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Effects of the blending sequence and interfacial agent on the morphology and mechanical properties of injection molded PC/PP Blends

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Summary

The effects of blending sequence and the addition of an interfacial agent (triblock copolymer styrene-butylene ethylene/styrene, Kraton G1652) on the morphology and the mechanical properties of Polycarbonate (PC)/Polypropylene (PP) blends prepared by injection molding were studied. This study presents an analysis of impact resistance, tensile properties and morphology of the raw materials and the blends at different compositions. The blends, before being injected, were prepared in a twin-screw extruder by different sequences of blending. The results indicate that the blending sequence and the presence of humidity significantly affect the properties and morphology of the blends. For ternary blends (PC/PP/Kraton), only one-step mixing before injection molding proved to be sufficient to improve mechanical properties. Increasing the amount of blending steps did not present a significant change in properties. With the addition of the interfacial agent, higher impact resistance and particle size reduction were observed.

Introduction

In the last years, the use of polymer blends is of great industrial importance due to economic reason and simple manipulation. Injection molding is one of the most important fabrication process used in to polymer blend preparation [1]. PC/PP blends have been used in very diverse applications, due to the characteristics of each polymer [2-8]. PC is transparent and hard with high thermal and dimensional stability, characteristics that make it a widely used engineering resin [8, 9]. On the other hand PP can be found in very diverse applications despite its low dimensional stability and its limited impact and thermoforming properties [6, 10]. In order to increase its applications, attempts have been made to enhance these properties by blending with other polymers [5-7].

Studies on the thermal, mechanical, and rheological properties of PC/PP blends are available [2-6, 9]. They showed that the final blend morphology is related to the rheological behavior, composition, viscosity ratio, and elasticity of the blend. A relation between particle size, composition, and viscosity ratio was reported [2, 3]. The PC/PP system is mainly characterized by an absence of interfacial adhesion [9], attributed to an elevated thermal expansion coefficient [4].

For immiscible polymer blends an interfacial modifier is added to improve the compatibility between both phases [10, 11]. This additive is very important to improve the interaction between both phases and to create better distribution of the dispersed phase [11-12]. In immiscible polymer systems, the morphology of the dispersed phase can be spherical particles or in fibrillar and laminar forms [2, 10]. In this study, a triblock of SEBS was used as copolymer, because it was shown [11-12] to be a good compatibilizer for PC/PP blends. Gupta and Srinivasan [11] have worked with this system using PP as a matrix phase and found that the pseudoplasticity of the blend is modified with the addition of SEBS and PC. The most significant contribution of SEBS towards the elasticity of the blend compared to that of PC in their respective binary blends is attributed to the higher deformability and interfacial interaction of SEBS. The addition of SEBS copolymer to PP/HIPS blends causes a reduction in the particle size of the dispersed phase and improves the impact resistance [10]. This effect can occur due to diffusion and the ability of the copolymer to remain within phases, promoting a reduction of interfacial energy and avoiding particle coalescence.

An important point to deal with is the blending sequence. Since blending is one of the main operations in polymer processing [13], good phase dispersion is crucial to obtain high quality products [14], i.e. the processing conditions have great influence on the microstructure of the blends and their mechanical properties [15]. In systems for which the interfacial modifier has a higher affinity for one of the components, these considerations become important. Cimmino et al. [16] studied the effect of mixing procedure on PA6-EPM blends stabilized with EPM functionalized with maleic anhydride (EPM-g-MA). They considered (a) one-step mixing, in which all the components are introduced into the mixer simultaneously, and (b) two-step mixing, in which the EPM and EPM-g-MA are premixed prior to mixing with PA6. They obtained a very fine morphology and excellent impact strength when the blends were prepared by two-step mixing. Willis et al. [17], working with PA-polyolefin blends, showed that an ionomer (Surlyn 9020, used as compatibilizer) has more affinity for the PA phase. The migration of modifier to the interface is facilitated when it is initially mixed with the component for which it has the least affinity. Ha et al. [18] studied the effect of the blending sequence in polyolefin ternary blends. They observed that the blend properties are controlled by the morphology, where the domain size is determined by the viscosity ratio of the premixed binary blend. Recently, Lin et al. [19] investigated the effect of mixing protocol on the morphology of compatibilizer polymer blends. They explained that the mixing protocol determines the initial interfacial distribution of compatibilizer and thus, influences the final morphology.

Melt blending continues to be one of most important methods to create new materials from commercial homopolymers. In this study, an analysis of the morphology and mechanical properties of PC/PP blends prepared by injection molding is presented and the effect of mixing protocol on the final properties is discussed.

Experimental

Materials

The materials used in this work were polycarbonate (PC) 1080 pellets with M.I.=80 g/10 min (at 300°C @ 1.20 kg) as continuous phase and polypropylene (PP) H700-12 (also pellets) as dispersed phase with M.I.=12 g/10 min (at 230°C @ 2.16 kg), both from Dow Plastics. The copolymer was KRATON G1652 (K) with M.I.=5 g/10 min (at 230°C @ 5 kg), manufactured by Shell Co. Initially the PC and some blends were used without previous drying in order to compare its performance to that of the materials previously dried. In the rest of this study all materials were dried at 80°C for three hours, in a MATSUI DMZ2-40 dryer, at a dew point of -40°C, before extrusion and injection molding.

Blending sequence

PC/PP blends were prepared at ratios of 90/10, 80/20 and 70/30 (wt/wt). To study the compatibilizing effect, the copolymer (Kraton) was added to blends with the same ratios in proportion of 5, 10 and 15 w% w.r.t. the dispersed phase (PP). The blends were prepared in a co-rotating twin-screw extruder Leistritz Micro 27 GL/GG-36D. Temperature settings along the barrel were: 190, 200, 210, 220, 225, 230, 235, 235, 235°C from feed hopper to exit at a screw speed of 100 rpm. The blend was extruded through a filamentary die (3 mm diameter circular holes) and subsequently pelletized in a Randcastle pelletizer/cutter Model RCP-2.0 with controlled material strain rate. Three types of blending were used in this study before injection: (I) without premixing, introducing PC, PP and Kraton (K) directly; (II) one-step mixing, all three components were mixed in the twin-screw extruder and (III) two-step mixing, PP and Kraton were premixed followed by subsequent mixing with PC.

The blends previously compounded by extrusion were subsequently processed in an all-electrical 80 ton injection molding machine (NISSEI ES-1000). The screw diameter is 36 mm with L/D of 18:1. The barrel temperature profile used was 235/250/265/265^{o}C with a mold temperature was 60^{o}C. The screw speed was 80 rpm, the maximum injecting pressure used was 65 MPa and the screw position (shot size) was 35 mm. The holding time was 3.5 s and the cooling time 20 s.

Mechanical analysis

Impact tests were carried out with a Gardner impactor according to ASTM D 5420. Tensile strength tests were performed on a universal testing machine (UNITED SFM 100), and operated in accordance with ASTM D 638 (samples type IV). The crosshead speed was 5 mm/min at room temperature and a minimum of five samples were measured for each material.

Morphological analysis

For the morphological study, small samples were taken after twin-screw extrusion and specimens from the injection molded samples were cut from the center of the piece. They were immersed in liquid nitrogen and then fractured parallel to the flow direction and the exposed surfaces were analyzed by scanning electronic microscopy (JEOL JSM 5400 LV). Image analysis was done with Image-Pro Plus 4.5 software.

Rheological analysis

The rheological characterization of the resins was performed using a twin-bore capillary rheometer Rosand, model Rh-2200, with a capillary die of 1 mm diameter and length to diameter (L/D) ratios of 16. The Bagley and Rabinowitsch corrections were applied automatically to the capillary rheometry data. A master curve of viscosity (Figure1) was prepared using a shift factor ($a_T = \eta_o(T)/\eta_o(T_{ref})$) as reported in Table 1. The experimental values were fitted to a Carreau viscosity model as:

$$\eta = \frac{\eta_o}{\left[1+(\lambda\dot{\gamma})^2\right]^{\left(\frac{1-n}{2}\right)}} \qquad \textbf{(1)}$$

The rheological parameters (η_o, λ, n, and a_T) are presented in Table 1.

Results and discussion

Figure 1 shows the viscosity master curve of $\eta(T)/a_T$ vs $\dot{\gamma}\, a_T$ for pure materials at a reference temperature of 265°C. Since both curves intersect, this offers the possibility of obtaining different morphologies due to changes in viscosity ratios (p). Everaet et al. [20] separated the effect of droplet break-up and coalescence for poly(propylene) in polystyrene/poly(2,6-dimethyl-1,4-phenylene ether) blends for a viscosity ratio range between 0.05 and 20. Their results showed a clear dependence of blend morphology on viscosity ratio: (a) highly viscous matrices (p<<1) enhance droplet break-up due to their efficient shear stress transfer toward the dispersed phase and (b) low viscous matrices (p>1) often act as a lubricant for the dispersed phase reducing droplet break-up. The influence of p on droplet break-up is reflected in the particle sizes.

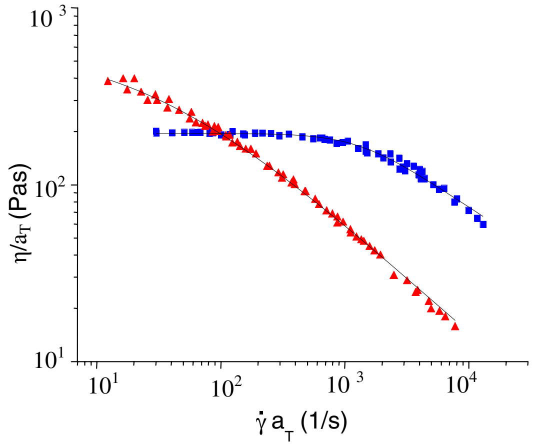

Figure 1. Master curve $\eta(T)/a_T$ vs $\dot{\gamma}\, a_T$ for: (■) polycarbonate; (▲) polypropylene. (-) Equation (1). The reference temperature used is 265°C.

Table 1. Numerical values of the Carreau parameters of Equation (1)**.**

Polymer, T(ºC)	η_o (Pa s)	λ (s)	n (-)	a_T (-)
PC, 235	795	0.0021	0.40	4.07
PC, 250	375	0.0018	0.58	1.92
PC, 265	195	0.0009	0.56	1.00
PP, 235	691	0.0789	0.49	1.73
PP, 250	573	0.0790	0.52	1.43
PP, 265	399	0.0517	0.52	1.00

Effect of humidity

The effect of the PC humidity on the mean fracturing energy (MFE) for different blends is presented in Figure 2. There is a substantial difference of MFE when drying is involved, because the presence of humidity in PC greatly reduces the MFE required to fracture the samples. This can be explained by the fact that PC is highly hygroscopic. Therefore, the absorbed humidity has a tendency to form bubbles during blending. Consequently, fracture points at the bubbles are more likely to appear in the samples. The same effect is observed for all blends. Aguirre et al. [21] observed a drastic decrease in tensile and impact properties when the PC was reprocessed after exposed to a certain relative humidity. The effect of humidity on the material is evident in Figure 3, where specimens for impact tests of dry and wet pure PC are presented. It is observed the formation of a large amount of bubbles that cause fracture points, which affect material resistance and generally diminish their properties (Figures 2 and 4).

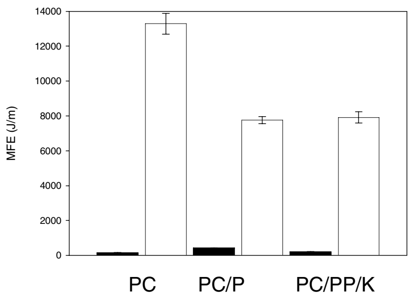

Figure 2. Impact resistance of polycarbonate blends: (■) undried, (□) dry. PC/PP (90/10), PC/PP/K (89/10/1).

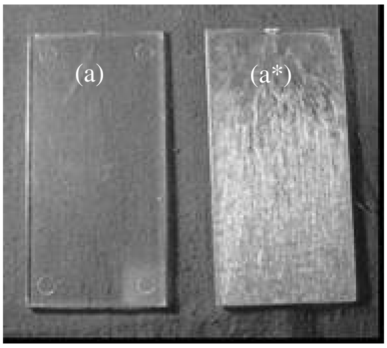

Figure 3. Photograph of impact test samples of pure PC: (a) dry, (a*) undried.

Influence of compatibilizer

The effect of humidity on the tensile tests for several PP compositions is presented in Figure 4. All the samples had higher values of elongation at break when drying was involved. There is a tendency for the materials with larges amount of PC to support

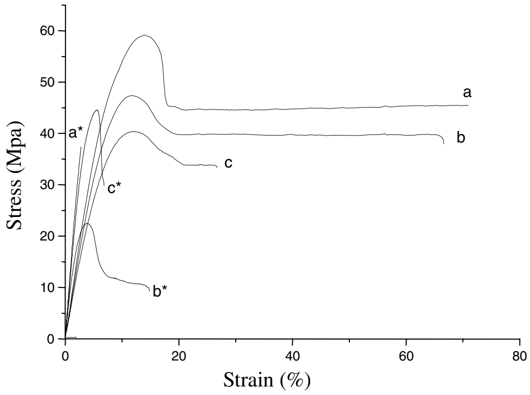

Figure 4. Tensile stress as a function of tensile strain for PC/PP blends: (a) PC, (b) PC/PP (90/10), (c) PC/PP (80/20), (*) undried.

greater elongations at break. This effect decreased with the dispersed phase (PP) content. For samples when the PP concentration increases, large PP particles (see Figure 5) facilitate the presence of failures.

The addition of the interfacial agent improved the interaction between both polymers. Consequently, during melt processing, stress transfer between the phases decreased the particle size of the dispersed phase. This kind of result has been reported for other systems [22-24]. Figure 5 displays a series of SEM micrographs of PP/PC mixtures

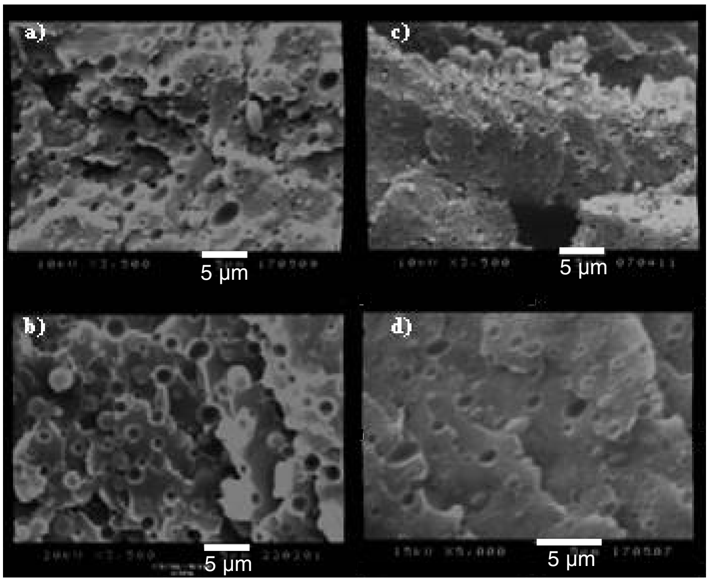

Figure 5. Scanning electron micrographs of samples fractured in liquid nitrogen: (a) PC/PP (90/10), (b) PC/PP (80/20), (c) PC/PP/K (89/10/1), (d) PC/PP/K (78/20/2).

without (Fig.5a and 5b) and with (Fig. 5c and 5d) compatibilizer. The micrographs were obtained after twin-screw extrusion and for two-step mixing. The average size of the dispersed phase for samples with different compatibilizer contents is reported in Table 2. In general, a reduction in the size of the dispersed phase is observed when the compatibilizer is used. The low values of particle size may also be associated to the viscosity ratio (p). From Figure 1 and for typical shear rate values in the extruder die (~100 s^{-1}), p values are of the order of one. For this condition, a minimum particle size is observed [20,22].

The effect of SEBS addition on the blends MFE at 10 and 20% of PP in PC is presented in Figure 6. Generally, blends at 10% PP sustain a larger load prior to reaching the fracture point than those at 20%. This is consistent with the fact that the MFE needed to fracture pure PC (13,300 J/m) is greater than the necessary energy for pure PP (9,300 J/m). Increasing the amount of PP in blends will decrease their MFE. The size of the minor phase in immiscible polymer blends has a significant effect on the properties such as the impact strength [10]. Figures 5 and Table 2, confirm that smaller particle sizes are obtained in the blends with 10% PP which also exhibit larger MFE than 20% PP blends.

Table 2. Particle size as a function of SEBS content for PC/PP blends.

Blend (% PP)	Compatibilizer (%) w.r.t. PP	Particle size (μm) ± SD
10	0	1.2 ± 0.3
	5	0.8 ± 0.2
	10	0.4 ± 0.1
	15	1.0 ± 0.2
20	0	1.3 ± 0.4
	5	0.8 ± 0.3
	10	0.6 ± 0.2
	15	0.5 ± 0.2
30	0	5.2 ± 1.2
	5	1.8 ± 0.4
	10	0.9 ± 0.3
	15	0.7 ± 0.2

Considering the addition of the copolymer (SEBS) as an interfacial agent, it is observed in Figure 6 that MFE increases with SEBS concentration for all PP compositions. This result is associated to the particle size (Table 2) reduction due to the presence of the copolymer. Srinivasan and Gupta [12] improved the tensile and flexural properties of PP/SEBS blends by blending with a rigid polymer (PC). They suggested that interactions with SEBS/PP are better than in PP/PC. The PC content in their case was varied from 0 to 30% while in our case PC content was varied from 70 to 100 %.

Figure 7 shows the influence on tensile strength of blends with SEBS content for 10 and 20% PP in PC. In general, increasing the amount of PP lowers the fracture strain, the elastic modulus and yield strength [25]. However, by increasing the amount of interfacial agent in the blend, a reduction in particle size is obtained. Thus, deformation

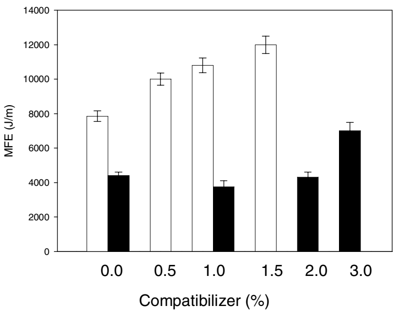

Figure 6. Impact resistance as a function of SEBS content: (□) PC/PP (90/10) and (■) PC/PP (80/20).

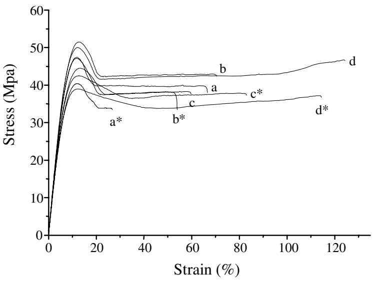

Figure 7. Stress-strain curves for PC/PP blends at several compatibilizer contents in PC/PP10: (a) 0% (b) 0.5%, (c) 1.0%, (d) 1.5% and in PC/PP20: (a*) 0 %, (b*) 1.0%, (c*) 2.0%, (d*) 3.0w%.

of the sample requires more stress because the strain at the fracture point increases as a result of better phase adhesion.

Influence of blending sequences

Figure 8 presents the impact resistance of injection molded PC/PP blends using 3 different blending sequences: (I) without premixing, (II) one-step mixing and (III) two-step mixing. For the binary blend of PC/PP the difference in MFE is notable when simultaneous blending is used compared to the MFE obtained for PC/PP samples without blending. MFE values are: for process I, 413 J/m and for process II, 7854 J/m. This indicates that the blend was efficient; a well-known phenomenon, attributed to

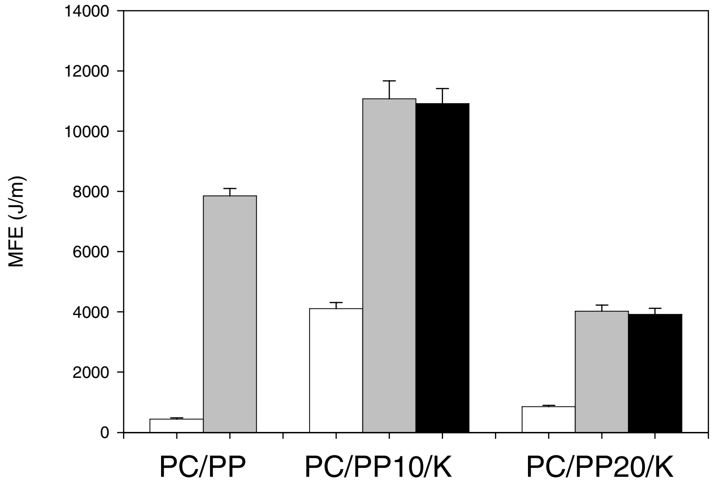

Figure 8. Impact resistance of injection molded PC/PP samples made by different blending sequences: (□) I, without premixing; (▨) II, one-step mixing and (■) III, two-step mixing. Composition PC/PP (90/10), PC/PP10/K (89/10/1) and PC/PP20/K (78/20/2).

the phase dispersion of the ingredients inside the extruder [16]. Pre-mixing provides a better dispersion of PP by reducing the particle size [3]. For ternary blends the tendency is maintained, according to the results presented in the Figure 8. Increasing the amount of blending steps (process III) does not represent a significant change in properties. Favis [3] reported that the strain and decomposition process is carried out in the first two minutes where blending dominates, and the effect of a longer processing time is minimal. Aguirre-Flores and Sánchez-Valdez [21] observed that the properties suddenly fall after being submitted to a third processing. The loss of properties may be caused by the degradation of the polymer due to exposure to high temperatures (325 °C) and elevated shear strain as in the case of injection molding. In our case for the two-step mixing we do not expect to have important degradation and more because the melt temperature using at the twin-screw extruder was 235°C. Additionally all materials were dried in order to minimize possible degradation.

Conclusions

The mechanical properties of injection molded PC/PP blends were modified by compatibilizer addition, sequence of blending and the presence of humidity. For ternary blends (PC/PP/Kraton), before being injection molded, only one-step mixing is sufficiently to improve the mechanical properties. Dispersion is guaranteed with a single premixing process and increasing the amount of blending steps does not present a significant change in properties. The morphological results indicate that the compatibilizer acts as an interfacial agent by reducing particle size. In general, impact resistance and tensile properties of PC/PP blends were improved by compatibilizer addition. The presences of humidity (particularly in PC) significantly affected the final properties of the materials.

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