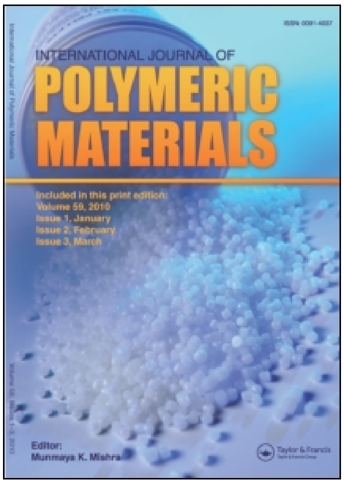

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Effects of Reactive Extrusion and Interchange Catalyst on the Thermal Properties of Polycarbonate/Poly (Ethylene Terephthalate) System

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This study was performed in order to evaluate the effects of transesterification reactions on the thermal properties of the PC/PET system, as a function of homopolymer and exchange catalyst concentrations. DSC results support well that when transesterification occurs, the glass transition temperature of the PC-rich phase decreases with the increase of the catalyst's concentration. The evaluation of the PC-rich phase composition using Wood's equation showed its strong dependence on the catalyst concentration and on the initial amount of homopolymers in the system. Furthermore, it was found that the thermal stability of the studied blends falls in between those of the two homopolymers and shows an evident improvement relatively to that of the neat PET.

Keywords: PC/PET blend, thermal stability, transesterification

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INTRODUCTION

Blending is one of the most popular and cost-effective ways to produce new polymeric materials, especially when the performances of two or more components are synergistically combined. For this purpose, reactive extrusion is very widely advised and adopted for the chemical modification of the existing polymers and for blending of the immiscible ones. But despite its economical and environmental advantages, this process is still a complex technology because it involves interactions between chemistry, rheology and morphology [1,2].

Polycarbonate/polyethylene terephthalate (PC/PET) is one of the polymeric systems which recently gained a great scientific and industrial interest, both for representing a large potential market in a number of technical fields and also for involving transesterification reactions that give interfacial copolymers during catalyzed reactive blending. Several researchers in the area of polymer transreactions have pointed out that the control of the exchange rate can provide a new route for preparing copolymers in the processing equipment. Such copolymers are expected to have variation in microstructure and properties different from copolymers prepared directly by polymerization [3–7].

The phase relationship of the PC/PET system was described as complete miscibility [8], partial miscibility [9–11] and even total immiscibility [3,12–15]. In this context, Barlow and Paul [10] reported that for all the systems containing more than 60% of PET, only one glass transition temperature (Tg) was detected, while all the compositions below this range showed two Tg. Later, Hanrahan et al. [12] studied solvent-cast PC/PET blends and found by differential scanning calorimetry (DSC) and by dynamic mechanical analysis (DMA) that all their results support the total immiscibility for all the compositions, which appeared to contain two separate PC and PET amorphous phases. These contradictory results were explained by Porter and Wang [3], who attributed all the discrepancies to the occurrence of transesterification between PC and PET because of the presence of residual synthesis catalyst.

Exchange reactions between the carbonate groups of PC and the ester groups of PET begin at the interface and cause the conversion of homopolymer chains to block copolymers, when the exchange rate is still weak. The block structure of the synthesized copolymer is, after more intense transreactions, converted to a random one, especially when transesterification also concerns copolymer chains for which the reactions must be faster and easier. But, without the deliberate incorporation of a transesterification catalyst, ester-carbonate interchanges do not occur at all or produce practically unnoticeable effects on the final properties of the blend. In this context, Ignatov et al. [16–18] detailed the different activities evolved by some PET synthesis catalysts and found that tetrabutylorthotitanate (TBOT) is the most effective, because when it is freshly dispersed on homopolymer pellets before melt mixing, significant variations are noticed in the properties of the system. In a previous article [19], we have also reported that in the presence of TBOT, transesterification causes important variations in the mechanical, thermal, rheological and morphological properties of PC/PET blends. However, the activity of TBOT can also be inhibited when phosphites are incorporated in the system, because these compounds interact with carboxyl and hydroxyl end groups and chelate the Titanium atom [20].

The principal purpose of this work is to gain insight into the behavior of PC/PET blends, stabilized with triphenylphosphite (TPP), after promoting transesterification reactions in the presence of TBOT during a twin-screw extrusion. We will try also to evaluate the fractions of PC and PET in the PC-rich phase as a function of the TBOT concentration, by using the DSC results and according to Wood's equation. Finally, the present article will consider the modifications induced in the thermal stability of the system after reactive blending in the presence of TBOT and TPP.

EXPERIMENTAL

Materials

The homopolymers PC and PET used in this work are, respectively, Lexan 129 manufactured by General Electric Company and Polyclear supplied by Kosa. The transesterification catalyst and inhibitor tetrabutylorthotitanate, $[(C_4H_9\text{-}O)_4Ti]$, and triphenylphosphite, $[(C_6H_5\text{-}O)_3P]$, respectively, were purchased from Fluka. All the products were used without further purification. Polymers were dried for 24 h at 120°C before melt blending.

Melt Blending

PC/PET blends were prepared by melt mixing, using a Clextral corotating 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 the PET pellets. The resulting extrudates were quenched in water, pelletized and then dried at 120°C. In order to prevent the occurrence of further exchanges between PC and PET during thermal characterization, TPP was dispersed on all the catalyzed blend pellets before extruding then 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).

Measurements

Differential Scanning Calorimetry (DSC)

The values of the melting temperature (T_m) and the crystallinity (χ^c) of blends obtained after the second extrusion 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 of 25 to 300°C and heating rate of 10 K/min under inert atmosphere. The crystallinity was calculated according to the equation

$$\chi^c = \frac{\Delta H_m}{\Delta H_m^0} \tag{1}$$

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. A value of ΔH_m^0 equal to 140 J/g was used [21].

Scanning Electron Microscopy (SEM)

Micrographs of 30/70 and 70/30 PC/PET blends prepared with 0.25 phr of TBOT 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 were also obtained from etched samples of 0.25 phr TBOT catalyzed 70/30 and 30/70 PC/PET blends. Etching was performed in dichloromethane (CH_2Cl_2) to dissolve PC and to make the PET domains more discernible.

Thermogravimetric Analysis (TGA)

The tests were performed on a TA instrument by heating the samples from 25 to 700°C at 10 K/min. From the thermograms expressed as DTG curves and depicting the derivative of the weight loss as a function of time, it was possible to estimate the temperatures at which each stage of the degradation process starts and finishes, Td_0 and Td_f, respectively. In this context, Td_{max} and M_{res} indicate respectively the temperature at which the weight loss is the maximum and the residual mass.

RESULTS AND DISCUSSION

Thermal Behavior of PC/PET Blends

The thermograms illustrated by Figures 1–3 reveal the presence of the glass transition temperatures of both PC and PET. The appearance of the two glass transition regions reflects the existence of two amorphous phases and the immiscibility of the system. Also, the observed values are close to, respectively, the characteristic Tg of neat PET at approximately 80°C and PC at 140°C, which confirms that for the uncatalyzed blends, the two detected amorphous phases are essentially formed of neat homopolymers.

For the systems extruded with 0.05, 0.20 and 0.25 phr of TBOT, the Figures 1–3 also clearly illustrate that after blending with an interchange catalyst, two Tg values are still observed for all the concentrations; therefore, two amorphous phases are present. But, on comparing the Tg measured values in this last case with those characteristic of the uncatalyzed blends, we notice that on increasing the TBOT concentration, the characteristic Tg of the PC-rich phase shifts to lower temperatures whereas the Tg of the PET-rich phase varies slightly. The detected variations are probably the consequence of an induced compatibilization, promoted by the occurrence of transesterification reactions, which provide the opportunity for PC units

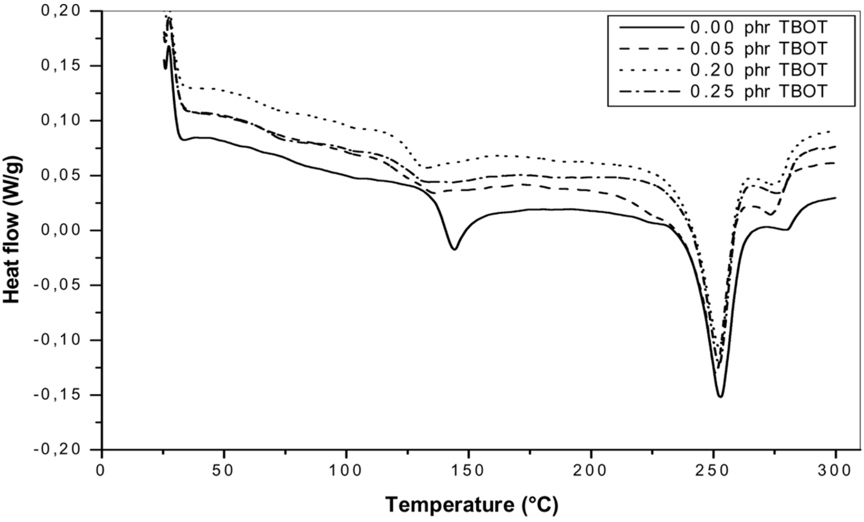


FIGURE 1 DSC thermograms of 70/30 PC/PET blends extruded with different concentrations of TBOT.

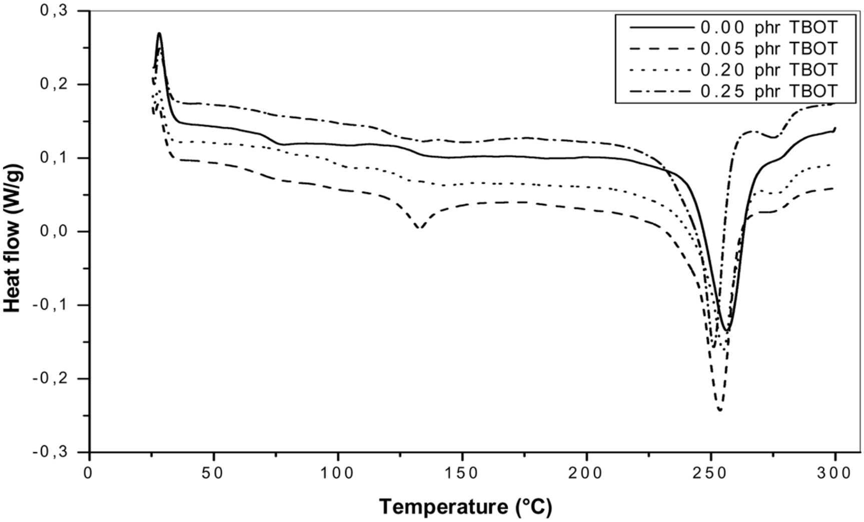


FIGURE 2 DSC thermograms of 50/50 PC/PET blends extruded with different concentrations of TBOT.

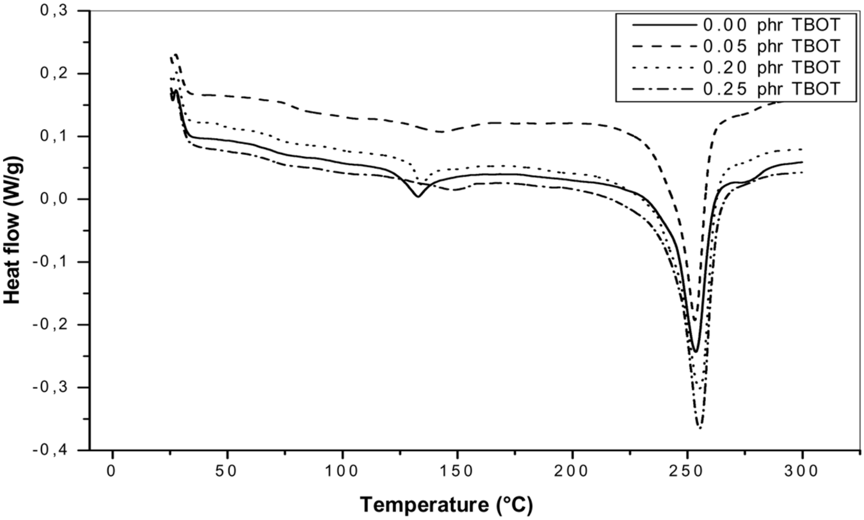


FIGURE 3 DSC thermograms of 30/70 PC/PET blends extruded with different concentrations of TBOT.

to pass into the PET phase and for PET ones to enter the PC domains. All these exchanges contribute to the creation of copolymers that act as interfacial agents and improve the compatibility of the two phases.

Moreover, the results revealed that Tg variations are much more significant for the PC-rich phase than for the PET-rich phase. This observation has already been attributed to the fact that the glass transition of PET occurs when the PC amorphous phase is still in its glassy state, which hinders the PET chains' mobility and permits only slight variations to occur in its transition temperature [22]. Mbarek et al. [23] have attributed this same situation to the fact that the PC phase is more deeply affected by transesterification than the PET one.

On the other hand, the melting temperatures of the studied blends vary only slightly with the composition of homopolymers and the concentration of TBOT. Thus, the uncatalyzed and catalyzed blends exhibit approximately the same melting temperature which is situated around 255°C. In contrast, Figure 4 depicting the variations of crystallinity versus the TBOT concentration shows a very strong dependence of this parameter on homopolymers composition. The higher the PET content in the blend, the higher the crystallinity of the whole system.

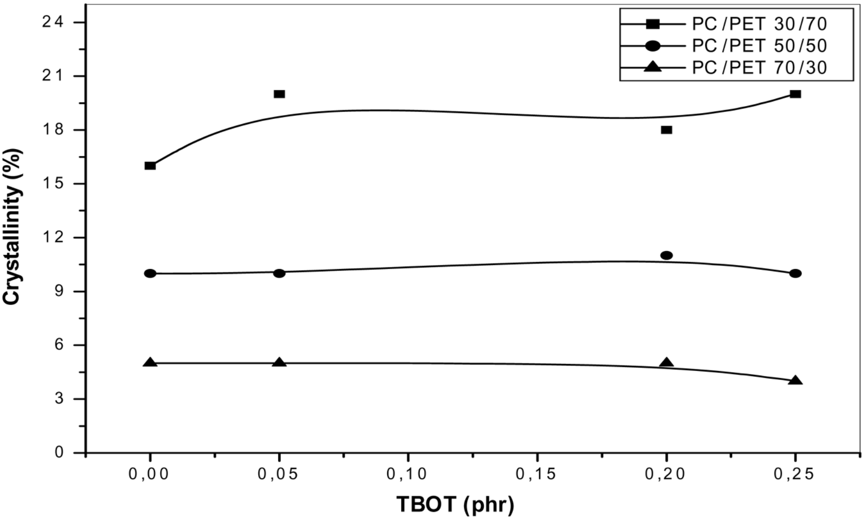


FIGURE 4 Variations of crystallinity versus TBOT concentration and PC/PET composition.

Evaluation of PC and PET Apparent Weight Fractions

From the evaluated PC and PET Tg values, it was possible to estimate the apparent weight fractions of PC and PET dissolved in the PC-rich phase in which Tg variations were much more important. These apparent weight fractions are determined by following Wood's [24] equation which is often used to describe the dependence of Tg on the composition in the case of random copolymers:

$$T_g = \omega_1 \cdot T_{g1} + \omega_2 \cdot T_{g2} \tag{2}$$

where Tg is the observed glass transition of the copolymer, ω_1 is the weight fraction of polymer 1 having Tg_1 and ω_2 is the weight fraction of polymer 2 having Tg_2. Kim and Burns [25] used this equation but rearranged as following:

$$\omega'_1 = \frac{T_{g1,b} - T_{g2}}{T_{g1} - T_{g2}} \tag{3}$$

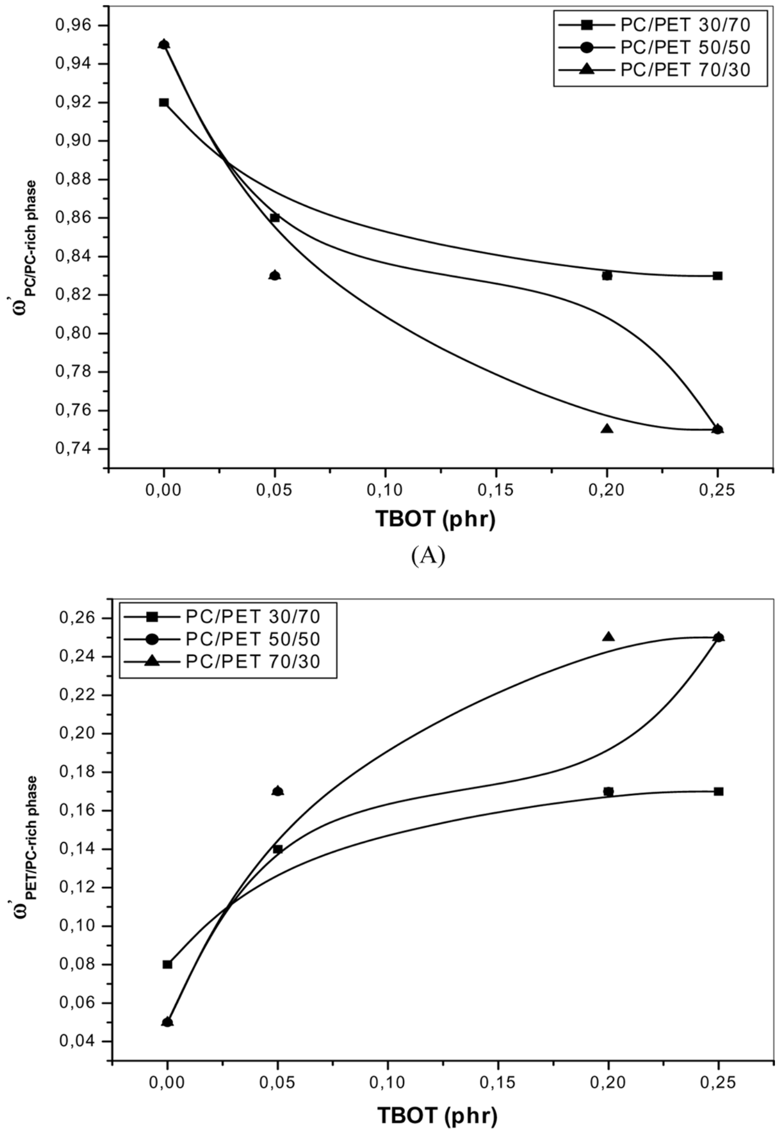
where, ω'_1 is the apparent weight fraction of polymer 1 in the polymer 1-rich phase and $Tg_{1,b}$ is the observed glass transition temperature of polymer 1 in the blend.

Figure 5 gives the variations of ω'_{PC} and ω'_{PET} in PC-rich phase versus homopolymer composition and TBOT concentration in plots (A) and (B). These confirm that for the uncatalyzed blends, no transesterification reactions are promoted. Thus, the PC-rich phase contains only a unique component which is the neat PC, and no traces of copolymers are assumed to be present because only very small Tg modifications were detected.

In the presence of the transesterification catalyst, the apparent weight fractions determined according to Wood's equation well support the occurrence of a compatibilizing effect due to the promotion of ester-carbonate reactions, which have generated copolymers in each of the two phases of this binary system. Thus, on increasing the TBOT concentration, we observe a noticeable decrease of PC apparent weight fractions. In contradistinction, an evident increase of the PET ones is detected which expresses the mutual exchange between PC and PET chains to form copolymer in the interfacial region between the two components.

Microscopic Observations

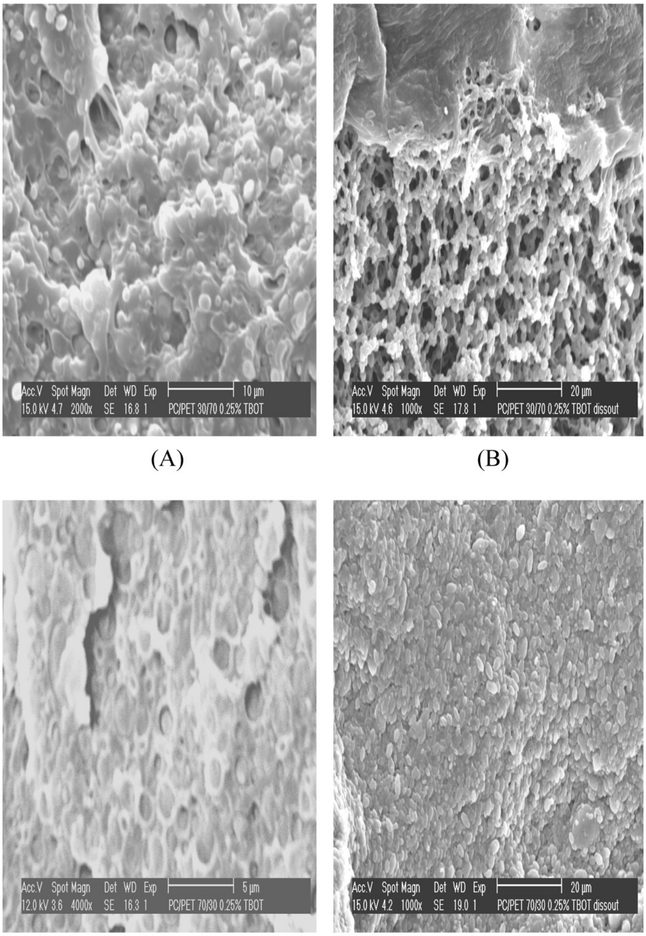
The micrographs represented in Figure 6 illustrate clearly the biphasic morphology of the 30/70 and 70/30 systems extruded in the



(A)

(B)

FIGURE 5 Variations of the apparent weight fractions in the PC-rich phase evaluated according to Wood's equation as a function of TBOT concentration and homopolymers composition: (A) PC apparent weight fractions and (B) PET apparent weight fractions.



(A) (B)

(C) (D)

FIGURE 6 Micrographs of PC/PET blends extruded with 0.25 phr of TBOT: (A) non etched 30/70 system, (B) etched 30/70 system, (C) non etched 70/30 system and (D) etched 70/30 system.

presence of 0.25 phr of TBOT. For the non-etched 30/70 PC/PET blend, the micrograph (A) reveals the PET matrix in which PC nodules having various diameters seem very well dispersed.

But, the micrograph (B), illustrating the morphology of the etched sample of this system, permits us to deduce that because of the difference in viscosity between PC and PET, these micro-domains that contained PC and are represented here as voids, are irregular and, contrary to PET ones, they do not exhibit similar forms and dimensions.

On the other hand, the micrograph (C), representing the morphology of the 70/30 PC/PET system, shows that the dispersion of PET in the PC-rich phase is better than that of PC in the PET-rich phase. This fact can also be confirmed when we observe the micrograph (D) of this blend etched in CH_2Cl_2. PET nodules are analogous and they are totally encapsulated in the PC phase, which explains the total absence of micro-domains that contain the extracted PC.

Study of the Thermal Stability of the PC/PET System as a Function of Composition

Theoretical Aspects of the Thermal Decomposition of PC and PET

According to Zimmermann [26], PET thermal degradation begins between 250°C and 300°C, but volatile product evolution becomes rapid above 350°C. The breakdown of PET chains involves at first non-homolytic scission at ester linkage and produces acid and vinyl ester end groups. There-after, the reaction of the vinyl ester with hydroxy ester end groups in the PET by transesterification leads to the elimination of acetaldehyde, which is the principal observed volatile product. But these are not the only reaction products, since CO, CO_2, CH_4, C_2H_2, C_2H_4 and benzene have also been observed.

However, PC is more thermally stable than PET, because it begins to lose weight at temperatures above 350°C. The products of degradation include chain fragments, bisphenol-A, phenol, diphenyl carbonate and CO_2. The first processes to occur in the degrading polymer are believed to be hydrolysis and phenolysis at the carbonate group. Branching reactions occur also due to thermal rearrangement of the carbonate group and eventual gelation takes place due to the removal of volatile products formed during degradation [27].

Experimental Study of the Thermal Stability of PC/PET Blends

The present part of the study concerns the determination of the influence of reactive extrusion with TBOT and TPP on the thermal stability of the PC/PET system. A preliminary test was performed on the 70/30 system extruded with 0.15 phr of TBOT in air and then under inert atmosphere. Since, only small differences were detected between the obtained differential thermograms (DTG) so we have carried out all the tests in air.

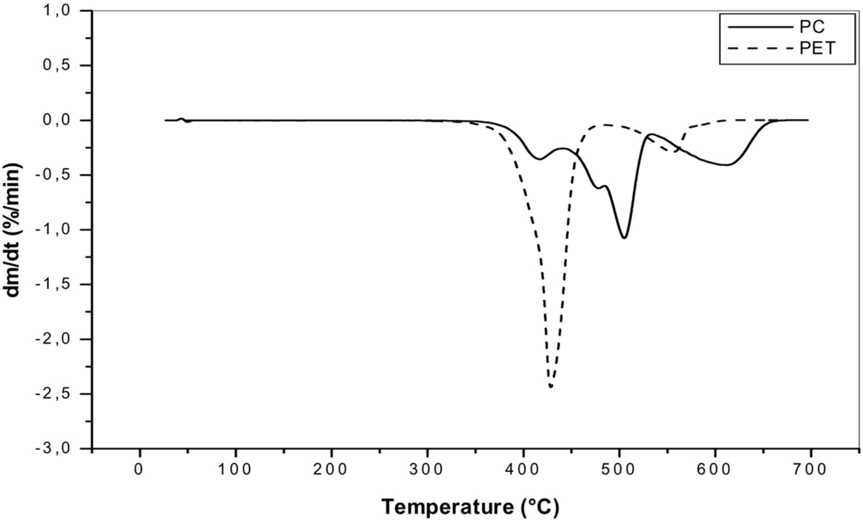


FIGURE 7 DTG thermograms of neat PC and PET.

Figure 7 gives the DTG curves of homopolymers and shows that the decomposition process of PET involves two steps while that of PC occurs in three steps.

The first step of PC decomposition starts near 350°C and ends around 440°C. The weight loss is approximately 10% at the Td_{max} of 416°C and 17% at the Td_f of 440°C. The second stage begins at this later temperature and finishes at 534°C with a weight loss of 65%. This stage is faster than the first one and is characterized by a weight loss of 50%. The third stage starts close to 534°C and finishes around 655°C with approximately no M_{res}.

For PET, the first stage of decomposition starts near 300°C and is achieved around 480°C with an important weight loss of 90%. This stage is particularly fast and characterized by a Td_{max} close to 428°C, at which the weight loss is 52%. The second stage begins at 496°C and finishes with approximately no M_{res} around 555°C.

For the systems 30/70, 50/50 and 70/30 extruded without TBOT, the DTG curves represented in Figure 8, show that the decomposition process of these blends occurs essentially in two main stages with a noticeable improvement of the thermal stability relative to that of the neat PET as is reported in Table 1. The values of the decomposition parameters confirm that these blends possess an intermediate stability between those of PC and PET and suggest also that whether PC represents the major component of the system or the minor one, its

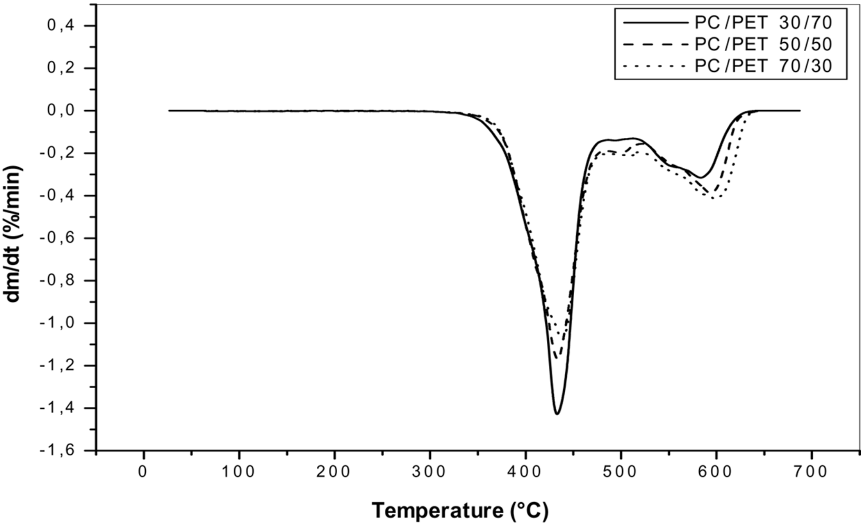


FIGURE 8 DTG thermograms of 30/70, 50/50 and 70/30 PC/PET blends extruded without TBOT.

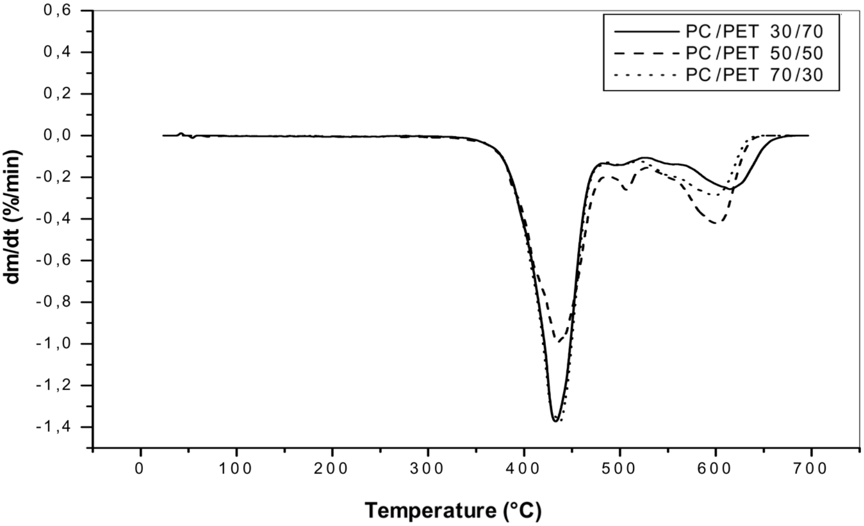


FIGURE 9 DTG thermograms of 30/70, 50/50 and 70/30 PC/PET blends extruded with 0.15 phr of TBOT.

TABLE 1 Values of the Decomposition Parameters of 30/70, 50/50 and 70/30 PC/PET Blends

	0 phr TBOT			0.15 phr TBOT		
Parameter	30/70	50/50	70/30	30/70	50/50	70/30
			First stage of decomposition			
Td_0 (°C)	314	316	318	335	338	336
Td_f (°C)	480	480	480	526	486	488
Td_{max} (°C)	432	435	438	432	439	438
Weight loss (%)	64	59	59	65	65	60
			Second stage of decomposition			
Td_0 (°C)	514	520	522	532	524	518
Td_f (°C)	633	641	643	671	647	650
Td_{max} (°C)	584	594	600	614	599	598
Weight loss (%)	36	41	41	32	35	40

incorporation is sufficient to improve the thermal stability of the entire blend.

On the other hand, Figure 9, depicting the DTG curves of these systems extruded with 0.15 phr of TBOT, shows that the thermal stability is also noticeably influenced by the ester-carbonate transreactions. The DTG thermograms of the three studied compositions involve essentially two stages characterized by decomposition parameter values different from those describing the equivalent stages for the uncatalyzed blends, as is reported in Table 1.

On considering that the most important decomposition parameters, from a practical point of view, are Td_0 and Td_{max} of the first stage of the decomposition process, it is interesting to plot their variations versus the composition of the blend. Thus, Figure 10 supports well the notion that transesterification reactions producing copolymers are very favorable to the attainment of more thermally resistant materials, because both temperatures show a noticeable increase over to those of the uncatalyzed blends as is illustrated in plots (A) and (B).

The same trend is also observed while studying the 50/50 PC/PET system, extruded with 0, 0.15 and 0.25 phr of TBOT. Table 2 confirms that despite the difference in homopolymer amounts, the decomposition parameter values of these materials are very close to those of the previously mentioned blends. Indeed, Figure 11, illustrating the DTG curves of these systems, supports the above results which show that in this case, the thermal stability depends greatly on the thermal behavior of PC and PET, and slightly on the composition of the combined components.

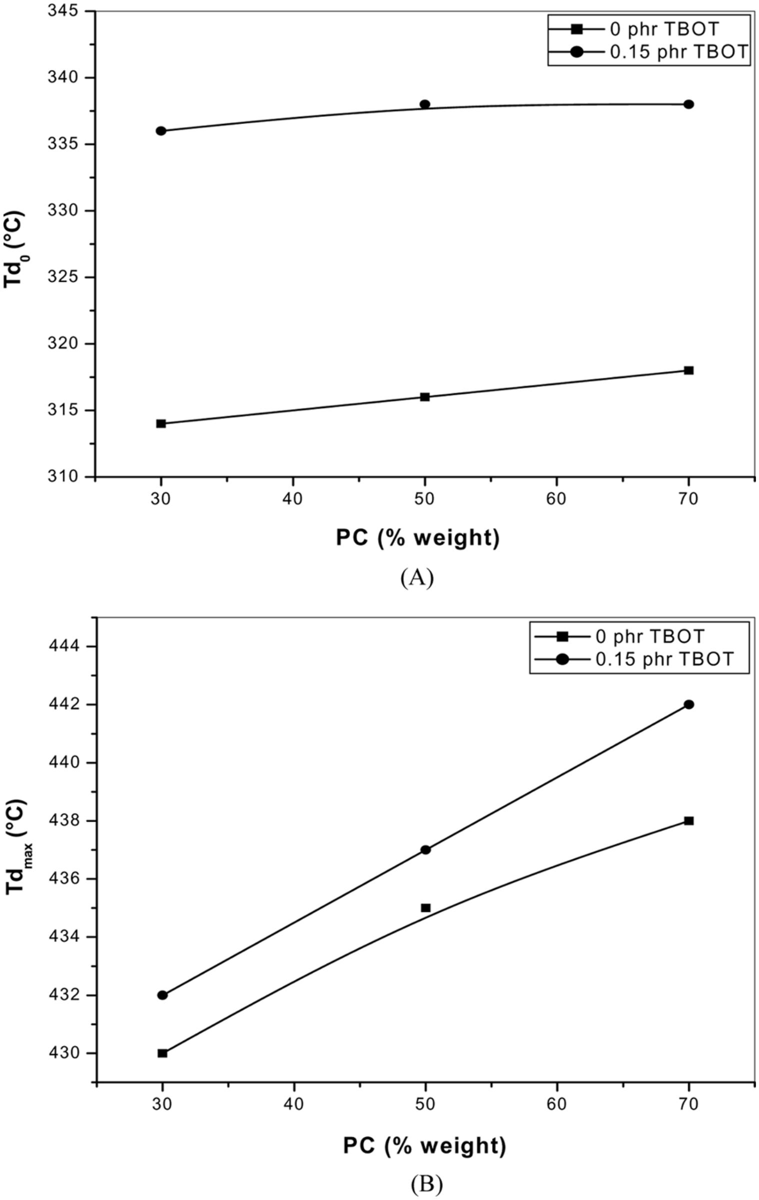


FIGURE 10 Variations of: (A) Td_o and (B) Td_{max} of the first stage of the decomposition process of PC/PET blends extruded with 0 and 0.15 phr of TBOT as a function of PC composition.

TABLE 2 Values of the Decomposition Parameters of the 50/50 PC/PET System Extruded with 0, 0.15 and 0.25 phr of TBOT

Parameter	0 phr TBOT	0.15 phr TBOT	0.25 phr TBOT
		First stage of decomposition	
Td_0 (°C)	316	338	316
Td_f (°C)	480	486	483
Td_{max} (°C)	435	439	438
Weight loss (%)	59	65	61
		Second stage of decomposition	
Td_0 (°C)	520	524	529
Td_f (°C)	641	647	672
Td_{max} (°C)	594	599	611
Weight loss (%)	41	35	39

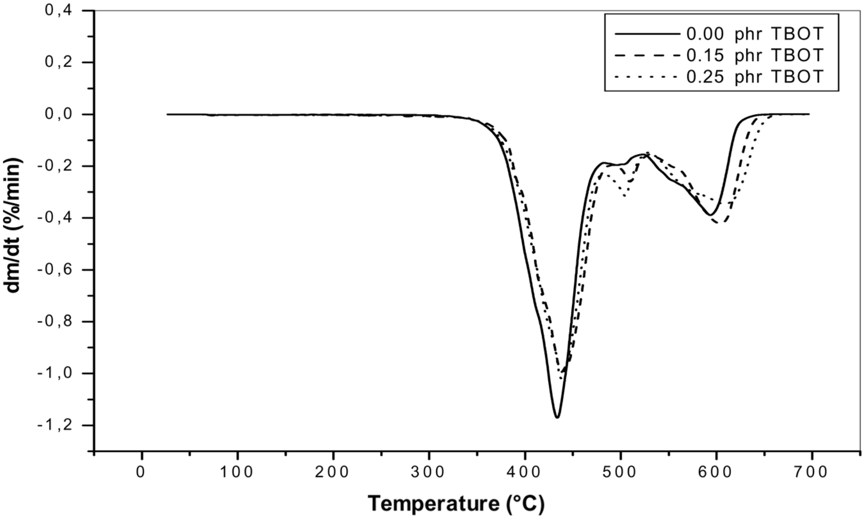


FIGURE 11 DTG Thermograms of 50/50 PC/PET catalyzed blends extruded with 0, 0.15 and 0.25 phr of TBOT.

CONCLUSION

In this article, Wood's equation was employed to determine PC and PET apparent weight fractions in the blends extruded in the presence of TBOT, a transesterification catalyst. The thermal stability of the system has also been investigated as a function of homopolymers' composition and TBOT concentration.

From Tg values of PC/PET uncatalyzed blends, it was concluded that without the transesterification catalyst, there was no induced compatibilization. Thus, the evaluation of PC and PET apparent weight fractions in the PC-rich phase confirmed that this domain is based on only one neat polymer, which seems to be its sole component.

After extrusion with TBOT, the noted decrease of the PC-rich phase Tg value indicated that a degree of partial miscibility is attained as a result of the interfacial generation of copolymers. The calculation of PC and PET apparent weight fractions supported the fact that the extrusion process conserved the binary morphology of the system, but imposed noticeable variations on the composition of the two phases forming the blend.

According to the thermogravimetric analysis results, the thermal stability of the blend was intermediate between those of the combined homopolymers. This fact suggested that after blending PET and PC with transesterification reactions, the thermal stability of the whole system was noticeably improved.

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