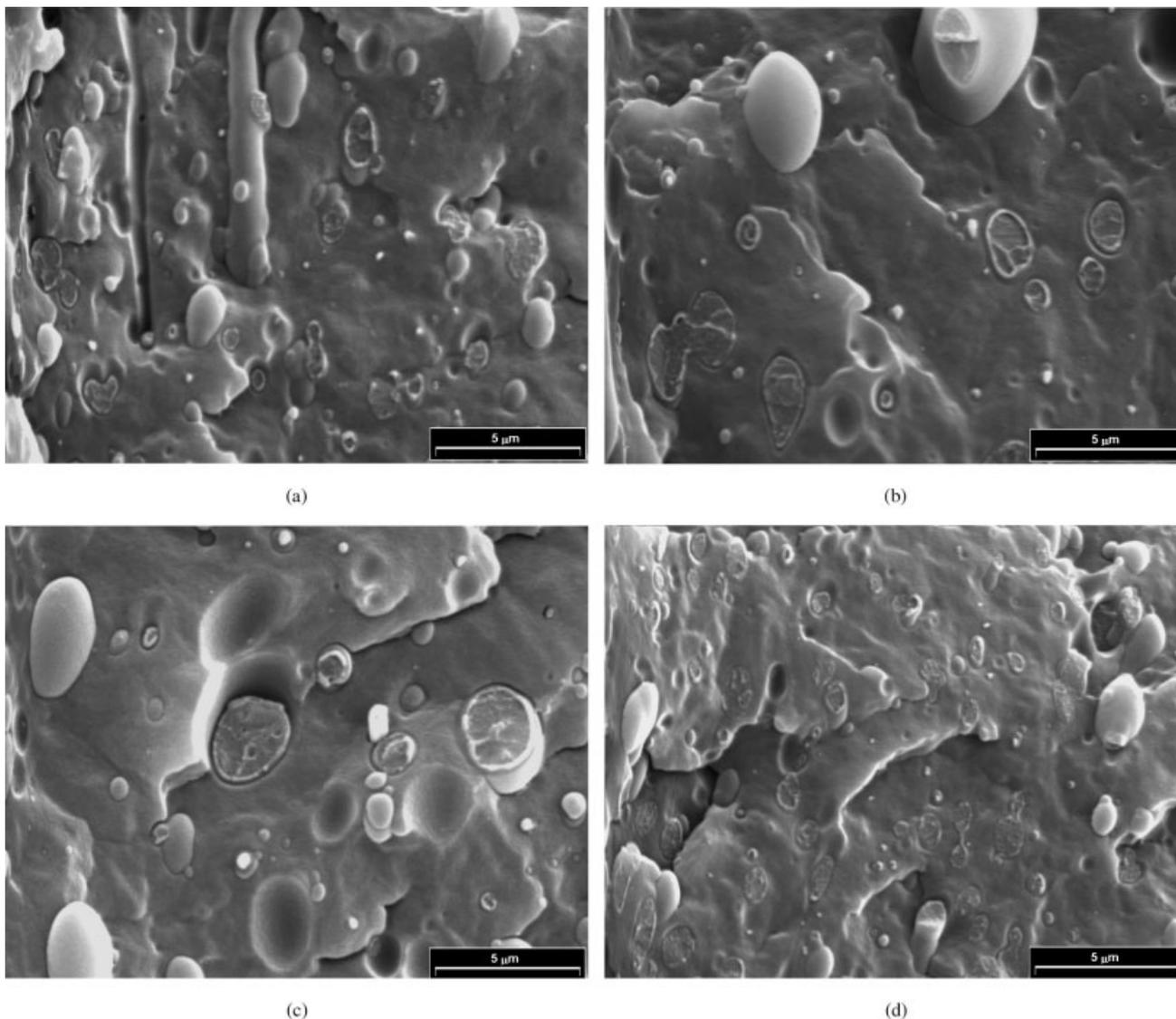


FIG. 2. SEM micrographs of blend fracture surfaces. (a) PB, (b) CB 01, (c) CB 1.0, and (d) CB 10. Mixing time: 24 min.

matching between the compatibilizer structure and the blend homopolymers.

During the mixing process, the PB particle size is determined mainly by two competitive mechanisms: drop “breakup” favoring dispersion, and drop aggregation by coalescence. Under the same shear field and temperature, the blending variable to be considered is mixing time. The D_0 for 24 min (Table 2) is $1.45 \mu\text{m}$, while the one for 36 min (Fig. 1) is $0.99 \mu\text{m}$, then D_0 (36 min) is 68% of D_0 (24 min). This significant change reveals that the main mechanism, within the range of mixing times studied, is drop breakup.

At low TMC concentrations, the migration mechanism and the emulsifying effect seem to be unaffected by the mixing time. The ratio $D_{c-0.1 \text{ wt}\%}/D_0$ is ~ 0.89 for both mixing times (Table 2 and Fig. 1). In contrast, for higher concentrations the greater the mixing time, the greater the reduction of D_p becomes. For example, for 1 wt% of TMC $D_{c-1 \text{ wt}\%}/D_0$ is 0.66 for 24 min and 0.50 for 36 min. This behavior can be explained in

terms of the difficulty in placing the greatest amount of TMC at the interphase. At low TMC concentrations, there are relatively few compatibilizer molecules competing to go into a large number of interfacial vacancies (please note that, in this paper, “vacancy” means interphase zone without compatibilizer), and so the migration can be completed by mixing 24 min or less. Then, the results observed are the same for both mixing times. On the other side, at higher TMC concentrations, many more molecules have to be placed in the same number of vacancies. The compatibilizer occupies the vacancies progressively, and less free places remain to be filled each time. Therefore, at high TMC concentration, longer mixing time is needed to complete the compatibilizer migration.

Morphological Features

The morphology of the compatibilized blends (CB) was studied by SEM of blend surfaces, fractured at

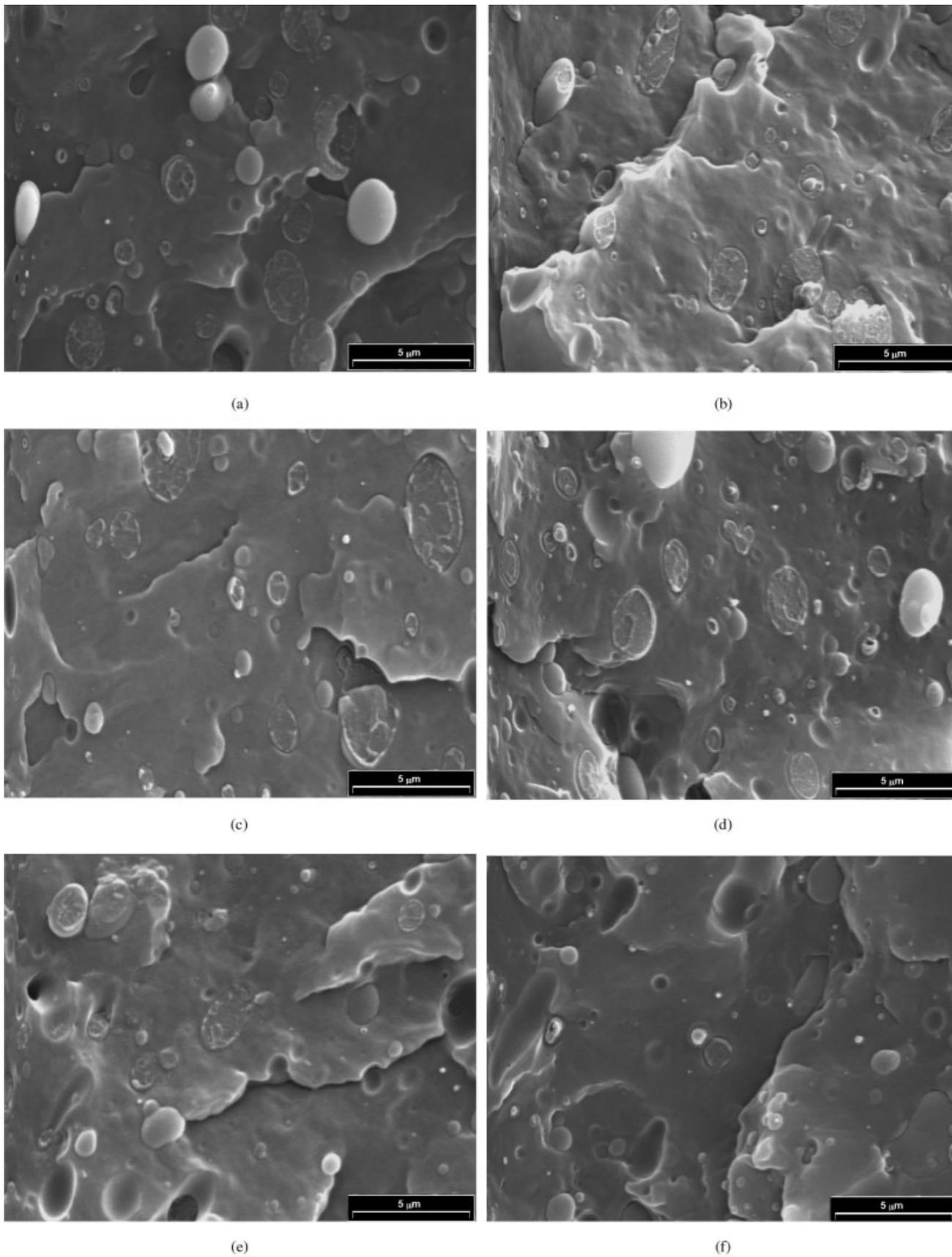


FIG. 3. SEM micrographs of blend fracture surfaces. (a) PB, (b) CB 01, (c) CB 03, (d) CB 05, (e) CB 07, and (f) CB 1.0. Mixing time: 36 min.

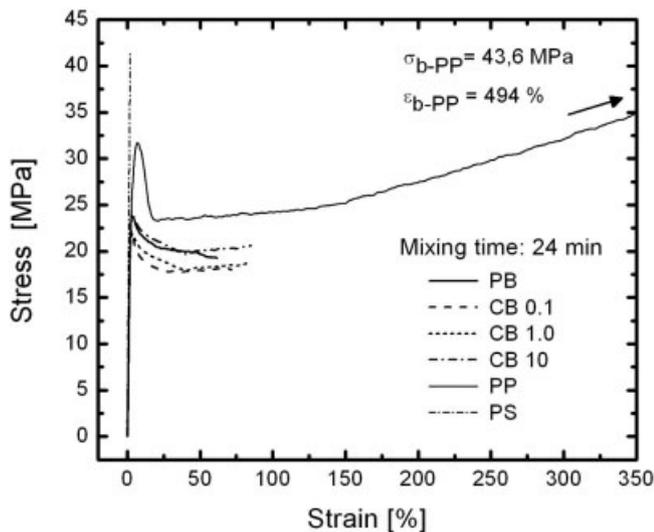


FIG. 4. Stress–strain behavior for homopolymers, PB and CB, mixed during 24 min.

cryogenic temperature. Twelve different-magnification micrographs were analyzed for each blend. The effect of the interfacial adhesion on compatibilization was assessed through the proportion of transgranular type of fracture with respect to the intergranular one. Figure 2 shows the micrographs corresponding to blends mixed during 24 min. The interfacial adhesion does not show any improvement until a TMC addition of 10 wt% (Fig. 2d), where only a few particles exhibit transgranular fracture. Also, a gradual decrease of particle size with the TMC addition is appreciated.

For the blends mixed during 36 min, both particle size reduction and interfacial adhesion improvement are clearly seen from Fig. 3. The transgranular fracture portion increases from 0.3 wt% up to 0.7 wt% of TMC added, remaining constant for greater TMC concentrations. These results are in agreement with the CMC value reported in emulsifying effect. At 0.7 wt%, the saturation of the interphase is completed and the largest possible improvement of interfacial adhesion is achieved. It can be inferred that, for higher TMC concentrations, the excess of compatibilizer accumulates in the homopolymer phases not affecting the interphase behavior. Similar deduction was also reported by other authors [2–4]. It has to be noted that this excess cannot be observed by SEM, because the homopolymer phases do not undergo any change in the fracture surface morphology. They show a neat surface, specially the matrix (Fig. 3).

The effect of mixing time is shown in Figs. 2c and 3f. The sample corresponding to 36-min mixing (Fig. 3f) presents a larger proportion of transgranular fracture surface than the 24 min one, indicating that the interphase in Fig. 3f is better compatibilized than in Fig. 2c. As was explained earlier, the amount of interfacial agent that reaches the interphase increases with mixing time for high concentrations.

Mechanical Properties

The effect of compatibilization on the blends mechanical behavior was assessed by tensile tests. Stress–strain curves were obtained from CB specimens prepared at different TMC concentrations and mixing times. The Figs. 4 and 5 show the traces corresponding to PB, CB, and homopolymer matrices grouped by mixing time. The samples prepared by 24-min mixing (Fig. 4) ruptured before the cold drawing-strengthening zone (positive slope) was reached. It can be inferred from this behavior that the interfacial PP/PS adhesion is lower than the shear strength of the matrix. The samples break when the primary (stable) necking is already achieved, without later necking displacement along the specimen length. This is in accordance with a premature debonding of PP/PS interphase not allowing further PP crystals reorganization. The reduced adhesion between phases is probably due to a nonhomogeneous compatibilizer distribution at the interphase, coming from insufficient mixing.

The blends mixing during 36 min showed a greater elongation to break, well in the cold draw strengthening region (Fig. 5). It has to be noted that the CB traces are almost parallel to the PP curves, suggesting that the same mechanism of rupture is occurring for pure PP as for CB. It is also observed that the interphase remains bonded beyond the necking formation and displacement. The compatibilizer is contributing to interfacial adhesion, and the elongation to break depends now on TMC concentrations as will be discussed later. Figures 4 and 5 show that the yield strength of CB samples does not change appreciably with TMC concentration.

Figure 6 shows the yield strength vs TMC concentration for samples prepared at both mixing times. Even if a yield strength increase with particle size reduction was expected, there is no appreciable variation that could be assigned to domain changes. Taking into account that the particle size

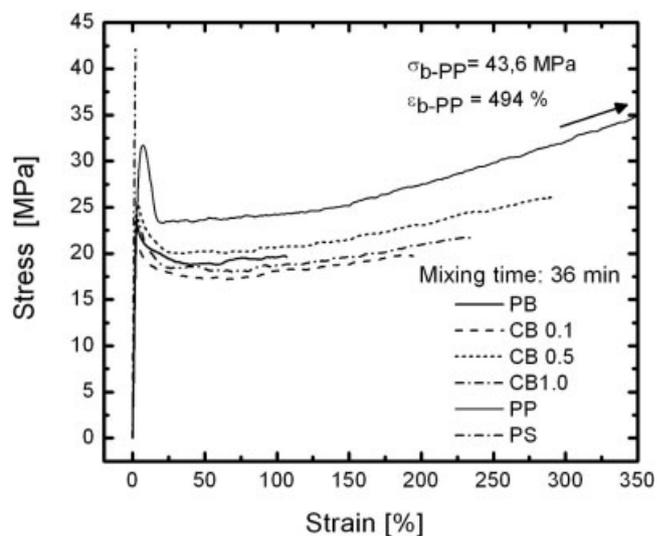


FIG. 5. Stress–strain behavior for homopolymers, PB and CB, mixed during 36 min

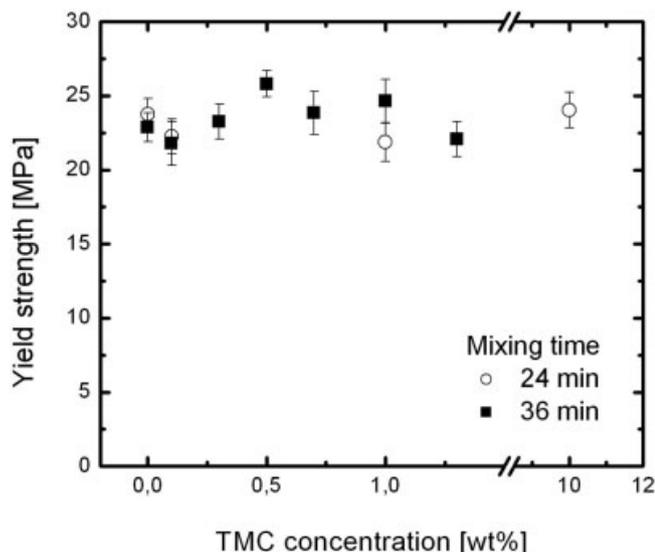


FIG. 6. Variation of yield strength with TMC concentration for blends prepared during 24 and 36 min.

range is extremely small (0.5–1.0 μm), it can be assumed that the largest particles are below some critical diameter needed to concentrate stresses and induce fracture [13]. A similar behavior was reported for PP/PS blends compatibilized by an aromatic vinyl monomer grafted PP [14]. The tensile modulus, measured for the homopolymer matrices and the PB and CB samples, are shown in Table 3. Both modules agree with the predicted range by the rule of mixtures, within the experimental error.

Figure 7 shows the variation of elongation to break as a function of TMC concentration for both mixing times. This property is sensitive to changes in interfacial adhesion. At the low mixing time, the elongation to break does not show

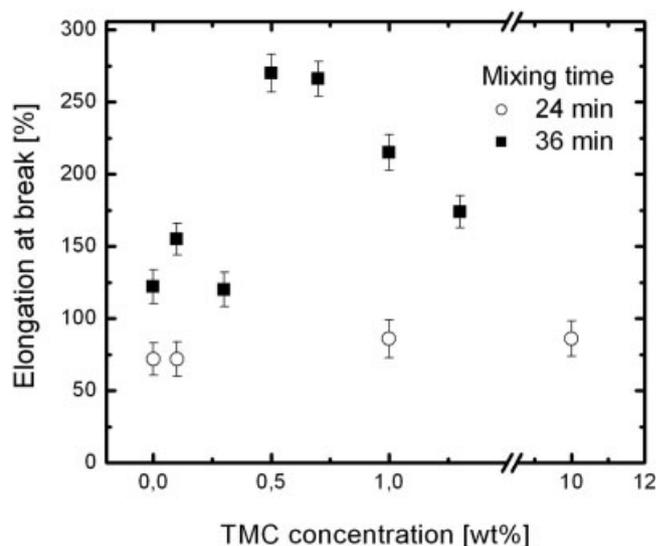


FIG. 7. Variation of elongation at break (under tensile test) with TMC concentration for blends prepared during 24 and 36 min.

major changes for small TMC additions. An increase of only 20% is observed when 1 wt% or more of TMC is added. This result suggests that the mixing process seems not to be effective to bring the necessary amount of compatibilizer to the interphase.

The blends mixed during 36 min revealed more significant results. The elongation to break increases with TMC concentration up to a maximum at 0.5–0.7 wt%, and then decays to a value higher than the initial one (PB). The maximum, which occurs at the same TMC concentration as CMC, is about three times higher than the initial value. Up to this point, the results are in agreement with the emulsifying effect and interfacial adhesion improvement observed (Fig. 3). The decaying behavior after the maximum may be due to the copolymer in excess within the homopolymer phases. It is well known that above CMC this copolymer forms micelles within the homopolymer phases [2, 11, 15, 16]. Such micelles might be detrimental to the elongation to break. Other authors for addition compatibilization of immiscible blends also reported this undesirable behavior. However, no detailed explanation was given [10 “Chapter 4”, 17, 18].

It is worth to be noted that the blend reaches the greatest ductility (300% larger than the PB) with a relatively low TMC concentration, as compared with the data reported in the literature. For example, Halimatudahliana et al. [19], working with PP(80)/PS(20) blends, adding 7.5 wt% of PS-*b*-PEBu-*b*-PS block copolymer, obtained a 180% increment in elongation to break.

CONCLUSIONS

The tailor-made copolymer, prepared via F-C reaction, exhibited a notable performance as addition compatibilizer for PP/PS blends. Improvements in blend morphological aspects as well as in mechanical properties were appreci-

TABLE 3. Elastic modulus (E) and standard deviation ($\sigma(E)$), for homopolymers, PB and CB, mixed during 24 and 36 min.

Sample	E (GPa)	$\sigma(E)$ (GPa)
Homopolymers		
PP	1.27	0.07
PS	2.07	0.24
Blends mixed 24 min		
PB	1.41	0.15
CB 01	1.27	0.09
CB 1.0	1.33	0.12
CB 10	1.35	0.11
Blends mixed 36 min		
PB	1.42	0.14
CB 01	1.43	0.13
CB 03	1.47	0.09
CB 05	1.49	0.10
CB 07	1.33	0.17
CB 1.0	1.41	0.13
CB 1.3	1.39	0.18
Theoretical value ^a	1.43	—

^a Calculated following rule of mixture [13].

ated. A 50% particle size reduction was achieved with low TMC concentration (0.7 wt%), indicating a considerable reduction of the interfacial tension. Also, the observed increase in transgranular fracture proportion is consistent with a better interfacial adhesion. In regard to mechanical properties, an increase of three times in ductility, as compared to the PB values, was achieved using very low TMC concentrations (0.5–0.7 wt%). No appreciable detriment in yield strength or modulus was observed in these CB. On the other side, the process effectiveness and mechanical properties showed to be sensitive to the excess of copolymer in the homopolymer phases. So, a process optimization, particularly the mixing time, is necessary to achieve the CMC condition without leading to the generation of copolymer in excess.

This compatibilization method combines a small amount of compatibilizer required, with low-cost reactants and ease processing. These features present the proposed alternative as potentially applicable to the recycling of mixed plastics from urban and industrial wastes.

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