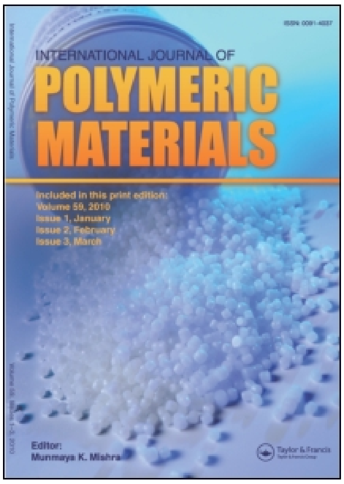

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Influence of the Addition of Tetrabutyl Orthotitanate on the Rheological, Mechanical, Thermal, and Morphological Properties of Polycarbonate/Poly(Ethylene terephthalate) Blends

M. Guessoum[a]; N. Haddaoui[a]
[a] Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Département de Génie des Procédés, Faculté des Sciences de l'Ingénieur, Université Ferhat ABBAS, Sétif, Algeria

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M. Guessoum
N. Haddaoui
Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP),
Département de Génie des Procédés, Faculté des Sciences de
l'Ingénieur, Université Ferhat ABBAS, Sétif, Algeria

The effects of the incorporation of tetrabutyl orthotitanate (TBOT) on the mechanical, thermal, rheological, and morphological properties of polycarbonate (PC)/ poly(ethylene terephthalate) PET blends were investigated. Blends were prepared using a screw extrusion with TBOT's rates varying from 0 to 0.25 phr. Rheological and mechanical investigations showed that the blends properties decreased by chain scissions induced by the degradation of PET and by volatile products release. Differential scanning calorimetry (DSC) revealed that the crystallinity of PET in PC/PET blends is affected by many parameters and does not depend only on PC and TBOT concentrations whereas dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) support the occurrence of a little compatibilization.

Keywords: polycarbonate, poly(ethylene terephthalate), transesterification

INTRODUCTION

Among the strategies of polymer reactive blending, the compatibilization of polycondensates by interchange reactions has attracted the attention of a number of scientists for both academic and industrial reasons [1–16]. This alternative has proved to be a quiet fascinating method to generate in-situ and at the interface, block or graft

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Address correspondence to M. Guessoum, Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Département de Génie des Procédés, Faculté des Sciences de l'Ingénieur, Université Ferhat ABBAS, Sétif 19000, Algeria. E-mail: guessoum_melia@yahoo.fr

copolymers that improve interfacial adhesion and thus whole blend properties [11–12].

The bisphenol-A polycarbonate/poly(ethylene terephthalate) PC/PET is an immiscible polymer blend that combines two high-performance plastics, PC which has a high impact strength, and PET, which has a high resistance to solvent. However, their immiscibility is a strong limiting factor to their use for obtaining a material with both characteristics.

Like all polycondensates, PC and PET can involve a large number of reactive sites, contained in their skeletons. Ester and carbonate groups can undergo several different exchange reactions that can result in the compatibilization of the system by the synthesized copolymer that affects the thermal, mechanical, rheological, and morphological properties [3,6–8,11–12]. Devaux et al. [13–14] studied extensively exchange reactions in PC/PET polymer blend and concluded that exchange between PC and PET occurs essentially by transesterification and that alcoholysis and acidolysis occurs, but not extensively. However, the use of catalysts is necessary to have sufficient exchange, because in the melt blending temperature range, transesterification reaction rates are relatively very low. In this case, tetrabutyl orthotitanate (TBOT) has proved to be a very effective catalyst in transesterification reactions between PC and PET. But, it presents the disadvantage of catalyzing also other side reactions [15–16]. In this way, Fiorini et al. [10,16–20] investigated the efficiency of TBOT and a series of lanthanides-based catalysts and established that TBOT is a very active catalyst for the transesterification reactions whereas the terbium derivative appeared to be the least active one. But, they also concluded that the use of TBOT promotes side reactions leading essentially to gas release and discoloration.

This article considers the effects of the addition of TBOT and the composition of the system on the rheological, mechanical, thermal, and morphological properties of PC/PET polymer blends. The objective is to show its efficiency in the compatibilization of the blend and at which extent side reactions induced by the transesterification will affect these properties.

EXPERIMENTAL

Materials

The PC and PET used in this work were, respectively, Lexan 129 from General Electric and Polyclear T 86 W from Kosa. The transesterification catalyst and inhibitor used were respectively the tetrabutyl

Orthotitanate (TBOT) [$Ti(OC_4H_9)_4$] and the triphenyl phosphite (TPP) [$(C_6H_6{-}O)_3P$] from Fluka.

Blends Preparation

Blends of dried PC and PET were prepared by melt mixing using a co-rotating twin screw extruder (screw diameter = 25 mm, L/D = 36) at a screw speed of 130 rpm and at a temperature of 270°C. For the catalyzed blends, the TBOT was initially dispersed on PET pellets. The resulting extrudates were quenched in water, pelletized, and dried at 120°C. In order to prevent the occurrence of further exchanges between PC and PET during compressing moulding, TPP was dispersed on the catalyzed blends pellets before extruding all the blends in a Controlab single screw extruder (Screw diameter = 25 mm, L/D = 20) at a screw speed of 50 rpm and a temperature profile (240–260°C).

The compositions of the prepared PC/PET blends (in weight percent) are 30/70, 50/50, and 70/30 in presence of TBOT varying from 0 to 0.25 phr with an increment of 0.05 phr.

Samples Preparation

For mechanical tests samples preparation, the blends were dried for 24 h at 120°C before compressing them in a Davenport compression molding machine at a temperature of 250°C and a compression pressure of 220 Kg/cm^2.

Measurements

Melt Flow Index (MFI)

It was performed on the pelletized blends with a melt flow indexer model 5 instrument at 260°C under a load of 1.2 Kg according to the standard procedure ASTM D1238.

Mechanical Properties

Unnotched Izod impact strength was performed on compressed samples according to the standard procedure ISO 180 using a Ceast pendulum instrument (4 Joules).

Differential Scanning Calorimetry (DSC)

Crystallization (T_c) and melting temperatures (T_m) were evaluated on the basis of thermograms of the first scanning of samples obtained on a Mettler 30 DSC, under the following conditions (temperature range: 25 to 300°C, heating rate of 10°C/min under inert atmosphere).

The crystallinity χ^c was calculated according to the following equation:

$$\chi^c = \Delta Hm - \Delta Hc / \Delta Hm^\circ$$

where ΔHm and ΔHc are, respectively, the melting and the crystallization enthalpies of the samples, and ΔHm° the equilibrium melting enthalpy of a pure PET crystal. A value of ΔHm° equal to 140 J/g was used [21].

Dynamic Mechanical Analysis (DMA)

The glass transition temperatures $T_{g_{PC}}$ and $T_{g_{PET}}$ of PC and PET, respectively, were characterized by Dynamic Mechanical Analysis (DMA). The tests were performed on compressed samples of uncatalyzed and catalyzed 0.1, 0.15, 0.20, and 0.25 phr of TBOT 30/70 blends, using a rheometrics dynamic analyzer RDA II. The samples were scanned from 35°C to 200°C at 2°C/min and at a frequency of 1 Hz.

Scanning Electron Microscopy

Micrographs of, respectively, uncatalyzed and catalyzed PC/PET 50/50 blends prepared with 0.10, 0.15, 0.20, and 0.25 phr of TBOT, all obtained after the first extrusion, were taken using a Philips scanning electronic microscope (SEM) from the surface of samples, fractured in liquid nitrogen and covered with a conductive gold layer. Micrographs of etched and non-etched samples of 0.25 phr TBOT catalyzed 70/30 and 30/70 blends were also performed. Etching was undertaken in dichloromethane (CH_2Cl_2) to dissolve PC and to make the PET phases more discernible.

RESULTS AND DISCUSSION

Rheological Properties

It was noticed that the melt flow index of the uncatalyzed blends increases with the amount of PET present in the blend as represented in Figure 1. The MFI values measured for the homopolymers are 3.6 g/10 min for PC and 26.4 g/10 min for PET. Further, it was observed that there is also an increase in the MFI values as catalyst concentration increases. These observations support well the occurrence of a decrease in the molecular weight of PET. This degradation process with chain scission occurs quicker with PET than for PC and is favored by the addition of TBOT.

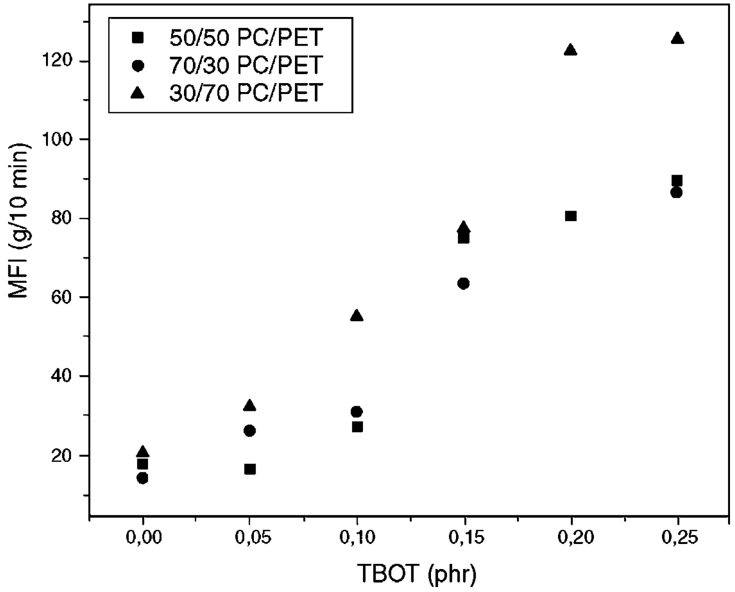

FIGURE 1 Effect of TBOT concentration on the melt flow index of PC/PET blends.

Mechanical Properties

The values of Izod impact strength of uncatalyzed PC/PET blends vary between the values of the 2 homopolymers, which are 6.10 KJ/m^2 for PET and 13.30 KJ/m^2 for PC. The higher the content of PET in the blend, the lower the impact strength, as shown in Figure 2. This is an expected result, because addition of a semicrystalline polymer such as PET to the polycarbonate would increase the notch sensitivity of the blend. With the incorporation of TBOT, it was very difficult to obtain samples by compression molding without imperfections resulting from the release of volatile products. The authors have attempted to eliminate them by changing the conditions of compression but unfortunately, the impact strength of all the blends showed a very sharp decrease that confirms that the imperfections have not totally disappeared and decreased significantly the mechanical properties. In fact, the values of impact strength decrease over all the range of the blend compositions.

Thermal Properties

After the extrusion of the neat PET, the evaluation of its degree of crystallinity by DSC gave a value of approximately 40%. After

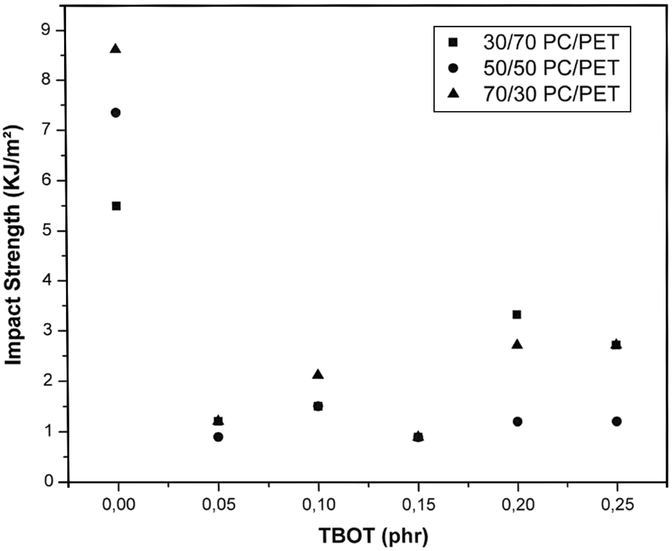

FIGURE 2 Effect of TBOT concentration on the Izod impact strength of PC/PET blends.

blending, the effect of the incorporation of PC on the crystallinity of PET is revealed by Figure 3. The presence of PC hinders the crystallization of PET that crystallizes at relatively higher temperatures and reveals lower degrees of crystallinity. It was expected that the higher the PC content in the blend, the lower the crystallinity of PET, as it was deduced by Ma et al. [22] who reported that in polymer blends composed of an amorphous polymer and a crystallizable one, the crystallinity of the crystallizable polymer can be greatly hindered by the amorphous component.

Figure 3 reveals that the degree of crystallinity is governed neither by the PC content in the system nor by the concentration of TBOT, because in all the prepared blends, the values are very close. Therefore, we propose that these observed variations of the crystallinity, relative to the value concerning the extruded neat PET, are probably due more to the process of extrusion which had induced blends with equivalent thermal and mechanical histories that govern the crystallization.

Also, the effects of transreactions between PC and PET cannot be neglected because by their promotion, these reactions contribute greatly in the alteration of the process of crystallization by the

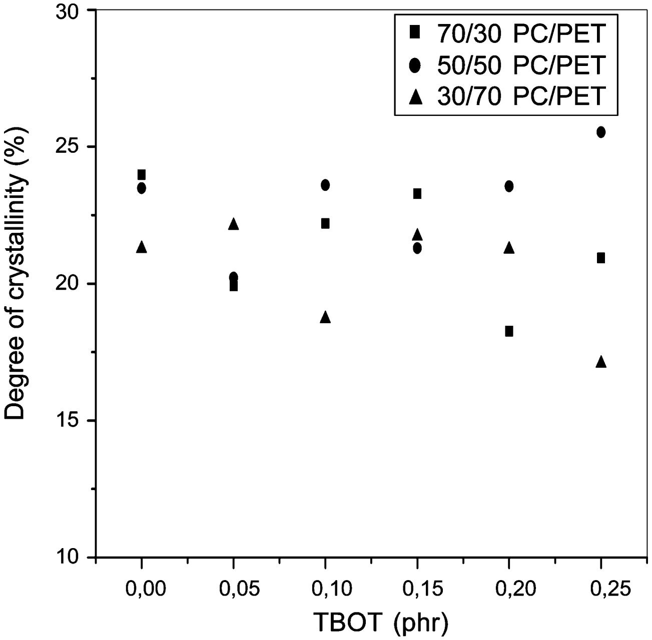

FIGURE 3 Effect of TBOT concentration on the degree of crystallinity of PC/PET blends.

synthesis of copolymers, as has been reported by Kong and Hay [23] who proposed that when exchanges between PC and PET occur, the crystallinity of PET is still occurring but is significantly reduced. Therefore, we can notice from Figure 4 that the PET component in the blends still can crystallize showing the melting endotherm and the crystallization exotherm in the DSC thermograms, but its crystallization becomes more complicated with the interference of many parameters such as the addition of TBOT, the presence of PC and the occurrence of degradation processes.

Figure 5 shows that T_c is more affected by the composition of the blend than the degree of crystallinity, because the lower the content of PET in the system, the lower is the value of T_c. It appears also that the effects of this last factor are much more noticeable than the effects of transreactions which probably had not extensively occurred and so small variations were observed on the values of T_c.

Also, Figure 6 shows that the melting temperature varies slightly, which means that only small exchanges were possible within the relatively short time of residence in the extruder. All the compositions of

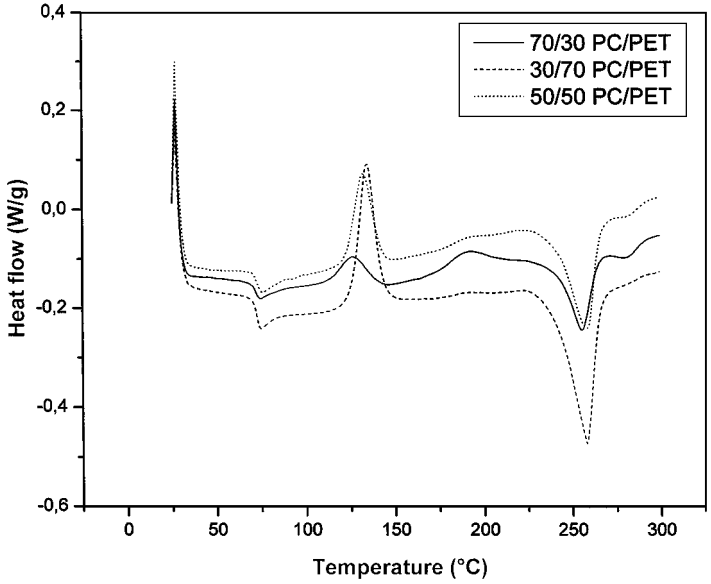

FIGURE 4 DSC thermograms of PC/PET blends extruded with 0.25 phr of TBOT.

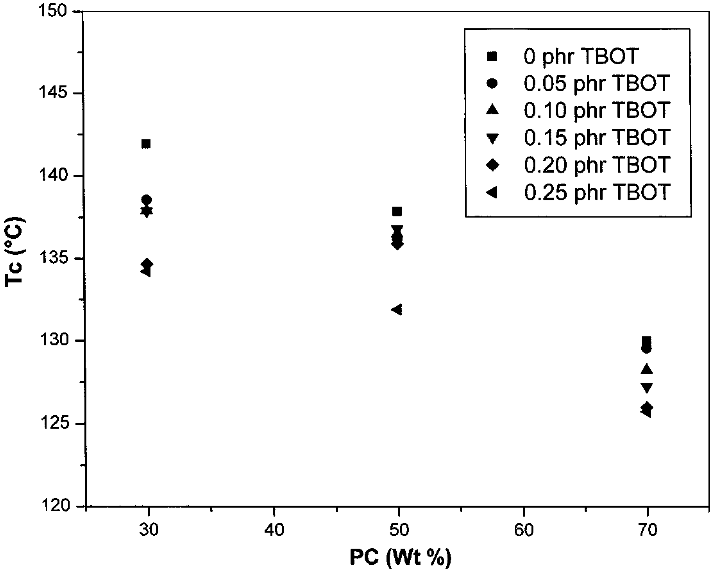

FIGURE 5 Effect of TBOT concentration and blend composition on the crystallization temperature of PC/PET blends.

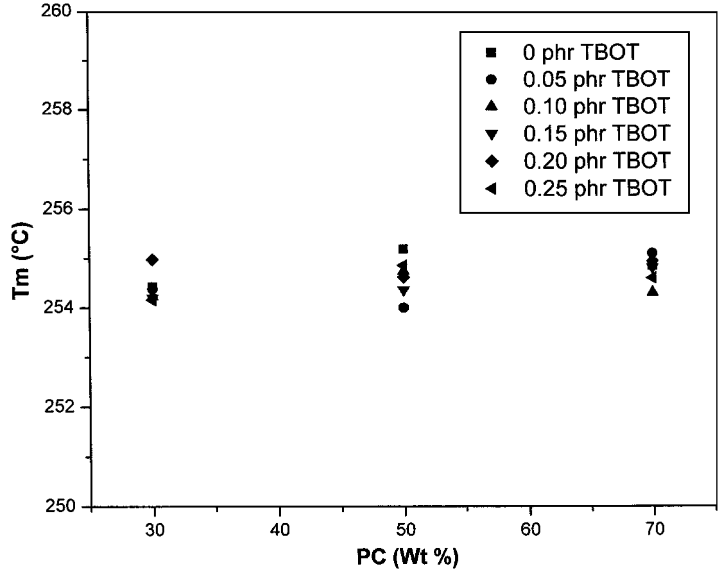

FIGURE 6 Effect of TBOT concentration and blend composition on the melting temperature of PC/PET blends.

uncatalyzed and catalyzed blends exhibited approximately the same melting temperature which value is situated around 255°C.

Dynamic Mechanical Properties

Figure 7 shows a DMA thermogram of a 50/50 uncatalyzed PC/PET blend. The appearance of two glass transition temperatures reveals the substantial immiscibility of the system. The same trend was shown by all the tested uncatalyzed and catalyzed compositions: two maxima were noticed in the curves of the shear dynamic modulus G″ reflecting two values of the glass transition temperatures, the first for the PET-rich phase and the second for the PC-rich phase.

T_g values of the PC and PET phases determined first for the uncatalyzed blends are represented by the maxima of the curves of G″ Figure 8. The appearance of two glass transitions reflects the presence of two amorphous phases because the two values of T_g are close to the characteristic values of, respectively, PET at approximately 80°C and PC at 140°C.

When blending with TBOT, two T_g values are still observed for all the amounts of the catalyst. Therefore, two amorphous phases are

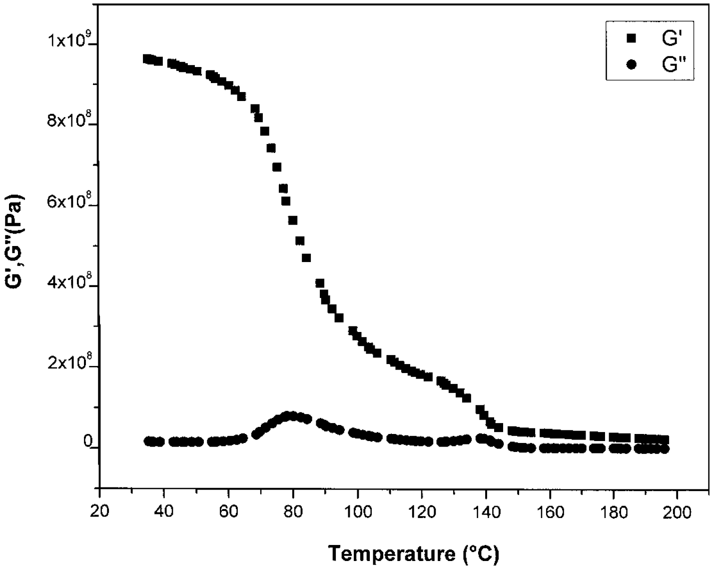

FIGURE 7 DMA thermogram of a 50/50 uncatalysed blend.

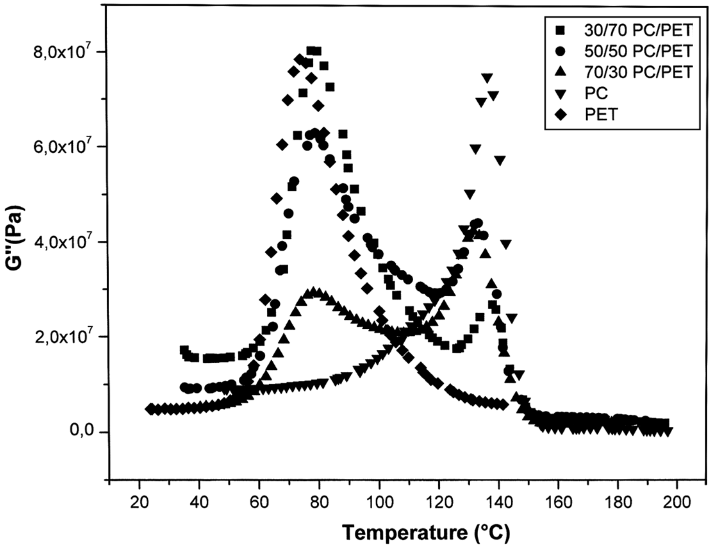

FIGURE 8 Variation of G″ of the homopolymers and the uncatalyzed PC/PET blends.

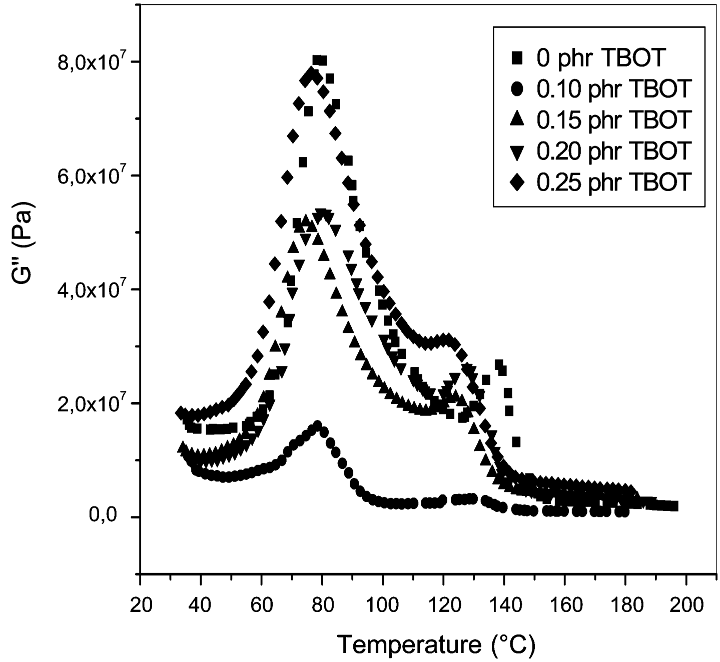

FIGURE 9 Variation of G″ of the catalyzed 30/70 PC/PET blends with the concentration of TBOT.

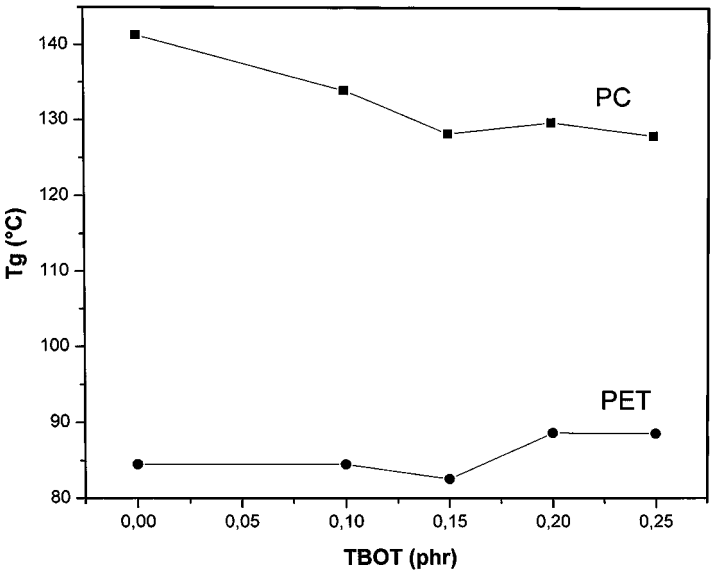

FIGURE 10 Effect of TBOT concentration on the glass transition temperatures of 30/70 PC/PET blends.

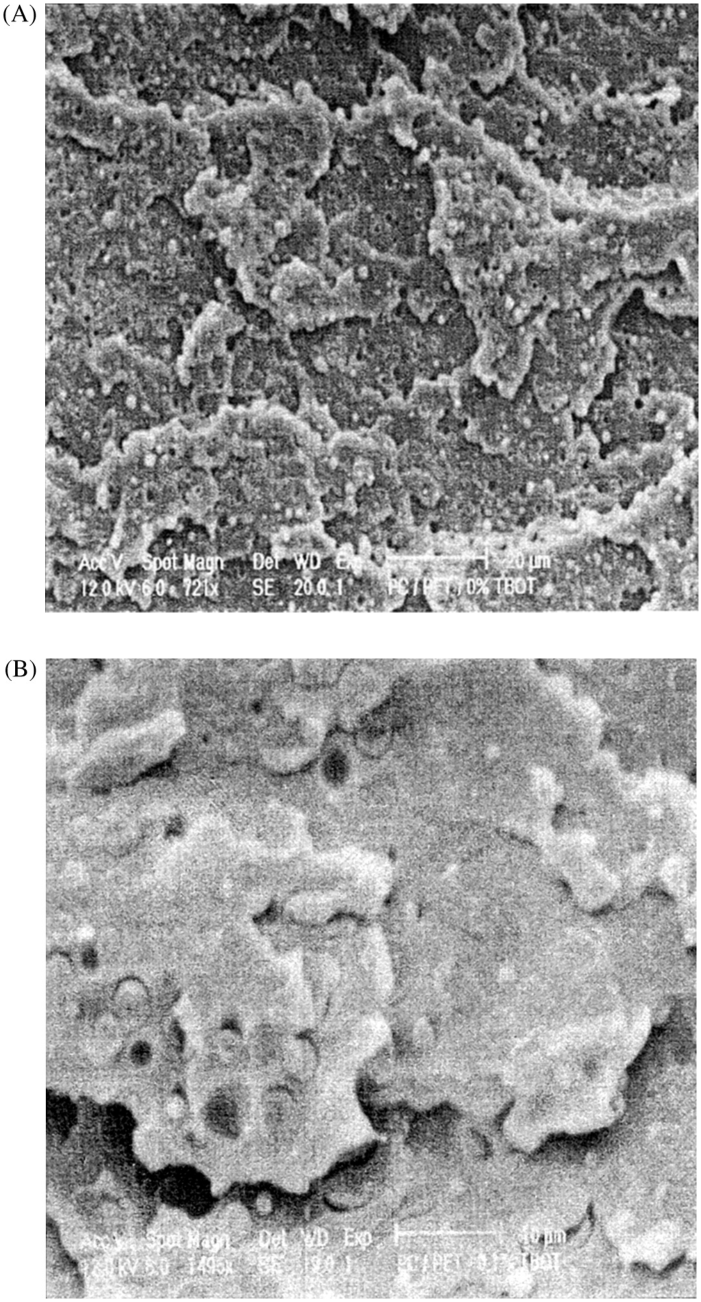

FIGURE 11 Scanning electron micrographs obtained from cryogenically fractured samples of 50/50 PC/PET blends: (A) (0 phr TBOT); (B) (0.1 phr TBOT); (C) (0.20 phr TBOT); (D) (0.25 phr TBOT).

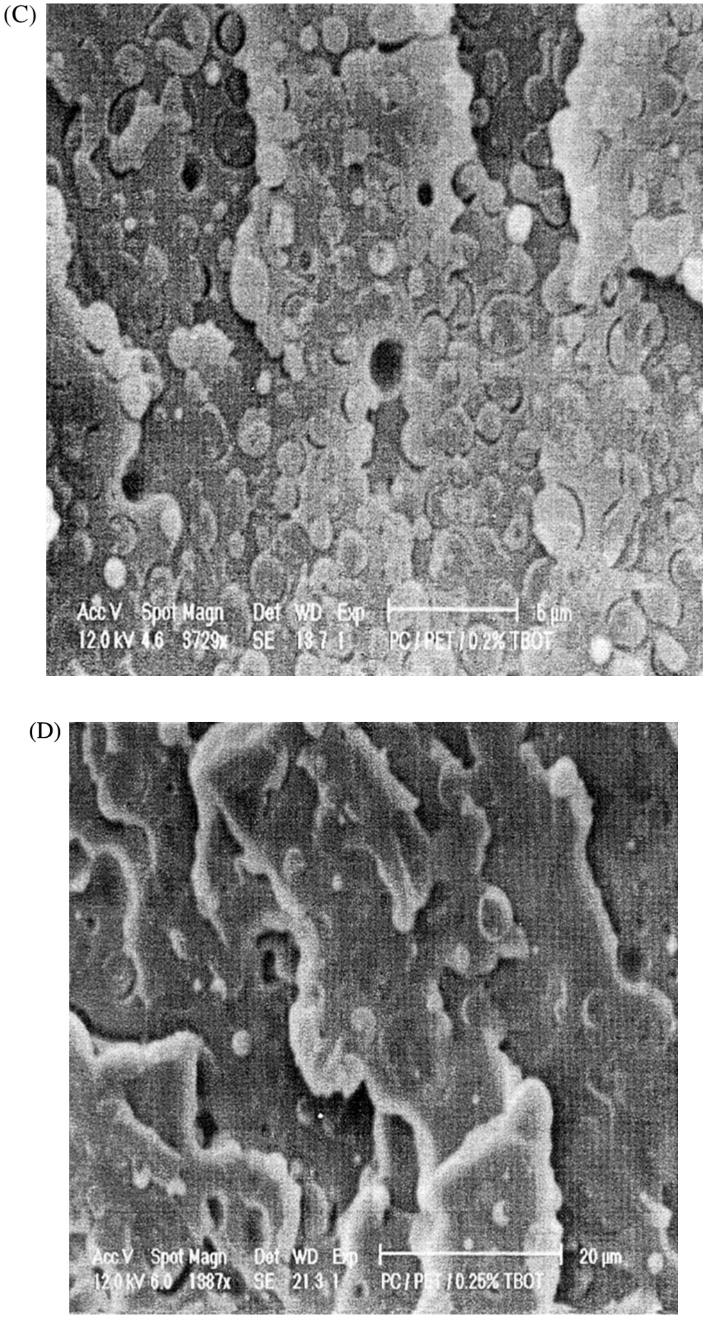

FIGURE 11 Continued.

present. This fact is well illustrated by Figure 9, which gives the variations of G″ with the concentration of TBOT.

Figure 10 represents the variations of the glass transition temperatures of a 30/70 PC/PET blend. By comparing the measured T_g values with those of the two homopolymers, it is possible to observe that the two values of P_g move toward one another. The T_g of the PC-rich phase shifts to lower values whereas the T_g of the PET-rich phase shifts to higher ones with increasing the rate of TBOT in the blend. These changes can be assigned to the beginning of homogenization promoted by the transesterification reactions that create copolymers that can improve the compatibility between the two polymers.

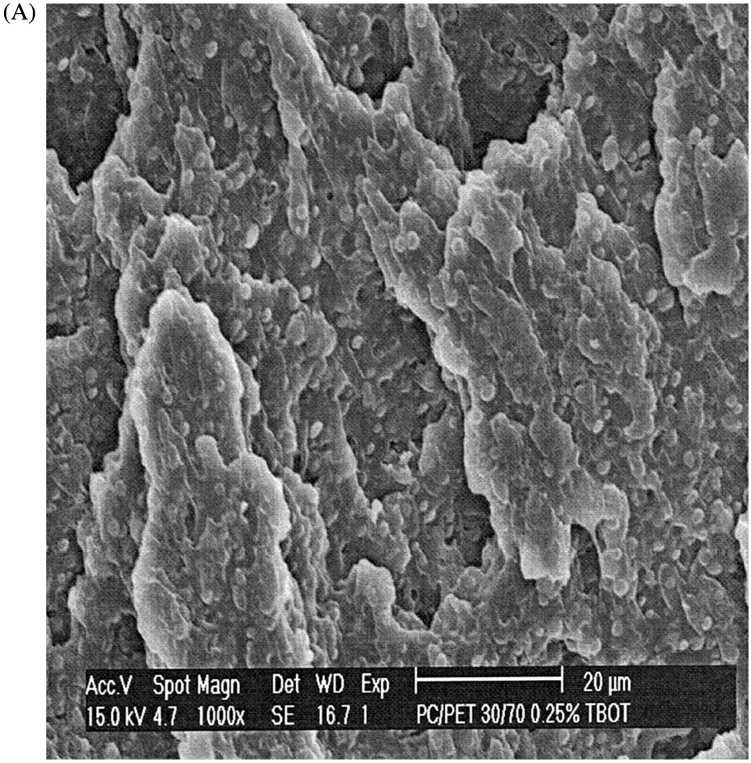

FIGURE 12 Scanning electron micrographs obtained from nonetched samples of 30/70 (A) and 70/30 (B) PC/PET blends extruded in the presence of 0.25 phr TBOT.

(B)

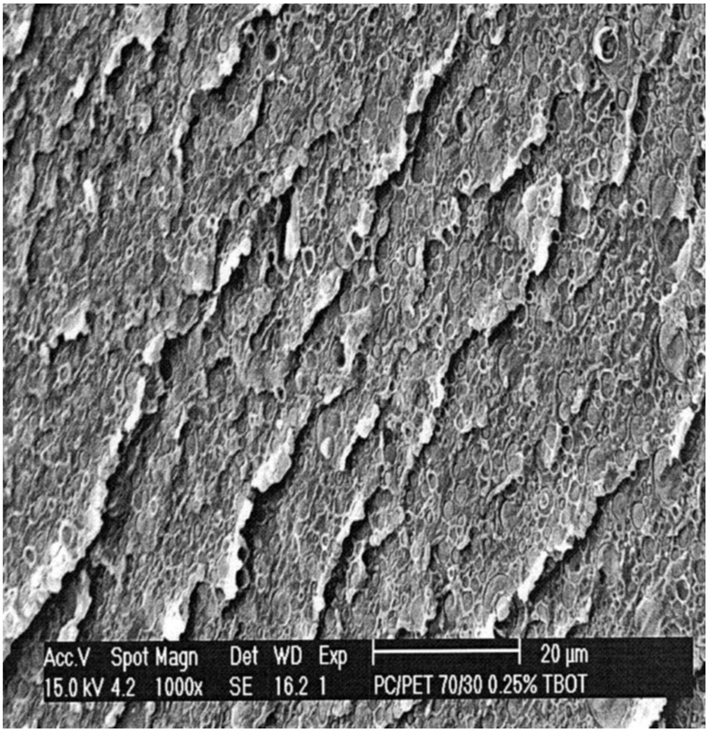

FIGURE 12 Continued.

Morphological Observations

Figure 11 shows the SEM micrographs of cryogenically fractured extrudate surface of PC/PET blends. The micrograph given by Figure 11A shows that the uncatalyzed blend has a biphasic morphology consisted of a matrix and a dispersed phase. This character confirms the incompatibility of PC and PET. The polycarbonate represents the dispersed phase and most PC particles have a spherical shape of about 1 to 2.66 µm. For the catalyzed blends, phase separation between the PC-rich phase and PET-rich phase is also very pronounced. The biphasic morphology is observed for all the blend compositions.

Figures 11B and 11C indicate that the dimensions of nodules vary from 1 to 3 µm for blends prepared with 0.1 phr of TBOT and that for those containing 0.20 phr of TBOT, the PC-rich phase has a uniform size scale of approximately 1.5 µm. For the system with

0.25 phr of TBOT, Figure 11D reveals that the spherical PC phase is still observed, uniformly distributed in the PET matrix but with a broad distribution of diameters varying from 0.7 μm to 2.85 μm. The Biphasic character indicates that for all the concentrations of TBOT, the (50/50) PC/PET system is still immiscible, but the values suggest that the observed reduction of the dimensions of the micro-domains indicates that when the percentage of TBOT increases, it progresses toward a finer dispersion.

Figure 12 (A and B) representing non-etched 30/70 and 70/30 PC/PET systems, show that the phase separation between PC and PET is also very clear. The biphasic morphology of these blends is much more revealed by the etched samples represented by Figure 13 (A and B) that reflect PET as a matrix in the first micrograph and as spherical nodules of the dispersed phase in the second.

(A)

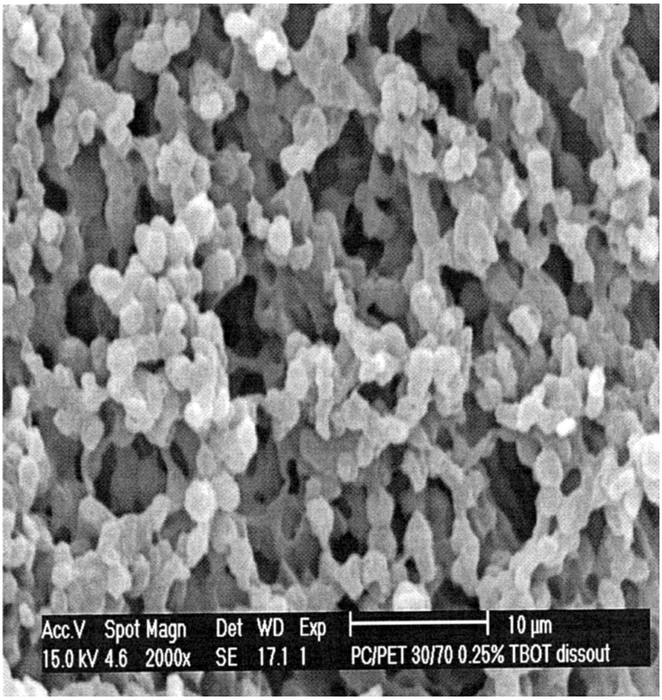

FIGURE 13 Scanning electron micrographs obtained from etched samples of 30/70 (A) and 70/30 (B) PC/PET blends extruded in the presence of 0.25 phr TBOT.

(B)

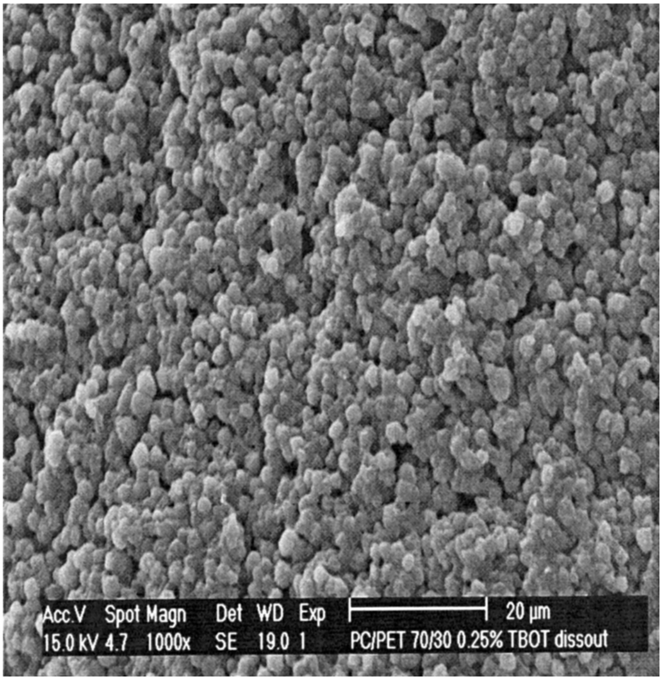

FIGURE 13 Continued.

CONCLUSION

The influence of tetrabutyl orthotitanate addition on rheological, mechanical, thermal, and morphological properties of PC/PET blends has been investigated. Melt flow index measurements confirm the increase of MFI of the blends with the increase of the amount of PET and TBOT, making the processing control of the blend difficult.

Moreover, TBOT addition caused the decrease of the impact strength of the PC/PET system, because while catalysing transesterification between PC and PET, TBOT also promotes side reactions that occur during the processing and result mainly in volatile products release. The imperfections caused by this disagreement do not permit highlighting, by this test, the positive effect of the produced compatibilization that has been extensively revealed by DMA and microscopic results.

The persistent immiscibility of the system has been noticed by DSC measurements. From this analysis, the independent crystallized component proves the tendency of PET to segregate in a separate phase. The crystallinity and the crystallization and melting temperatures of

PET show small variations with the modification of the concentrations of homopolymers and TBOT in the blend. This confirms that the extent at which exchange reactions had occurred was not sufficient to produce more significant variations on the thermal characteristics of PET. But, the appearance, from DMA thermograms, of two T_g values characteristic of the PC and PET rich phases and that approach each other with increasing the TBOT concentration, reflects the occurrence of an exchange-induced compatibilization that was also confirmed by SEM observations. Electron micrographs showed that on increasing the concentration of TBOT, transesterification generated a finer dispersion of one polymer in the other.

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