Effects of Blending Conditions and Catalyst Concentration on the Structural, Thermal and Morphological Properties of Polycarbonate/Poly (Ethylene Terephthalate) Blends

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The effects of mixing conditions and transesterification catalyst concentration on the structural, thermal and morphological properties of a 50/50 polycarbonate (PC)/poly (ethylene terephthalate) (PET) system were investigated by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and by solubility measurements. From the increase in the solubility of the blends in dichloromethane and the decrease of their degree of crystallinity, it was concluded that on increasing the mixing time and the catalyst concentration, transesterification becomes more important. Thermal analysis revealed also a noticeable increase of the crystallization temperature and a slight decrease of the melting temperature. These results suggest that when transesterification occurs extensively, the crystallization tendency declines progressively until finally a completely soluble material is obtained as revealed by solubility measurements.

Keywords: poly (ethylene terephthalate), polycarbonate, transesterification

INTRODUCTION

Reactive blending of polycarbonate (PC) and polyethylene terephthalate (PET) has proved to be a successful and economic route for producing new materials with modulated properties [1–4]. Both materials are widely used as engineering plastics, either alone or blended with other

thermoplastics to ensure certain performances that cannot be provided by using the neat homopolymers. For this reason, the reactive blending of PC and PET has received great interest as a way to acquire insight into all the parameters that may influence the ultimate properties of the final product.

Previous research [1–18] has focused on the study of the mechanisms of the reactions occurring during melt mixing, of the different experimental conditions' influences (time, temperature, equipment of blending), of catalysts and their efficiency in compatibilizing these systems, and finally on the effects of all the above parameters on the thermal, rheological, mechanical and morphological properties.

Montaudo et al. [19,20], Pilati et al. [21] and Berti et al. [22,23] found that the principal reactions that may produce particular effects on the properties of PC/PET blends are intermolecular ester-carbonate exchange reactions, alcoholysis, acidolysis, release of cyclic ethylene-carbonate and carbon dioxide and, finally, PET chains scission resulting from the thermal degradation. Such reactions may occur during melt mixing, but at very low rates, so the use of a catalyst is necessary to accelerate the exchange between the two polymers [22].

Fiorini et al. [24–28] studied extensively the efficiency of certain catalysts and found that tetrabutylorthotitanate (TBOT) is most active in catalyzing ester-carbonate exchange reactions in PC/PET systems, but it also allows the occurrence of side reactions which can have drastic effects on the properties of the blend. Marchese et al. [14] and Fiorini et al. [24–28] tested a series of various lanthanide-based catalysts and concluded that they were not as efficient as TBOT in producing copolymers, but they provide the opportunity for the control of the chemical structure during the reactive blending of PC and PET.

The purpose of this article is to study the extent of exchange reactions between PC and PET in the presence of TBOT as a transesterification catalyst, by employing a combination of techniques such as differential scanning calorimetry (DSC), electron microscopy (SEM) and the solubility test. Our objectives are aimed at the investigation of the effects of the time and the rotor speed of mixing and the concentration of TBOT, especially on the thermal, structural, and morphological properties of the system.

EXPERIMENTAL

Materials

The polymers used in this study were commercial PC (Lexan 129) of General Electric company and PET (Polyclear) of Kosa. The employed

transesterification catalyst is tetrabutylorthotitanate (TBOT), [($C_4 H_9$ $O)_4$−]Ti, supplied by Fluka. All these products were used without further purification.

Melt Blending

Before melt mixing, PC and PET pellets were dried for 24 h in an oven at 100°C. Reactive blending of the PC/PET systems using a weight ratio of 50/50 was performed in a Brabender (Haake Rheomix 300 P) at 270°C and at rotor speeds of 30, 80 and 130 rpm. After the melting of PC and PET pellets, the TBOT was introduced at a concentration of 0.05 phr with respect to the entire composition of the blend. During the process, samples were taken from the mixer after different mixing times (10, 15, 20, 25 and 30 min) and cooled in air. Samples were also taken after the same mixing times as for the first mixture, and from a 50/50 PC/PET blend mixed in the presence of 0.25 phr of TBOT at a rotor speed of 30 rpm. To study the effects of TBOT concentration, 50/50 PC/PET blends were prepared at a temperature of 270°C with a rotor speed of 30 rpm during 15 min in the presence of 0, 0.10, 0.15, 0.20 and 0.25 phr of TBOT.

Measurements

Solubility Measurements

This test was carried out by placing a sample of 0.10 g (m_0) of the PC/PET blends in a volume of 30 ml of dichloromethane (CH_2Cl_2). After stirring for a period of 24 h, the suspension was filtered and the soluble and insoluble fractions were recovered. A film of the soluble fraction was obtained after CH_2Cl_2 evaporation. The insoluble fraction was dried at 100°C and then weighed (m) to evaluate the solubility according to the following equation:

$$\text{Solubility}(\%) = \left(\frac{m_0 - m}{m_0}\right) \times 100$$

Differential Scanning Calorimetry (DSC)

Thermal analysis was carried out in a Mettler 30 DSC instrument at a heating rate of 10 K/min, by scanning the samples from room temperature up to 300°C, under nitrogen. The melting and the crystallization temperatures T_m and T_c respectively were evaluated on the basis of the thermograms of the first scanning of the samples. The crystallinity χ^c was calculated according to the following equation:

$$\chi^c = \frac{\Delta H_m}{\Delta H_m^0}$$

where, ΔH_m and ΔH_m^0 are respectively the melting enthalpy of the sample and the equilibrium melting enthalpy of a pure PET crystal. The value of ΔH_m^0 equal to 140 J/g was used as suggested by Wunderlich [29].

Scanning Electron Microscopy (SEM)

A Philips XL 20 scanning electron microscope was used to examine the morphology of the 50/50 PC/PET blends prepared with 0.05 phr of TBOT for mixing times of 10 and 30 min and at rotor speeds of 30 and 130 rpm. The test was performed by the observation of the surfaces produced on fracturing at liquid nitrogen temperature and after coating with a conductive layer of gold.

RESULTS AND DISCUSSION

Solubility Measurements

The first evidence of the occurrence of exchange reactions between PC and PET during melt mixing is provided by the results of the solubility test which are plotted in Figures 1 and 2. Figure 1 shows that for the blends prepared with 0.05 phr, a low concentration, of TBOT, the longer the mixing time, the higher are the values of solubility in CH_2Cl_2. These variations are explained by the fact that when the mixing time is short, the formation of a block copolymer with a limited solubility is favored. But, when the mixing is maintained for a longer
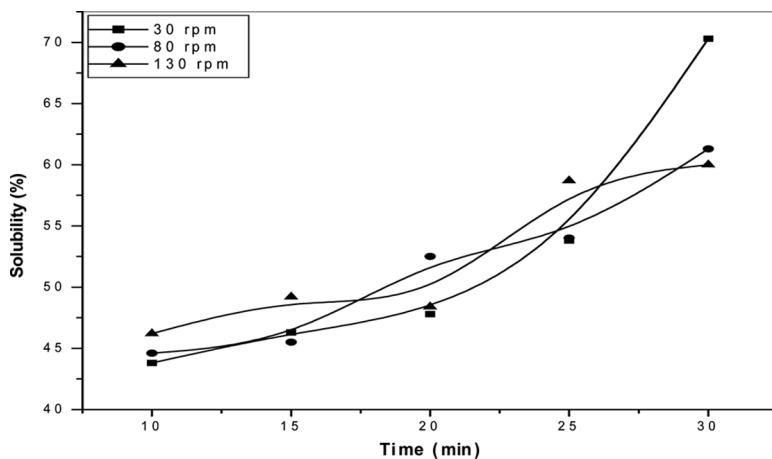
FIGURE 1 Variations of the solubility of 50/50 PC/PET blends prepared in the presence of 0.05 phr of TBOT with the time and the rotor speed of mixing.
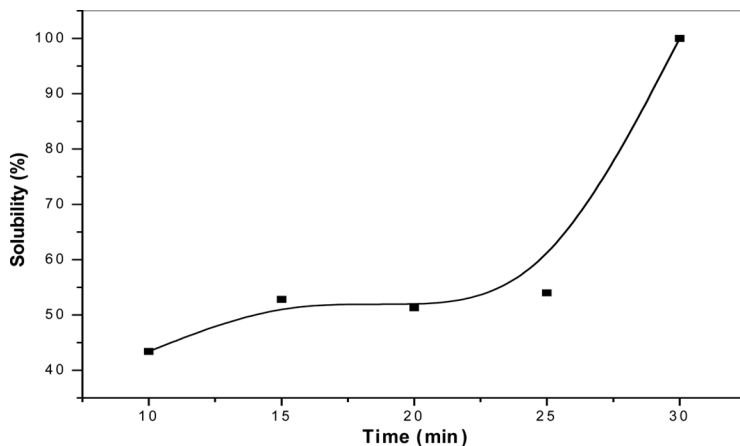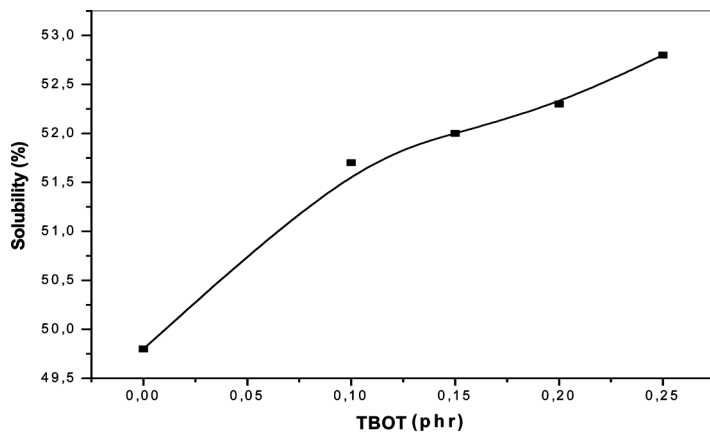
FIGURE 2 Effects of mixing time on the solubility of a 50/50 PC/PET system prepared in presence of 0.25 phr of TBOT at a rotor speed of 30 rpm.

period, more exchange occurs and the block copolymer lengths are progressively reduced, allowing the formation of a progressive statistical structure. Thus the resulting copolymer has a higher solubility in the CH_2Cl_2.

After varying the rotor speed of mixing, small changes were noticed in the values of the solubility. Transesterification reactions are molecular processes that occur first between portions of chains that are very close to each other. This neighborhood enclosing the chains disposed to interact is thought to be unaffected and unperturbed when the mixing speed is varied. Hence, on prolonging the mixing time, transreactions concern also the blocks contained in a main chain. So, the exchanges between the functions enclosed in these blocks can not be affected by the interface renewal, which is governed by the rotor speed of mixing but mainly by the time during which they are maintained in intimate contact.

For the blends prepared with 0.25 phr of TBOT, Figure 2 shows that the solubility increases with time of mixing, and after 30 min a completely soluble product is formed. This result is ascribed to the shorter sequences of PET in the blend which has been mixed for a long period with a substantial concentration of catalyst.

The effect of TBOT concentration on the solubility is revealed by Figure 3. The value of solubility of the uncatalyzed PC/PET blend is close to 50%, which indicates approximately the total absence of chemical interactions between the two homopolymers during melt mixing without catalyst. For the catalyzed blends, Figure 3 suggests

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FIGURE 3 Effect of TBOT concentration on the solubility of 50/50 PC/PET blends prepared at a rotor speed of 30 rpm during 15 min.

that a mixing time of 15 min was sufficient to produce only a low level of exchanges between PC and PET, and thus the solubility values of these blends have only slightly increased.

Thermal Analysis

The evaluation of PC and PET glass transition temperatures, Tg_{PC} and Tg_{PET} by DSC, provides the values of 140°C and 80°C, respectively. Thermal properties of PC/PET blends have showed a great dependence on the time of residence in the melt and on the concentration of TBOT. Figure 4 gives the variations of the crystallization temperature T_c of the blends prepared with 0.05 phr of TBOT versus the time of mixing. When the mixing process is prolonged, the crystallization of the PET component becomes more difficult as is indicated by the changes in the cold-crystallization temperature. T_c moves to higher temperatures while Figure 5 shows that T_m moves slightly to lower ones. The effect of rotor speed is not noteworthy because very small variations are observed when it is varied.

Figure 6 shows the crystallinity variations of the blends prepared in the presence of 0.05 phr of TBOT versus the mixing time. The crystallinity varies slightly because the low concentration of TBOT has not allowed a sufficient amount of copolymers that can alter significantly the crystallization behavior of the system.
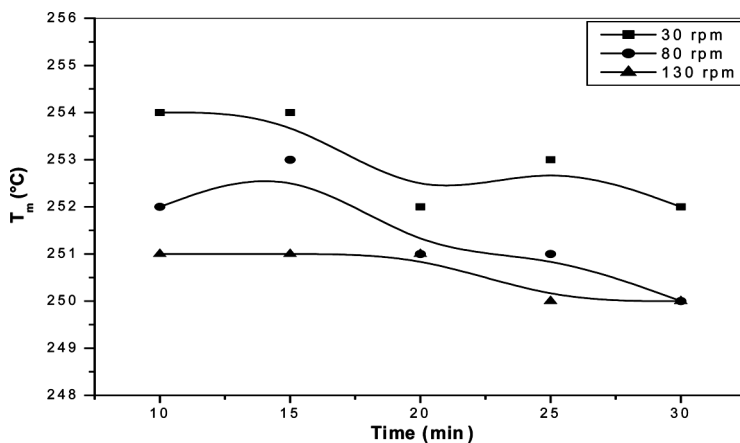
For the blends prepared with 0.25 phr of TBOT, Figure 7 reveals that the crystallization exotherm of the PET component decreases in
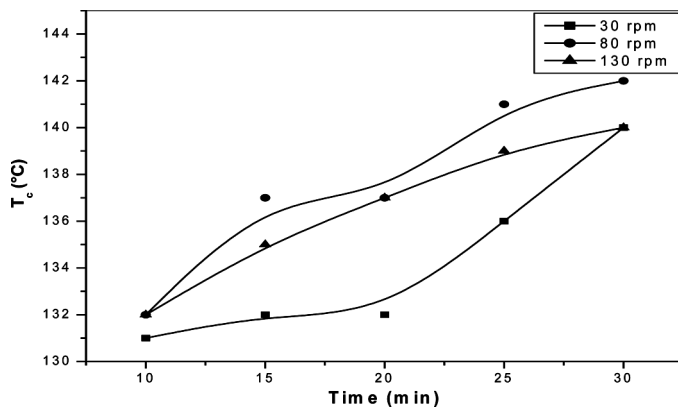
FIGURE 4 Effect of mixing time on the crystallization temperature of 50/50 PC/PET blends prepared with 0.05 phr of TBOT.

intensity and shifts to higher temperatures, while the melting endotherm decreases also but shifts to lower temperatures when the mixing time increases. These variations are much better illustrated in Figure 8 which shows a significant increase of the crystallization temperature and a decrease of the melting one.

After 30 min of mixing, the crystallization exotherm and the melting endotherm do not occur, as is well-illustrated by Figure 7. Moreover, only one glass transition temperature was observed at an

FIGURE 5 Effect of mixing time on the melting temperature of 50/50 PC/PET blends prepared with 0.05 phr of TBOT.
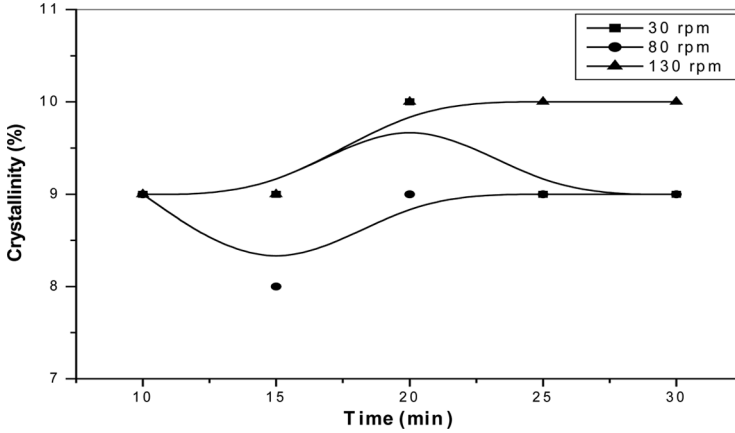
FIGURE 6 Effect of mixing time on the crystallinity of 50/50 PC/PET blends prepared with 0.05 phr of TBOT.

intermediate value between those of PC and PET. The evaluation of the T_g value of this material, based on PC and PET and on their copolymers, according to the equation given by Fox [30] and Couchman [31, 32]:

$$\frac{1}{T_g} = \frac{\omega_{PC}}{T_{gPC}} + \frac{\omega_{PET}}{T_{gPET}}$$
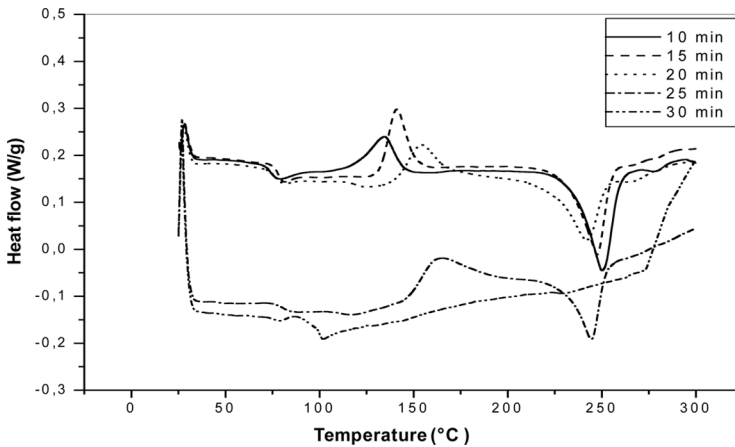
FIGURE 7 DSC analyses of 50/50 PC/PET blends prepared with 0.25 phr of TBOT for different mixing times.
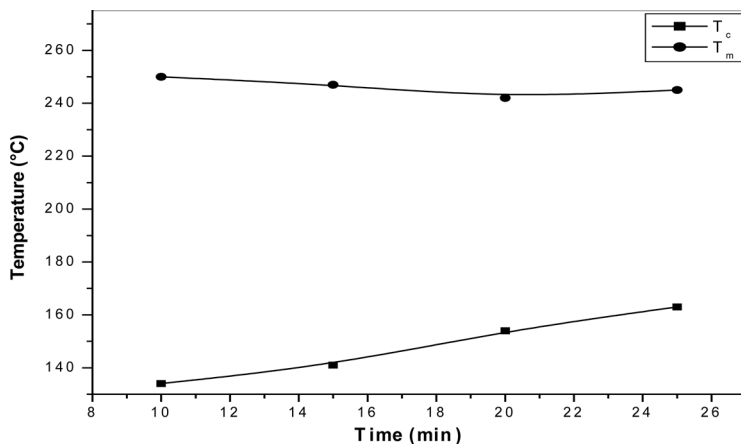
FIGURE 8 Effect of mixing time on the crystallization and melting temperatures of 50/50 PC/PET blends prepared with 0.25 phr of TBOT.

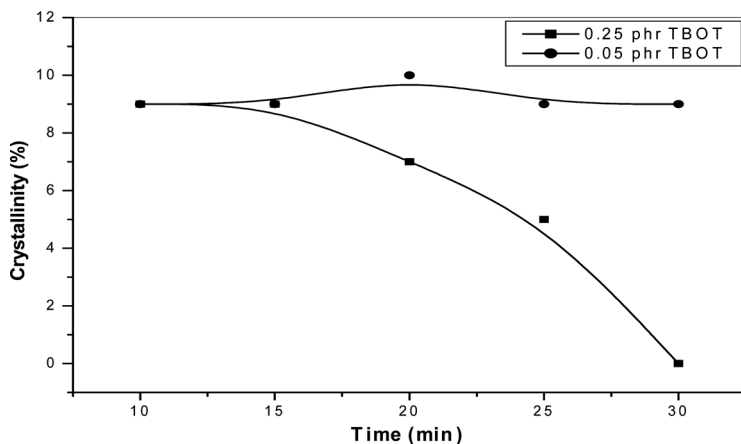provides an approximate value of 103°C, which is very close to the experimental value of 101°C.

The degree of crystallinity varies slightly for the blends containing 0.05 phr of TBOT, but it decreases considerably when the TBOT concentration is increased up to 0.25 phr and the mixing time is prolonged, as is plotted in Figure 9. For the blends prepared with

FIGURE 9 Effect of mixing time on the crystallinity of PC/PET blends prepared with 0.05 phr and 0.25 phr of TBOT at a rotor speed of mixing of 30 rpm.

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A

B

C
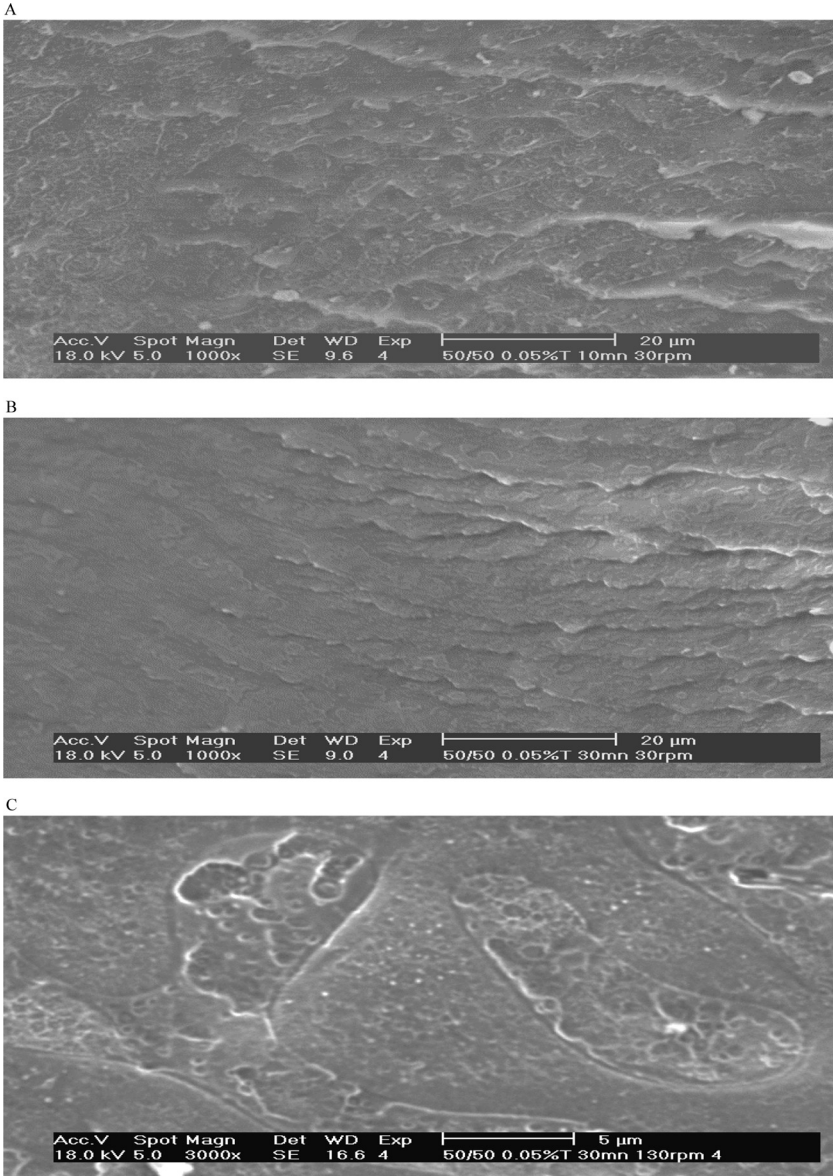
FIGURE 10 SEM micrographs of 50/50 PC/PET blends melt mixed with 0.05 phr of TBOT for: (A) 10 min at 30 rpm, (B) 30 min at 30 rpm and (C) 30 min at 130 rpm.

0.25 phr, the decrease of crystallinity is large and after 30 min of mixing, a completely amorphous material is obtained. This conclusion is well supported by the solubility results which revealed that from this blend, a totally soluble product is attained.

Microscopic Observations

The morphologies of 50/50 PC/PET blends melt mixed at 30 and 130 rpm in the presence of 0.05 phr of TBOT are represented by Figure 10. The micrograph A shows the biphasic morphology of the blend mixed at 30 rpm for 10 min. The system consists of a continuous PET phase in which the PC phase is dispersed in irregular micro-domains. The PC particles coalesced after a mixing time of 30 min, giving rise to the coarse morphology revealed by the micrograph B. In this case, PC micro-domains dispersed in PET matrix do not give the impression of being homogeneous, but they appear to include finer PET nodules. This conclusion seems more obvious in micrograph C, representing the morphology of the blend mixed for 30 min at 130 rpm and showing that the PC micro-domains contain also PET nodules with variable dimensions, introduced into the PC phase by the mixing and interchange reactions. So, it appears evident that the PET matrix as well as PC dispersed phase do not possess homogeneous consistencies, but they seem to contain domains of each other. This result is in absolute agreement with the occurrence of some compatibilization and an improvement in the dispersion of the homopolymers in each other.

CONCLUSION

The effects of the mixing conditions and the concentration of a transesterification catalyst on a 50/50 PC/PET blend were investigated. The study was detailed by solubility measurements and by the investigation of the thermal and morphological properties.

Solubility measurements suggested that the TBOT concentration and the time of residence in the melt play a key role in the transesterification between PC and PET because it is enhanced when the mixing time and/or the TBOT concentration are increased.

The thermal characterization of the studied blends revealed also that on increasing the mixing time and the TBOT concentration, the crystallization of PET becomes more difficult. This behavior is reflected by the depression of the crystallinity and the melting temperature and by the increase of the crystallization temperature.

For the blend mixed with 0.25 phr of TBOT for 30 min, the amorphous structure deduced from the thermal analysis and the total solubility of

the product is the consequence of the complete randomization induced by the occurrence of transreactions between PC and PET chains.

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