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Amorphous miscible PET/PC copolymers were prepared by blending the two constituent blend homopolymers at 50/50 wt% proportion in presence of cobalt acetylacetonate II and III (0.05 and 0.1 wt%) in the molten state. The reaction products were evaluated by solubility in methylene chloride (CH₂Cl₂), differential scanning calorimetry (DSC), thermogravimetry (TGA), and Fourier transform infrared spectroscopy (FT-IR). Two fractions were obtained by extracting the blend with CH₂Cl₂: one soluble, rich in PC, and another one insoluble, rich in PET. The DSC showed a unique glass transition temperature (T_g) (around 100°C) and the absence of melting temperature peak of PET, indicating that an amorphous copolymer was obtained. The T_g value coincides with Fox and Couchman's calculations and indicates the formation of a miscible system. TGA curves of the blends showed thermal degradation between that of the homopolymers. FT-IR showed a decrease of PC carbonyl band at 1773 cm⁻¹, a broadening of PET ester carbonyl band at 1720 cm⁻¹, a decrease of PET degree of order and a new band at 1063 cm⁻¹ attributed to the formation of aromatic-aromatic ester structure in the copolymer. The composition of CH₂Cl₂ insoluble and soluble phases were determined by FT-IR from calculation using the molar absorptivity of PC p-disubstituted ring band (558 cm⁻¹) and Lambert-Beer's law. The results

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indicated that exchange reactions took place, predominantly alcoholysis and acidolysis, and were to some extent dependent on the type and amount of cobalt complexes.

Keywords: cobalt catalysts, PET/PC blends, random copolymer, reactive blending, transesterification

INTRODUCTION

Since the middle of the 1970s, molten state polymer blending has been the simplest method to obtain new materials due to costs reduction and the fact of being the fastest way to generate materials with improving properties. For instance, blends of plastics and elastomers (PVC/NBR, PS/BR, PP/EPDM, PA/EPDM, etc.) are more and more recognized as a way of improving the impact strength of plastics. Nevertheless, few of them are miscible and most of them form multiple phase systems. The general characteristics, and in particular mechanical, thermal, and rheological properties depend on the mutual interaction of matrix and dispersed domains, and usually a compatibilizing agent is used in order to make better the final properties [1–2]. An alternative technology to improve blend compatibility is the reactive blending of polymers containing chemical groups capable to react to form new chemical structures. This methodology complements the polymerization process, having some advantages such as flexibility, versatility, low costs, and low environmental impact. Low molecular mass molecules and polymers containing ester groups can react with each other or with other ones containing hydroxyl and carboxyl acid groups leading to new products by transesterification/exchange reactions [3–5]. Poly(ethylene terephthalate) (PET) and polycarbonate (PC) are important engineering plastics, largely studied and mainly employed as bottles for carbonated beverages and compact discs (CDs) or digital video discs (DVDs), respectively [6–13]. Particularly, PC has exceptional impact, thermal, and mechanical properties but poor resistance to the attack of solvents and chemicals. Their blends intend to obtain the chemical resistance of PET without losing the good impact strength of PC. The reactive blending of PET and PC in the molten state, either catalyzed or not, involves transesterification and degradation reactions among acid and hydroxyl chain end groups beyond ester and carbonate groups in the homopolymers main chain. The extent of exchange reactions depends on the temperature, type, and amount of catalyst, way and time of processing, and composition, which may result in partially miscible mixture but also block or random copolymers. In spite of the significant amount of papers on

this subject, some controversy remains. Porter et al. [14] have studied the compatibility and transesterification for blends of PET/PC by melting mixing in the range of 260–300°C, without any external catalyst. The authors concluded that the system presented limited miscibility for all conditions of temperature and composition used. For Hanrahan et al. [15], the blend of PET/PC forms an almost completely immiscible system and PC exerts a significant influence on PET's melting behavior and heat of fusion. The microstructure of PET/PC blends in a wide range of compositions was also investigated [16]. The authors inferred that PET and PC were immiscible over the whole composition for both extruder-mixed and solvent-cast blends. Pilati et al. [17] have studied PET/PC blends and concluded that PET and PC are miscible due to the presence of residual catalysts in PET. These catalysts induced exchange reactions leading to copolymers that act as compatibilizing agents between phases. Barlow et al. [18–19] have found only one glass transition temperature (T_g) in compounds containing 60–70 wt% of PET whereas below this range, two values of T_g were observed. They concluded that PET rich blends are miscible and, on the contrary, PC rich ones separated into two distinct amorphous phases. The extent of transesterification reaction influences the mixture homogeneity. Divergent conclusions on the miscibility of PET/PC blends arise mainly from blending conditions [20–22].

The present work shows the action of cobalt complexes, never cited previously, to produce a miscible PET/PC system. In all cases, a miscible and amorphous copolymer was achieved.

EXPERIMENTAL

Material

Commercial PET and PC, respectively, supplied by BRASKEM and GE Plastics South America were used. Physical characteristics of both polymers given by the suppliers are listed in Table 1. The commercial

TABLE 1 Technical Characteristics of PET and PC

Property	PET (BG1180-W)	PC [Lexan 15X(R)]
Intrinsic viscosity (ASTM D 4603) (dl·g ⁻¹)	0.80 ± 0.02	—
Melt flow index (ASTM D 1238) (300°C/1.2 kg) (g/10 min)	—	2.5
Water absorption (ASTM D 570) (24 h/23°C) (%)	—	0.35
Density (ASTM D 792) (g·cm ⁻³)	1.39	1.2
Melting point (°C)	247 ± 3	—

cobalt acetylacetonate II and III were pink and green powders, respectively. Both were produced by J.T. Baker Chemical Co. and used as received.

X-Ray Fluorescence

After burning PET, the inorganic residue was characterized by X-ray fluorescence using a Rigaku equipment model RIX 3100. The ash was pressed in order to form a disk and was used to scan light and heavy elements.

Blending

PET/PC (50/50 wt%) blends were prepared in an Haake Reomix 600 internal mixer at 270°C, 60 rpm, for 10 min using 0.05 and 0.1 wt% of each complex. Before blending, the polymers were vacuum dried in an oven for 6 h, at 100°C. After blending, the material was ground to facilitate its handling.

Solubility

The sample was extracted with methylene chloride (CH_2Cl_2) for 24 h according to ASTM D 297 in order to verify the presence of one or two fractions [23]. The solvent was evaporated and the content of each fraction was determined.

Thermal Analysis

The calorimetric analysis was performed using a Perkin-Elmer differential scanning calorimeter (DSC-7). First, each sample was heated under nitrogen atmosphere from 40°C to 300°C at the maximum equipment heating rate (170°C/min) and kept for 2 min to destroy the thermal history. Subsequently, it was fast cooled to 30°C at 50°C/min. A second heating procedure was then carried out until 300°C at 10°C/min. Finally, the sample was cooled at 10°C/min. The melting temperature (T_m) was measured as the maximum of the endothermic melting peak from the second heating. Crystallization temperatures on heating and on cooling, T_{ch} and T_{cc} , respectively, were determined from exothermic peaks of heating and cooling runs at 10°C/min. T_g and ΔC_p were taken from the second heating cycle. The T_g value was also estimated using Fox and Couchman's equations [24a,b] in order to predict the miscibility. The PET crystalline fraction (X_c) was calculated from the ratio of PET endothermic peak area (ΔH_m) taking into account the enthalpy of fusion of 100% crystalline PET ($136 \text{ J}\cdot\text{g}^{-1}$) [25].

The thermal stability of the sample was studied in a Perkin Elmer TGA-7 instrument at 30–700°C, 20°C·min⁻¹ under nitrogen atmosphere. The starting/ending degradation temperatures and the curves profile were evaluated.

Film Preparation

In order to determine the composition of insoluble and soluble fractions of each blend, films from insoluble fractions were prepared in a Carver press. First, the material was kept for 1 min at 275°C for softening and then a pressure of approximately 2.7 MPa was applied during 1 min to form the film. Finally, the pressure was released, the mold removed, and the material cooled to room temperature, spontaneously. The film thickness was around 25 microns in average and was used for FT-IR analysis. Preparation of compression mold films from soluble fractions was unsuccessful because they were too fragile.

FT-IR Measurement

Qualitative and quantitative Fourier transform infrared spectroscopy (FT-IR) was performed. First, a qualitative observation of FT-IR spectra of the whole blend samples was carried out. In a second study, the degree of insertion of the PC units in PET and PET units in PC was quantitatively evaluated for the insoluble fraction of each system.

FT-IR Qualitative Analysis

The qualitative FT-IR analysis of each whole blend sample was performed in a Perkin Elmer spectrometer model 1720 × aiming to observe possible changes in the blend spectra. Each sample was completely dissolved in 1,1,1,2-tetrachloro-ethane (5 wt%/v) and the solution was cast in a KBr cell in order to obtain a film. The FT-IR spectrum was obtained using 40 scans and 2 cm⁻¹ resolution. The regions of carbonyl symmetric and asymmetric stretching were evaluated in order to observe shifting and broadening of peaks and new bands. The degree of transesterification and loss of PET crystallinity was also measured, using two characteristic band ratios: 1063 cm⁻¹/1580 cm⁻¹ and 1340 cm⁻¹/1580 cm⁻¹, respectively. For this calculation, the film thickness is not necessary because the relationship between bands was calculated in the same blend film and the effect of thickness must be neglected.

FT-IR Quantitative Analysis

In this study, the degree of insertion of PC units in PET and PET units in PC was evaluated quantitatively for each investigated system. All spectra were obtained using 40 scans and 2 cm^{-1} resolution. First, the molar absorptivity (ϵ) was determined for the characteristic PC *p*-disubstituted ring band at 558 cm^{-1} from the spectrum of pure PC films with different thicknesses. Based on Lambert-Beer's law, ϵ of that band was calculated after plotting absorbance versus film thickness. From the spectra of compression-molded films of the insoluble fractions, the absorbance was measured using the maximum of that band, and film thickness was also measured. Finally, by using band absorbance, film thickness, and molar absorptivity, the Lambert-Beer's law was applied and the PC content in the insoluble fraction was calculated. The PET content in this insoluble fraction was then determined from the difference from 100%. PET and PC contents in the soluble fraction were deducted from the percentage obtained in the insoluble fraction. The results were an average of three replicates.

RESULTS AND DISCUSSION

X-Ray Fluorescence

X-ray fluorescence was used initially to investigate residual metals capable of affecting transreactions, in addition to the employed catalysts. Antimony and cobalt were found as oxides, indicating that the PET used in this work contained antimony oxide (0.17 wt%) and cobalt acetate (0.03 wt%) as residual catalysts. This work considered the non-catalyzed blend as the one containing only the remaining catalysts (without acetylacetonate catalysts).

Solubility

Table 2 presents data on the content of the soluble fractions obtained from CH_2Cl_2 extraction. The table shows that PC was completely soluble whereas PET was practically insoluble in CH_2Cl_2 . After extraction, the non-catalyzed blend leaved about 50% of insoluble PET, indicating that PC can be completely removed from the blend by this treatment. Nevertheless, for the catalyzed samples, it was observed that the amount of PC extracted was lower and very close to the others, but for Co III (0.1 wt%). The difference in the solubility was attributed to exchange reactions catalyzed by the cobalt complexes.

TABLE 2 CH₂Cl₂ Soluble Fraction of PET/PC (50/50) Blends

Sample	Catalyst		CH ₂ Cl ₂ soluble fraction (%)
	Type	Concentration (wt%)	
PET	—	—	0.3
PC	—	—	100
PET/PC (50/50)	— ^a	—	50.2
	Co(Acac) ₂	0.05	30.5
	Co(Acac) ₂	0.10	31.5
	Co(Acac) ₃	0.05	38.0
	Co(Acac) ₃	0.10	54.0

^aResidual catalysts containing a mixture of antimony oxide and cobalt acetate.

DSC Analysis

Figure 1 presents the thermal curves and Table 3 summarizes the thermal parameters of the materials. The PET curve showed glass transition, crystallization on heating, and melting peak. The sample presented a relatively low degree of crystallinity, X_c . The curve of PC showed only the glass transition. For the non-catalyzed blend, the DSC curve was similar to PET; however, the T_{ch} appeared at lower temperature. In this case the degree of crystallinity was similar to PET alone and the T_g of PC was overlaid to T_{ch} peak of PET. With

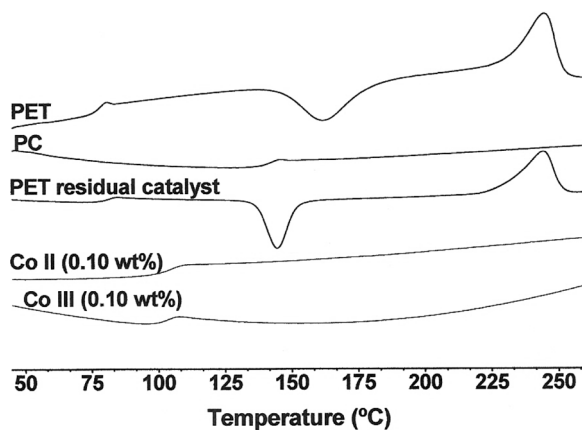


FIGURE 1 DSC traces for PET, PC, and PET/PC blends containing 0.1 wt% of Co II and Co III complexes.

TABLE 3 DSC Parameters for PET, PC, and PET/PC Blends

Sample	T_g (°C)	ΔC_p (J·g ⁻¹ ·°C ⁻¹)	T_{ch} (°C)	T_m (°C)	ΔH (J·g ⁻¹)	X_c (%)
PET	79	0.285	162	245	34.556	25.4
PC	143	0.242	—	—	—	—
PET/PC (50/50)	— ^a	0.092	141	244	18.227	26.8
Co III 0.10 wt%	102	0.265	—	—	—	—
Co III 0.05 wt%	101	0.230	—	—	—	—
Co II 0.10 wt%	103	0.274	—	—	—	—
Co II 0.05 wt%	101	0.268	—	—	—	—
Fox	99 ^b	—	—	—	—	—
Couchman	101 ^c	—	—	—	—	—

^aResidual catalysts containing a mixture of antimony oxide and cobalt acetate.

^bCalculated from Fox's equation.

^cCalculated from Couchman's equation.

respect to catalyzed blends, all curves showed only one T_g around 100°C and absence of crystallization and melting peaks, revealing that an amorphous and miscible material was developed. The T_g calculated by Fox and Couchman equations confirmed that statement.

TGA Analysis

TGA curves of homopolymers and blends are shown in Figure 2. The thermal degradation of PET and PC occurred as a single decay. PC exhibited higher thermal resistance than PET as evidenced by the higher values of starting and final degradation temperatures. The polymers left around 25 and 10% of a carbonaceous ash, respectively. With respect to the non-catalyzed blend, the degradation curve was similar to those of homopolymers, but occurred between them. It also showed a single decay but the degradation started at a temperature similar to PET and finished at PC final degradation temperature. The thermal curve of the blend with Co III (0.1 wt%) was chosen as representative for all blends obtained with Co catalysts. The degradation occurred in two decays. The second one is larger than the first one and occurred between both homopolymers curves. The blend degradation started at a lower temperature and finished at a similar temperature to PC. A carbonaceous residue also remained. Table 4 presents the TGA data.

FT-IR Measurement

Two studies involved FT-IR analyses. In the first one, the main modifications in the spectra of the samples were investigated

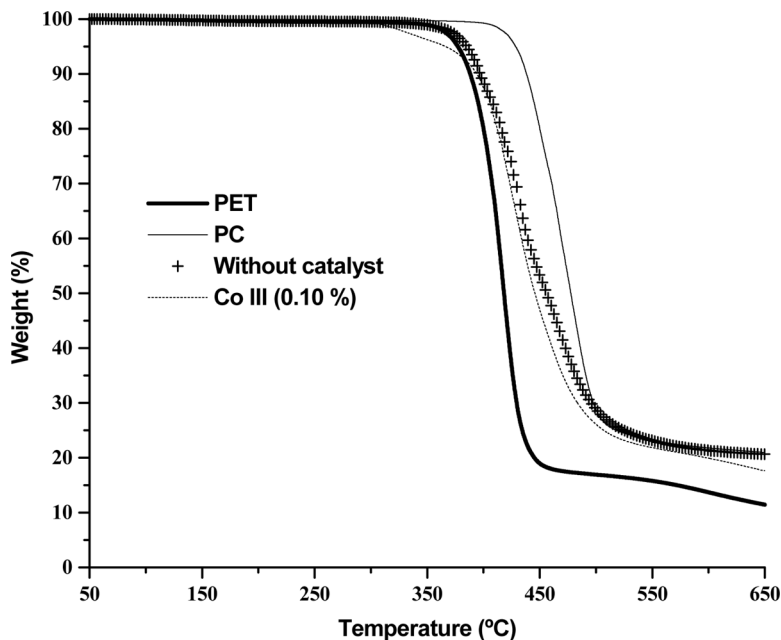


FIGURE 2 TGA curves of PET, PC, and PET/PC blends.

(qualitatively). In the second one, the quantitative determination of the PET and PC content in both insoluble and soluble blend fractions was performed [26–28].

FT-IR Qualitative Analysis

Three spectrum regions were evaluated: symmetric carbonyl stretching (C=O) at $1800\text{--}1700\text{ cm}^{-1}$, asymmetric carbonyl stretching

TABLE 4 TGA Parameters for PET, PC, and PET/PC Blends

Sample	Degradation temperature (°C)		Residue (%)
	Start	End	
PC	430	498	25
PET	394	432	10
PET/PC (50/50)	— ^a	471	25
Co III 0.10 wt%	305	470	15

^aResidual catalysts containing a mixture of antimony oxide and cobalt acetate.

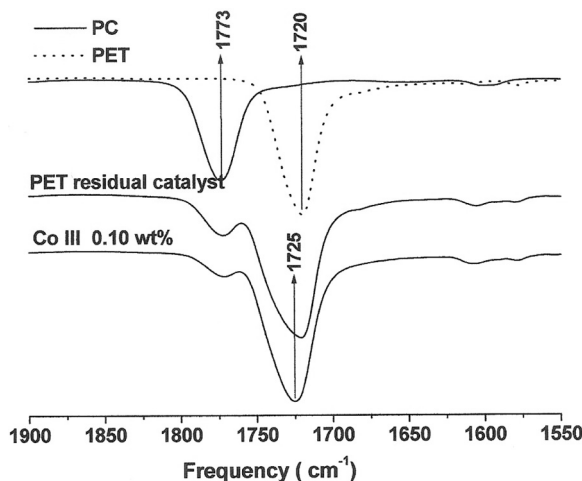


FIGURE 3 Infrared spectra of samples (1900–1550 cm^{-1}).

(C–C(=O)–O) and alcohol carbon-oxygen linkage stretching (O–C–C), both at 1300–1000 cm^{-1} .

As the spectra of the blends were similar, the spectrum of the blend with Co III (0.1 wt%) was selected and presented with the homopolymers and non-catalyzed sample in Figure 3. The maximum of the PC carbonyl band occurred at 1773 cm^{-1} and PET ester carbonyl appeared at 1720 cm^{-1} . In both blends, a decrease in the area of PC carbonyl peak as well as the broadening and shifting of PET carbonyl peak toward higher frequencies (1725 cm^{-1}) were noticed. The features shown by the catalyzed sample suggest the formation of a new structure.

Spectra of homopolymers, non-catalyzed blend, and blend with Co III (0.1 wt%) are shown in Figure 4. The asymmetric carbonyl stretching of PET appeared as two bands at 1263 cm^{-1} and 1245 cm^{-1} whereas PC showed the peak with maximum at 1230 cm^{-1} . Alcohol C–O stretching occurred at 1125 cm^{-1} for PET and at 1080 cm^{-1} for PC. In the case of the non-catalyzed blend, the mentioned infrared bands of PET were maintained, but for PC both a displacement of the band from 1230 to 1223 cm^{-1} and a decrease in intensity of the band at 1080 cm^{-1} were observed. In addition, the rise of a new band at 1063 cm^{-1} was noticed. With respect to the catalyzed blend, the bands related to asymmetric stretching of PET became sharper whereas the same band in PC appeared at 1223 cm^{-1} . Some changes in the absorption of alcohol C–O stretching

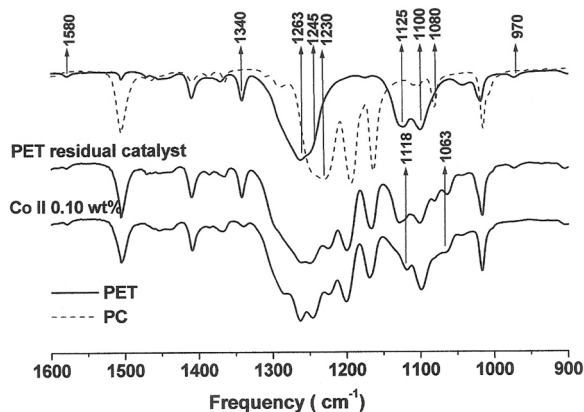


FIGURE 4 Infrared spectra of samples ($1600\text{--}900\text{ cm}^{-1}$).

bands were noted: the intensity of the band at 1125 cm^{-1} decreased and its peak maximum was shifted to a slightly lower frequency (1118 cm^{-1}) for PET due to the effect of cobalt complex, whereas the 1080 cm^{-1} band was overlaid for PC. As previously mentioned, a new band at 1063 cm^{-1} was detected. The absorption at 1100 cm^{-1} (C–H ring vibration) became sharper whereas the bands attributed to PET degree of order (1340 and 970 cm^{-1}) practically disappeared due to the action of the cobalt complex.

With the purpose of determining the degree of transesterification and loss of PET degree of order, an invariable band of PET at 1580 cm^{-1} (CH of aromatic ring) was selected. The ratios of bands at 1063 and 1580 cm^{-1} (degree of transesterification) and 1340 and 1580 cm^{-1} (loss of PET degree of order) were calculated for each blend film. These results are shown in Table 5. In fact, the degree of transesterification was practically constant and seemed to be independent of type/amount of catalyst. PET crystallinity was not affected by residual catalyst, but it decreased drastically (around 85%) in the blends containing cobalt complex, reaching to low values. Also, the loss of PET degree of order was independent of type/amount of cobalt complex.

The exchange reactions between PET and PC occurring during processing could be discussed according to the following reactions Schemes 1 and 2.

In Scheme 1, the attack of hydroxyl end groups of PET on carbonate linkage took place, activated by the residual catalyst in PET. The reaction products were PC of low molecular weight (structure III) and

TABLE 5 Degree of Transesterification and PET Degree of Order of Samples

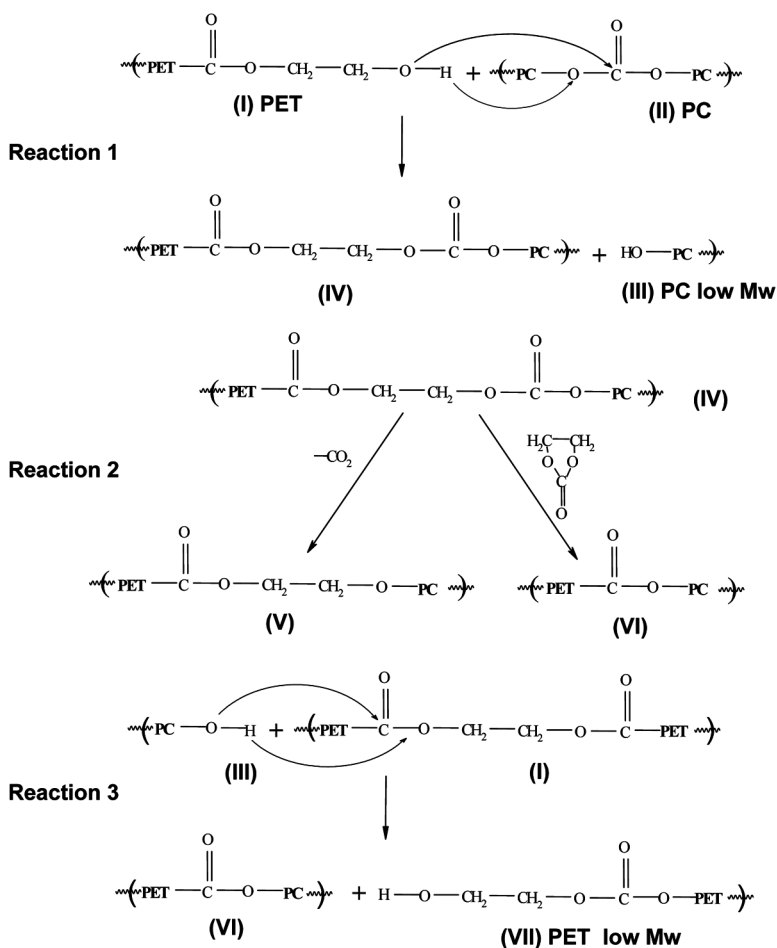
Sample	Catalyst type	Degree of transesterification (Ratio of peak height at 1063 and 1580 cm ⁻¹)	PET degree of order (Ratio of peak height at 1340 and 1580 cm ⁻¹)	Crystallinity ^b (%)
PET	—	—	7.04	25.4 ^b
PET/PC	— ^a	5.03	7.40	26.8 ^b
(50/50)	CoIII 0.1 wt%	5.44	1.13	4.0
	CoIII 0.05 wt%	4.45	1.14	4.0
	CoII 0.1 wt%	4.57	0.91	3.2
	CoII 0.05 wt%	4.69	1.13	4.0

^aResidual catalysts containing a mixture of antimony oxide and cobalt acetate.

^bReference value from DSC measurements.

aliphatic-aromatic carbonate (structure IV). After this reaction, reactions 2 and 3 may concomitantly occur. In reaction 2, decarboxylation of structure IV generates aliphatic-aromatic ether producing absorptions at 1240 and 1040 cm⁻¹. As the last band was not detected in the spectra of the blends, it was concluded that this reaction did not occur. If structure IV releases ethylene carbonate, an aromatic-aromatic ester must arise. In fact, the absorption at 1063 cm⁻¹ confirmed the occurrence of that structure. However, to interpret the loss of PET degree of order, it was supposed that the cobalt complex catalyzed the attack of low molecular weight PC (structure III) on ester linkage of PET (reaction 3). The resulting structures were aromatic-aromatic ester (VI) and low molecular weight PET (VII). Thus considering the reactions of Scheme 1, it could be concluded that alcoholysis was the main exchange reaction that has occurred in this PET/PC reactive blending. The residual catalyst catalyzed the reaction of PET on PC, whereas the cobalt complex was able to activate the reaction of PC on PET.

In Scheme 2, the residual catalyst catalyzed the attack of carboxyl end group of PET on carbonate linkage of PC. The structures III (aromatic-aromatic ester) and IV (low molecular weight PC) are generated. This reaction could explain the formation of a new ester linkage, but considering the loss of PET degree of order, the attack on PET ester linkage took place according to reactions 2 and 3. At first, the PC fragment (IV) activated by cobalt complex attacks PET ester linkage, resulting in structures V (new aromatic-aromatic carbonate) and VI (low molecular weight PET). The following reaction is decarboxylation of structure V, generating aromatic-aromatic ester (III). Therefore, taking into account the exchange reactions in Scheme 2,

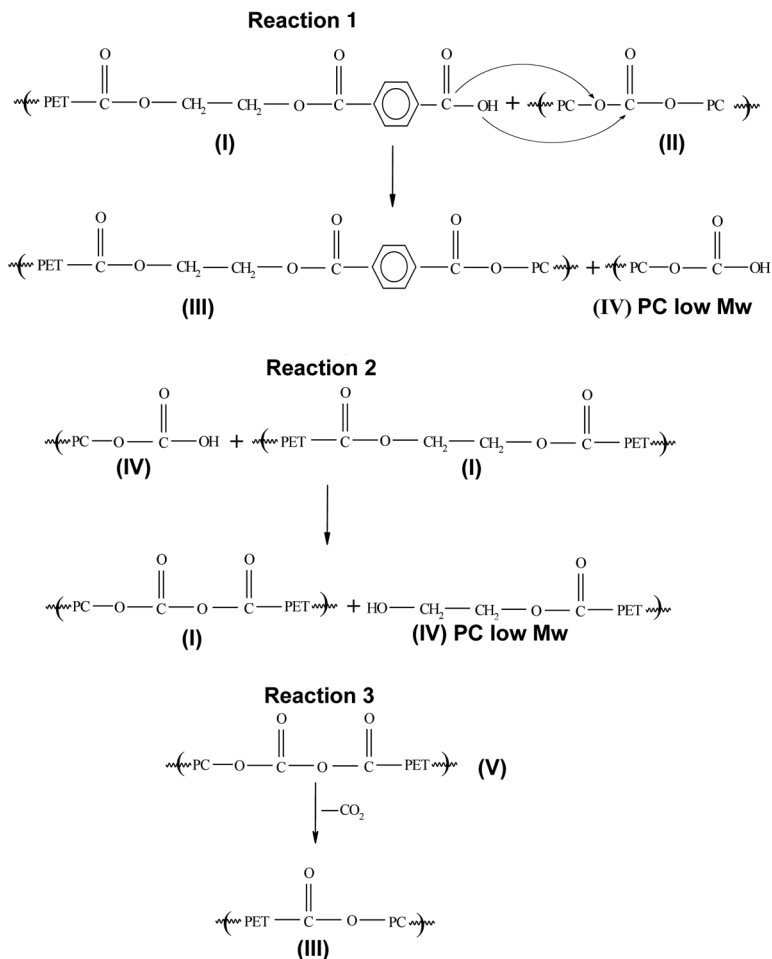


SCHEME 1 Alcoholysis of hydroxyl end group of PET on carbonate linkage of PC.

it could be inferred that acidolysis was the main reaction. Similar to what was found in Scheme 1, residual catalyst seems to have acted in the reaction of PET on PC and cobalt complex activated the reaction of PC on PET.

FT-IR Quantitative Analysis

From the plot of absorbance of PC *p*-disubstituted ring band (558 cm^{-1}) versus film thickness (Figure 5), the molar absorptivity (ϵ)



SCHEME 2 Acidolysis of carboxyl end group of PET on carbonate linkage of PC.

was calculated. The value of $34.3738 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ was used to determine the composition of the insoluble fraction using Lambert-Beer's law. The composition of the soluble portion was deducted from the composition calculated for the CH_2Cl_2 insoluble fraction. In Table 6, the composition of each fraction is presented. In general, the incorporation of PC in PET was higher than the opposite. The cobalt II complex promoted a higher degree of insertion of PC in PET than the cobalt III one. This tendency was practically independent of the concentration.

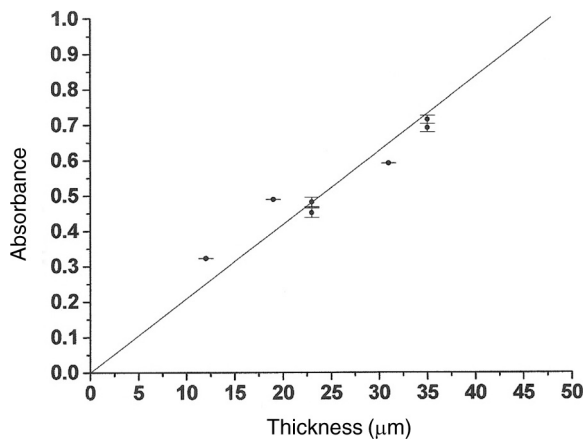


FIGURE 5 Lambert-Beer's plot of PC band at 558 cm^{-1} .

In other words, the rate of transesterification reaction was higher for the Co II than for the Co III complex. Considering the blends prepared with Co III complex, different copolymers were obtained depending on the catalyst content. In all cases, random copolymers with up to 40% of PC in PET and 30% of PET in PC were formed. The miscibility of the system was achieved when at least 20% of mutual insertion took place. The results are consistent with solubility and DSC analyses.

CONCLUSION

Cobalt complexes have promoted the formation of miscible and amorphous PET/PC copolymers. Residual antimony oxide/cobalt acetate in PET promoted the alcoholysis/acidolysis reaction of the PC component through hydroxyl/carboxyl end groups of PET. In

TABLE 6 Copolymer Composition by FT-IR

Sample		Insoluble fraction*		Soluble fraction*	
		X_{PET}	X_{PC}	X_{PET}	X_{PC}
PET/PC (50/50)	Co III 0.1 wt%	0.81	0.19	0.24	0.76
	Co III 0.05 wt%	0.69	0.31	0.20	0.80
	Co II 0.1 wt%	0.59	0.41	0.30	0.70
	Co II 0.05 wt%	0.61	0.39	0.26	0.74

* X_{PET} and X_{PC} weight fraction.

addition, PC fragments produced in previous steps attacked the PET ester linkage by action of Co complex, producing a decrease in PET degree of order. As a result, a PET/PC miscible system with absence of crystallinity and presence of a single T_g around 100°C was achieved.

REFERENCES

- [1] Mano, E. B. (1991). *Polímeros como Materiais de Engenharia*, Edgard Blucher, São Paulo.
- [2] Barlow, J. W. and Paul, D. R., *Polym. Eng. Sci.* **21**, 985 (1981).
- [3] Zhang, Z., Xie, Y., and Xie, D. Ma, *Europ. Polymer J.* **37**, 1961 (2001).
- [4] Fiorini, M., Berti, C., Ignatov, V., Toselli, M., and Pilati, F., *J. Appl. Polym. Sci.* **55**, 1157 (1995).
- [5] Fiorini, M., Pilati, F., Berti, C., Toselli, M., and Ignatov, V., *Polymer* **38**, 413 (1997).
- [6] Kim, Y. and Choi, K. Y., *J. Appl. Polym. Sci.* **49**, 747 (1993).
- [7] Pilati, F., Toselli, M., Messori, M., Manzoni, C., Turturro, A., and Gattiglia, E. G., *Polymer* **38**, 4469 (1997).
- [8] Chiu, S. J. and Cheng, W. H., *Polym. Degrad. Stab.* **63**, 407 (1999).
- [9] Lu, X. F. and Hay, J. N., *Polymer* **42**, 9423 (2001).
- [10] Gorlier, E., Haudin, J. M., and Billon, N., *Polymer* **42**, 9541 (2001).
- [11] Liangbin, L., Hui, H., Ling, Z., and Shiming, H., *Polymer* **42**, 2085 (2001).
- [12] Hagenaaars, A. C., Pesce, J.-J., Bailly, C., and Wolf, B. A., *Polymer* **42**, 7653 (2001).
- [13] Okamoto, M., *Polymer* **42**, 8355 (2001).
- [14] Porter, R. S., Wang, L. H., Huang, Z., and Hong, T., *J. Macromol. Sci.-Phys. B* **29**, 155 (1990).
- [15] Hanrahan, B. D., Angeli, S. R., and Runt, J., *Polymer Bulletin* **15**, 455 (1986).
- [16] Suzuki, T., Tanaka, H., and Nishi, T., *Polymer* **30**, 1287 (1989).
- [17] Pilati, F., Marianucci, E., and Berti, C., *J. Appl. Polym. Sci.* **30**, 1267 (1985).
- [18] Nassar, T. R., Paul, D. R., and Barlow, J. W., *J. Appl. Polym. Sci.* **23**, 85 (1979).
- [19] Murff, S. R., Barlow, J. W., and Paul, D. R., *J. Appl. Polym. Sci.* **29**, 3231 (1984).
- [20] Zhang, G. Y., Ma, J. W., Cui, B. X., Luo, X. L., and Ma, D. Z., *Macromol. Chem. Phys.* **5**, 604 (2001).
- [21] Banach, T. E., Berti, C., Colonna, M., Marianucci, E., Messori, M., Pilati, F., and Toselli, M., *Polymer* **42**, 7511 (2001).
- [22] Lee, S. S., Jeong, H. M., Jho, J. Y., and Ahn, T. O., *Polymer* **41**, 1773 (2000).
- [23] American Society for Testing and Materials, ASTM D 297.
- [24] a. Fox, T. G., *Bull. Am. Phys. Soc.* **1**, 123 (1956).
b. Couchman, P. R., *Macromolecules* **11**, 1156 (1978).
- [25] Starkweather, H. W., Zoller, P., and Glover, A., *J. Polym. Sci. Polym. Phys.* **61**, 295 (1983).
- [26] Silverstein, R. M. and Webster, F. X. (1998). *Spectrometric Identification of Organic Compounds*, John Wiley, New York.
- [27] Colthup, N. B., Daly, L. H., and Wiberley, S. E. (1964). *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York.
- [28] Humell, D. O. (1988). *Atlas of Polymer and Plastics Analysis*, V. 2 Part b/I, (Carl Hanser, Munich).