

Blends of Polyamide 6, Polycarbonate, and Poly(propylene oxide). I. Reactive Compatibilization–Morphology Relationships

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ABSTRACT: The relationship between reactive compatibilization and morphology of the polyamide 6–polycarbonate (PA6–PC) and polyamide 6–polycarbonate–poly(propylene oxide) (PA6–PC–PPO) blends were investigated by means of torque values, scanning electron microscopy, and Fourier transform infrared spectroscopy. The micrographs show that the blends processed for a long period of time presented a PC domain of smaller size and better adherence between the phases than the blends processed for a short period of time. This fact can be related with the presence of the block copolymer of PA6–PC synthesized *in situ* by the reaction of PA6 and PC and depend on temperature and mixing time. The presence of PPO does not impede the formation of copolymer but interferes on the size of the domain. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 857–864, 1998

Key words: polyamide 6, polycarbonate, poly(propylene oxide), blends, melt mixing, chemical reaction, torque, scanning electron microscopy, Fourier transform infrared spectroscopy

INTRODUCTION

Heterogeneous blends containing polyamide 6 (PA6) have been verified by several researchers with special concern for the need to improve impact resistance.¹ The success of blend properties depends on the following three important factors: chemical reactions, physical interactions, and processing steps. Reactive blends may occur during the melt mixing processes² with polyamide 6 through hydrogen bonding.^{3,4}

The compatibilization of the polyamide 6 and polycarbonate (PC) occurs through PA6–PC block copolymer synthesized *in situ* during long melt mixing process.^{1–11} The internal carbonate groups of PC may react with the amino terminal

groups of PA6 during the melt mixing process at 240°C. The formation of PA6–PC copolymers suggested that these copolymers can act as compatibilizers, inducing the compatibility in the heterogeneous blends of PA6–PC.^{1,2,8}

Polymers containing ether groups show some miscibility with PA6.³ When the poly(propylene oxide) (PPO) interacts with the PA6, the compatibility of the PA6–PPO blends is improved due to hydrogen bonding between C=O and N–H groups of PC and PA6, respectively.¹¹

In this work, the PPO influence on the PA6–PC blends through the variation of composition blends and mixing time during the melt mixing process was verified.

EXPERIMENTAL

Materials

The following homopolymers used in this study were commercial: PA6 (NYLODUR, NT2700) of

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Table I Compositions and Mixing Time of the PA6-PPO, PA6-PC, and PA6-PC-PPO Blends at 240°C

Blends	Composition (%)	Time (min)
PA6	100	10
PC	100	10
PA6-PPO	95/5, 90/10	30
PA6-PC	90/10	10, 30, 60
PA6-PC-PPO	85/10/5	10, 30, 60
PA6-PC-PPO	80/10/10	10, 30, 60

relative viscosity (η_r) = 2.65–2.75 (H_2SO_4), NH_2 equal to 35–40 mEq/kg, and melt flow index (MFI) equal to 4.13 ± 0.12 g/10 min (235°C, 1 kg), supplied by De Millus S.A. (RJ, Brazil); PC (LEXAN 141,111) of numerical average molecular weight (M_n) approximately equal to 45,000, supplied by Coplen Ind. and Com. (General Electric Co., SP, Brazil) and PPO of M_n approximately equal to 1000, supplied by Dow Química S.A. (SP, Brazil). The homopolymers were dried during 72 h before the processing.

Preparation of the Blends

The blends were mixed in a Haake Rheomix 600 cam mixer at $T = 240^\circ C$, at a rotational speed of 30 rpm, for 10, 30, and 60 min., and were compression-molded under 5000 lbf at 240°C during 7 min. The samples were analyzed through torque-time curves, scanning electronic microscopy (SEM), and Fourier transform infrared (FTIR) absorption spectra. The processing conditions and compositions of the blends are illustrated in Table I.

Torque Versus Time

The blends were analyzed through the torque of each blend relationship with the mixing time and the composition. Figure 1 shows the torque-time curves of the blends mentioned previously.

Morphology

The morphology of the blends were observed by SEM (JEOL, JSM-5300) at a 10–30 Kv electron accelerating voltage and magnitude of 500–5000. The samples were fractured in liquid N_2 , and the fractured surfaces were sputtered with gold before viewing under SEM.

FTIR Spectra

The blends were analyzed through a FTIR spectrometer, Perkin-Elmer 1720-X, at a nominal resolution of 2.0 cm^{-1} , equipped with multiple internal reflection accessory (MIR) with a TGS detector (deuterated triglycerine sulfate). The samples were analyzed under thin film form. Each sample spectrum was obtained by averaging 100 scans, with a transmission range of 4000–400 cm^{-1} .

RESULTS AND DISCUSSION

Torque

The torque measurements give the information concerning the PA6-PPO, PA6-PC, and PA6-PC-PPO blends through the mixing time and composition of these blends. Figure 1 shows that the PA6-PPO (95/5 and 90/10) blends presented the minimum torque values, smaller than PA6. The PA6-PC (90/10) blend presented torque values like the PC. This blend showed an increase of torque values around 15 and 45 min. The PA6-PC-PPO (85/10/5) blend presented medium torque values of PC and PA6 blends until a mixing time of 30 min; above this time, the torque values of the PA6-PC-PPO (85/10/5) blend decrease. The PA6-PC-PPO (80/10/10) blend presented an increase of torque values around 15 min; after this time, the torque values decrease below the PA6-PC-PPO (85/10/5) blend.

The decrease of the torque values when the

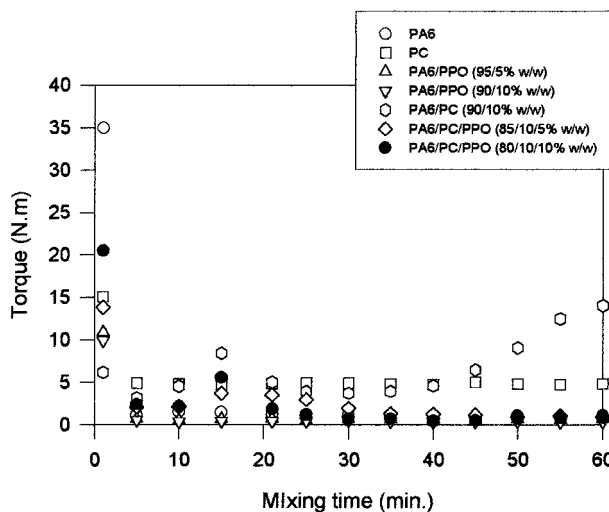


Figure 1 Torque as a function of the mixing time for pure PA6, PC, PA6-PPO, PA6-PC, and PA6-PC-PPO blends at $T = 240^\circ C$ for 60 min.

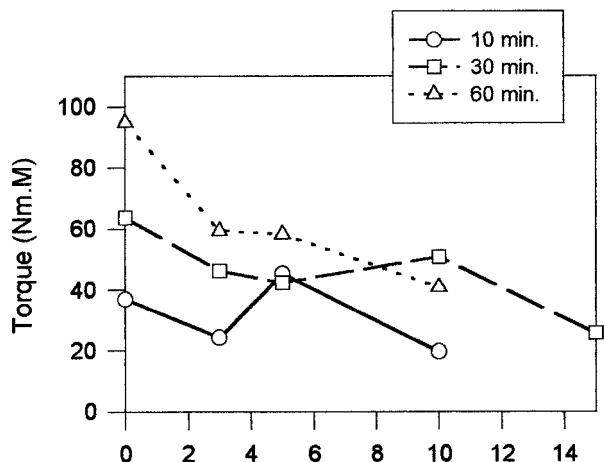


Figure 2 Torque values as a function of the percentage of PPO (% w/w) on the PA6-PPO blends.

PPO is present in the blends can mean plasticization of PA6 in the PA6-PPO and PA6-PC-PPO blends, while the increase of torque values in the PA6-PC can mean the occurrence of a chemical reaction between these homopolymers, forming a PA6-PC block copolymer.

Figures 2 through 4 show the relationship between torque, the percentage of PPO or PC (% w/w), and the mixing time on the blends. The composition of the blends and the mixing time have influence on the plasticization and the chemical reaction between PA6, PPO, and PC homopolymers. Figure 2 shows that the torque values decrease with 3% w/w of PPO in the PA6-PPO blends. The increase of the percentage of PPO to 10% w/w in the blends increase the torque values or remain constant. Above this composition, the

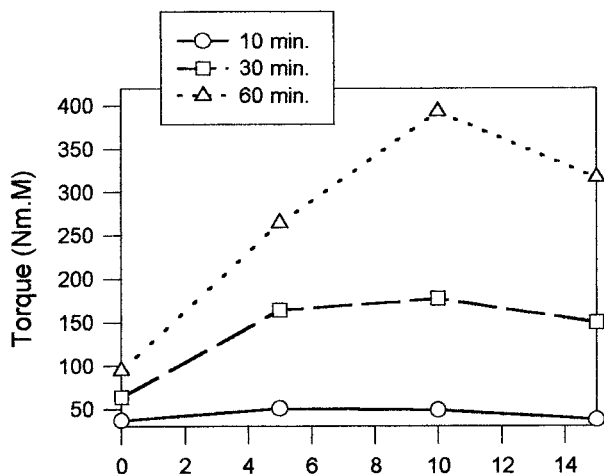


Figure 3 Torque values as a function of the percentage of PC (% w/w) on the PA6-PC blends.

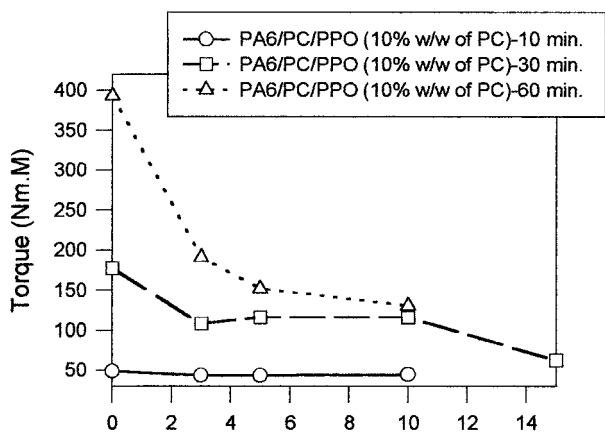


Figure 4 Torque values as a function of the percentage of PPO (% w/w) on the PA6-PC-PPO blends.

torque values decrease, depending on the mixing time. In Figures 3 and 4, it can be observed that the mixing time is very important to the chemical reaction between the PA6-PC. The composition is only important to these blends above 10% w/w of PC. The decrease of torque values (Fig. 4) indicates the possibility of occurring plasticization of the PA6 by PPO in the PA6-PC-PPO.

Morphology

The processing of immiscible polymers blends of PA6-PPO, PA6-PC, and PA6-PC-PPO at a short period of time may cause a growth in domain size. The compatibilizing action of the PA6-PC block copolymers formed by PA6-PC and PA6-PC-PPO blends processed for a long time was investigated by SEM analysis. Figures 5 through 7 present the scanning electron micrographs of PA6, PC (processed at 240°C for 10 min), PA6-PPO (processed at 240°C for 30 min), and PA6-PC and PA6-PC-PPO (processed at 240°C for 10, 30, and 60 min), respectively.

Figure 5 shows the micrographs of PA6 [Fig. 5(a)] and PC [Fig. 5(b)]. Through these micrographs, the continuous phases can be observed, meaning homogeneity of PA6 and PC systems. Figures 5(c) and (d) show the micrographs of the PA6-PPO (95/5 and 90/10) blends. These two systems present two well-defined phases (a continuous phase and a dispersed phase). The dispersed phase presents growth in domain size of PPO that may be caused by the morphology of insufficiently compatibilized PA6-PPO blends.

Figure 6 shows the PA6-PC blends processed at 240°C for 10, 30, and 60 min. In Figure 6(a), in the micrograph of PA6-PC blend (90/10 for

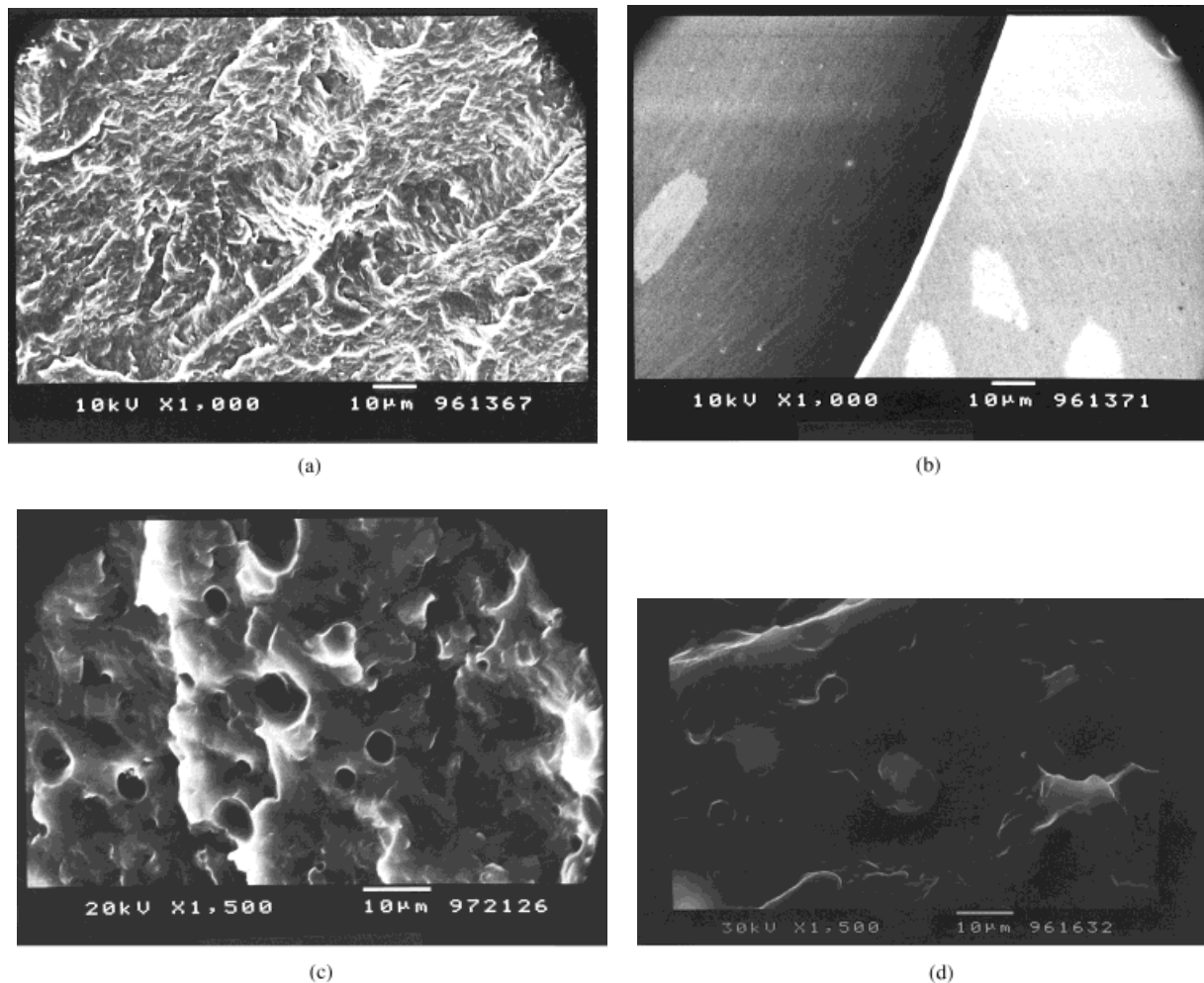


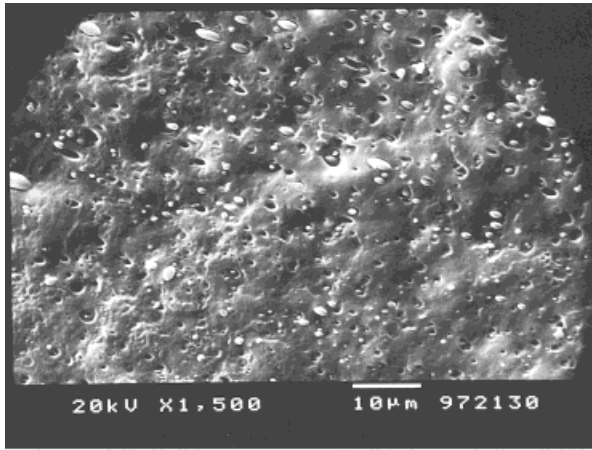
Figure 5 SEM micrographs of the fracture surface of (a) PA6 (100), (b) PC (100), (c) PA6-PPO (95/5), and (d) PA6-PPO (90/10) at $T = 240^{\circ}\text{C}$ for 10 and 30 min.

10 min), it can be observed that PA6 and PC phases are very distinguishable. However, Figure 6(b) shows the micrography of PA6-PC (90/10, for 30 min), and the partial interaction between both homopolymers can be observed; it does not present the separation of phases. This fact can be related to long melt mixing time. This time was sufficient to form the PA6-PC block copolymer, which will act as the compatibilizing of PA6-PC systems. Figure 6(c) shows the micrography of the PA6-PC blend (90/10 for 60 min). This micrography presents total compatibility between PA6 and PC and can also be attributed to the formation of the PA6-PC copolymer.

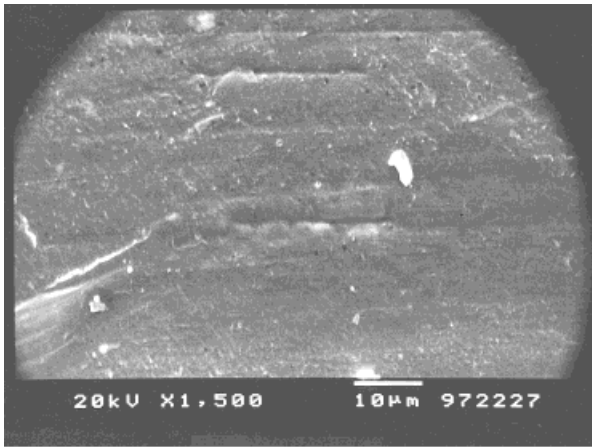
Figures 7 and 8 show the PA6-PC-PPO blends (85/10/5 and 80/10/10) processed at 240°C for 10, 30 and 60 min, respectively. Figure 7(a) presents the micrography of PA6-PC-PPO (85/10/5, at 240°C for 10 min), and the continuous and dispersed well-defined phases can be ob-

served. The presence of large domain size suggests incompatibility between the homopolymers of PA6, PC, and PPO. The PC and PPO represent the dispersed phases of the system. In Figure 7(b), the micrography of the PA6-PC-PPO (85/10/5, at 240°C for 30 min) shows that the melt mixing time is important in forming the PA6-PC copolymer, to improve the adhesion between these phases, and, consequently, to increase the compatibility of this system. Figure 7(c) presents the micrography of PA6-PC-PPO (85/10/5, at 240°C for 60 min). This figure is similar to the Figure 7(b), meaning that an increase in the melt mixing time causes a small improvement in the adhesion between the phases.

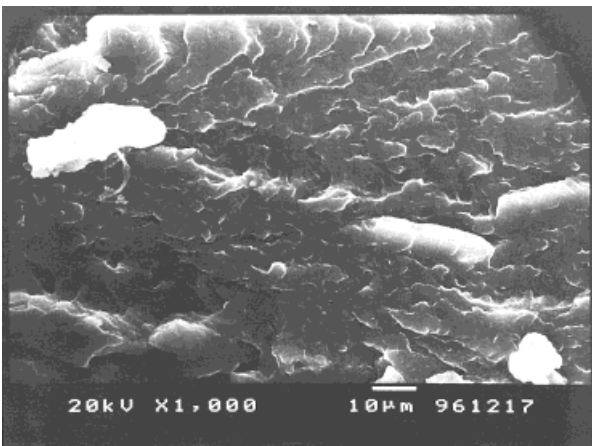
Figure 8(a) shows the micrography of the incompatibilized PA6-PC-PPO (80/10/10, at 240°C for 10 min) blend. In this figure, the presence of domain size can also be observed, suggesting incompatibility between the polymers



(a)



(b)

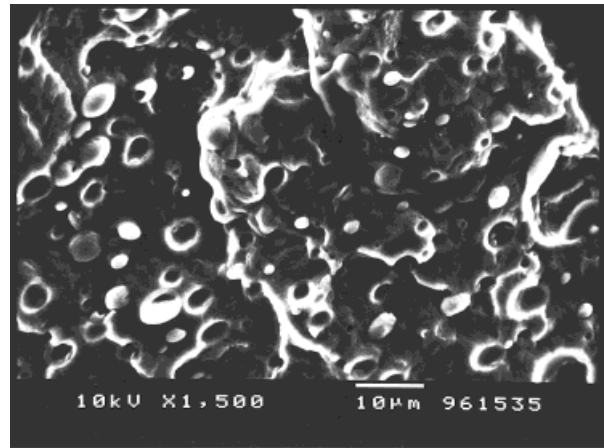


(c)

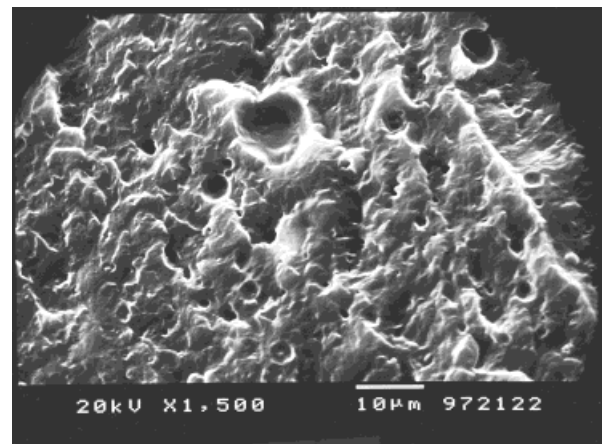
Figure 6 SEM micrographs of the fracture surface of the PA6-PC 90/10 blend for (a) 10 (b) 30, and (c) 60 min at $T = 240^{\circ}\text{C}$.

PA6, PC, and PPO. The presence of 10% w/w PPO in the PA6-PC blends modified the morphology of this system. In the micrographs of the PA6-

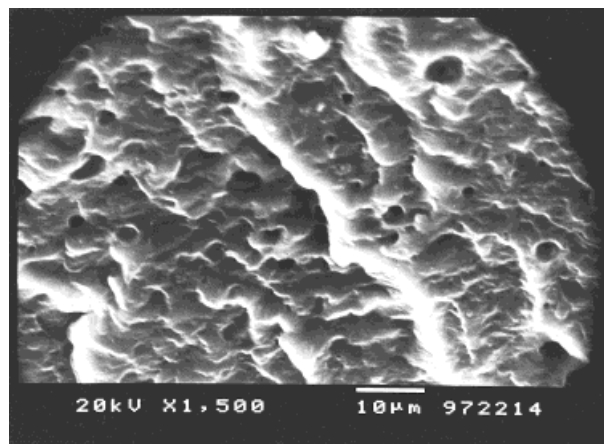
PC-PPO (80/10/10, at 240°C for 30 and 60 min) blends [Fig. 8(b) and (c)] can be observed that the melt mixing time also improves the adhesion



(a)

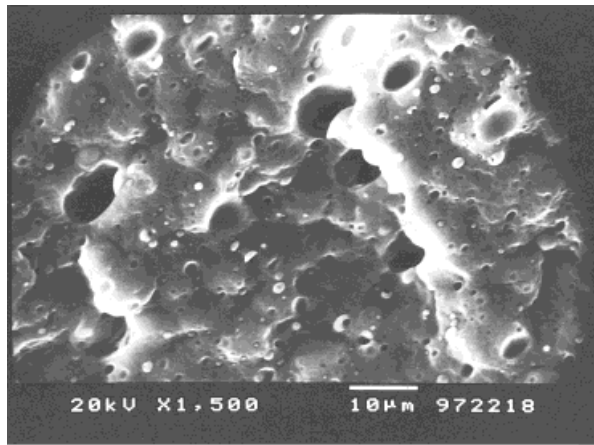


(b)

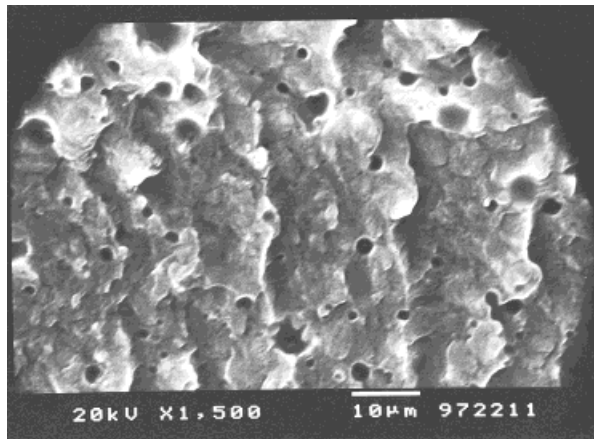


(c)

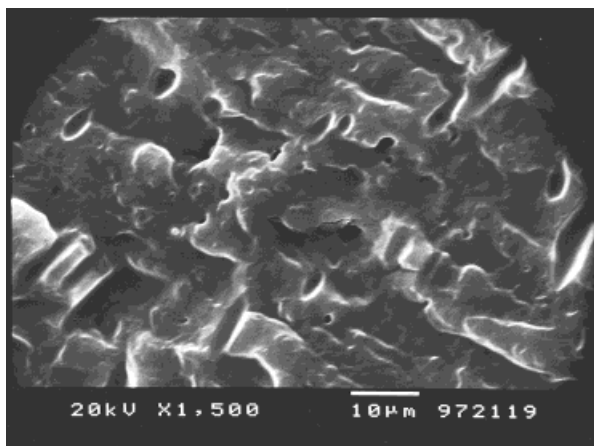
Figure 7 SEM micrographs of the fracture surface of the 85/10/5 PA6-PC-PPO blend for (a) 10, (b) 30, and (c) 60 min at $T = 240^{\circ}\text{C}$.



(a)



(b)



(c)

Figure 8 SEM micrographs of the fracture surface of the 80/10/10 PA6-PC-PPO blend for (a) 10, (b) 30, and (c) 60 min at $T = 240^{\circ}\text{C}$.

between the phases. These micrographs show that the PC and PPO domain sizes become smaller and more adherent to the PA6 matrix. Comparing the

systems PA6-PC-PPO (85/10/5) and PA6-PC-PPO (80/10/10), it can be verified that a small improvement in the morphology of the PA6-PC-PPO (80/10/10) system occurs. This fact can be attributed to the plasticization of the PA6-PC blend due to an increase of the quantity of PPO (10% w/w), improving and confirming the compatibilizing action of the PA6-PC block copolymer in the PA6-PC-PPO blends.

FTIR Spectra

The spectra of the PA6, PA6-PPO (95/5, 90/10), and PA6-PC (90/10) processed at 240°C for 10 and 30 min (Fig. 9) show the characteristic absorption bands of PA6 at 3230, 1640, and 1530 cm^{-1} attributed to the axial deformation of N-H and the C=O groups of amide I and II, respectively.

The presence of a short band at 1730 cm^{-1} can be attributed to absorption of free C=O group of PA6. It can be observed in the spectra of PA6-PPO blends (95/5 and 90/10, processed at 240°C for 30 min) [Fig. 9(b) and (c)] that a small increase of the band at 1730 cm^{-1} occurs. This fact

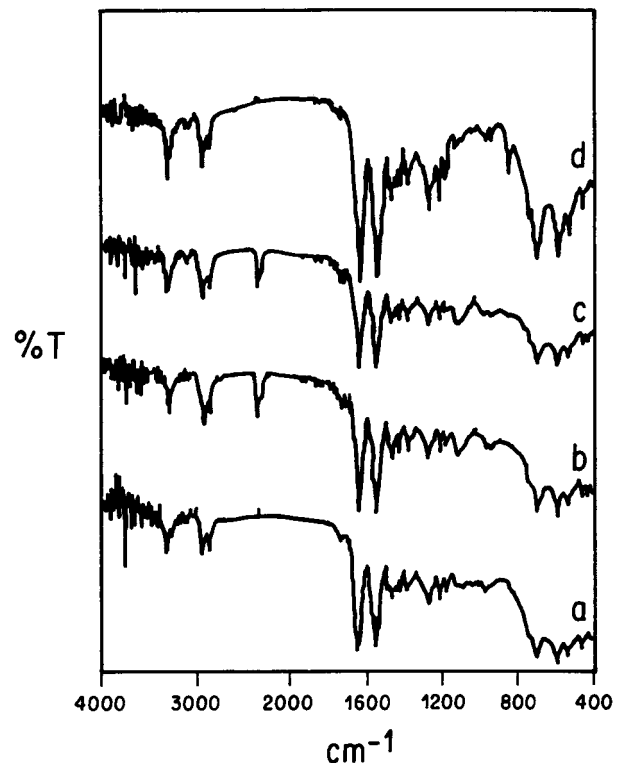


Figure 9 IR spectra of (a) PA6, 100 for 10 min, (b) PA6-PPO, 95/5 for 30 min, (c) PA6-PPO, 90/10 for 30 min, and (d) PA6-PC, 90/10 for 30 min at $T = 240^{\circ}\text{C}$.

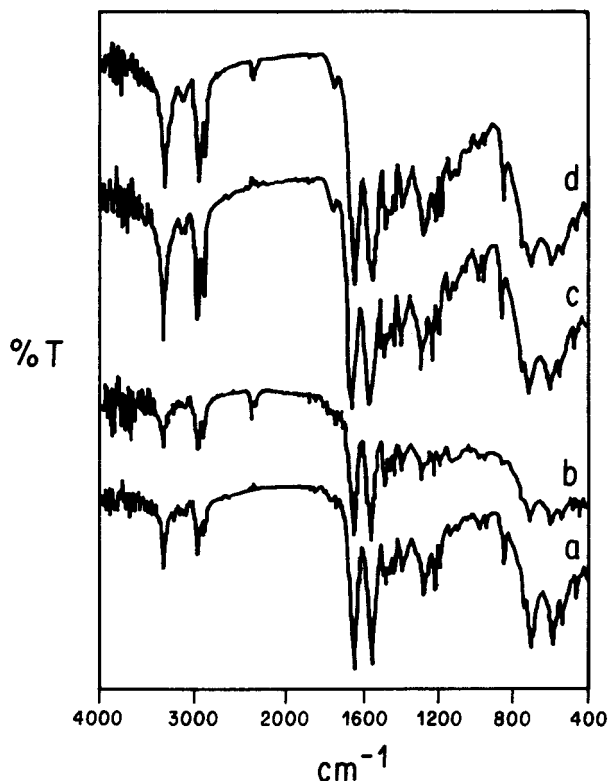


Figure 10 IR spectra of (a) 90/10 for 30 min, PA6-PC, (b) PA6-PC-PPO, 85/10/5 for 10 min (c) PA6-PC-PPO, 85/10/5 for 30 min, and (d) PA6-PC-PPO, 85/10/5 for 60 min at $T = 240^{\circ}\text{C}$.

can be attributed to the strong interaction between PA6 and PPO. The band at 1640 cm^{-1} can be attributed to hydrogen-bonded $\text{C}=\text{O}$. The increase of band at 1110 cm^{-1} can be attributed to the presence of PPO.

Figure 9(d) shows that the spectrum of PA6-PC (90/10, processed at 240°C for 30 min) presented a decrease of the 1730 cm^{-1} band and a small increase of the 1640 , 1240 , and 1450 cm^{-1} that can be due to the $\text{C}=\text{O}$ interaction and the presence of the $\text{O}-\text{CO}-\text{O}$ group. This fact can mean the formation of the PA6-PC copolymer.

Figures 10 and 11 show the spectra of PA6-PC-PPO (85/10/5 and 80/10/10, processed at 240°C for 10, 30 and 60 min). These systems also presented a small increase in the 1110 -, 1240 -, and 1450-cm^{-1} bands.

The band at 1730 cm^{-1} presented an increase in the PA6-PC-PPO (85/10/5) and PA6-PC-PPO (80/10/10) blends processed at 30 and 60 min. This fact can be attributed to the free $\text{C}=\text{O}$ group due to decrease of the formation of PA6-PC copolymer.

Comparing the 85/10/5 and 80/10/10, PA6-

PC-PPO systems, the 1110 , 1240 , and 1450 cm^{-1} bands are more intense in the PA6-PC-PPO (85/10/5) system due to the composition of this mixture with more quantity of PA6.

CONCLUSIONS

The composition and the melt mixing time modified the torque values in the PA6-PPO, PA6-PC, and PA6-PC-PPO blends. The small modification in the torque values to the mixtures processed at periods of time of 10 and 30 min in the presence of PPO can mean that the PPO do not sufficiently plasticize the PA6-PPO and PA6-PC-PPO blends. In the mixture processed at 60 min, the improvement in the plasticization of these systems was observed. The increase in the torque values to the PA6-PC blends (until 10% PC w/w) processed at long mixing times (30 and 60 min) indicate that this is the best composition at which a chemical reaction between these homopolymers can occur. The formation of the PA6-PC block copolymer and the plasticizing of the PA6 contribute to improving the compatibility of these systems. These facts were verified through the micrographs and FTIR spectra.

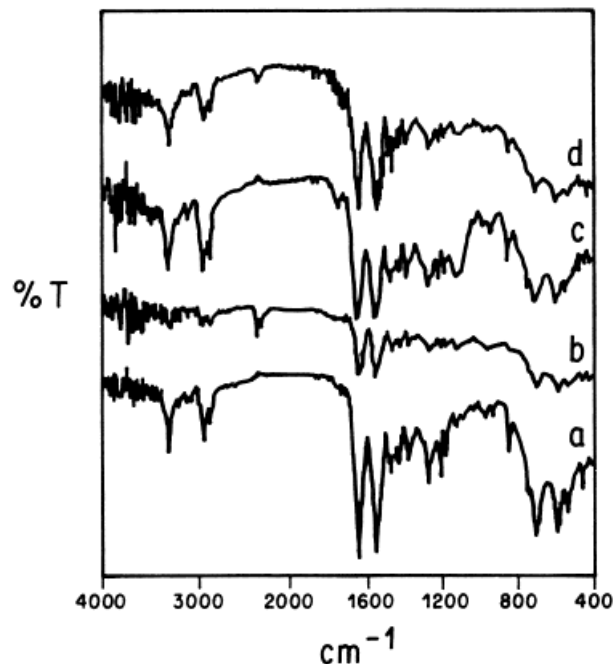


Figure 11 IR spectra of (a) PA6-PC, 90/10 for 30 min, (b) PA6-PC-PPO, 80/10/10 for 10 min, (c) PA6-PC-PPO, 80/10/10 for 30 min, and (d) PA6-PC-PPO, 80/10/10 for 60 min at $T = 240^{\circ}\text{C}$.

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