J Therm Anal Calorim (2010) 99:545–549
DOI 10.1007/s10973-009-0211-4

Effect of melt flow rate of polycarbonate and cobalt catalyst on properties of PET/PC (80/20 wt%) reactive blending

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Received: 16 February 2009 / Accepted: 10 June 2009 / Published online: 9 July 2009

Abstract The influence of PC melt flow rate (MFR) on phase behavior, thermal and rheological properties of catalysed and non-catalysed poly(ethylene terephthalate)/polycarbonate (PET/PC) (80/20 wt%) reactive blending were investigated. Two types of PC named PC1 and PC2 with MFR 3.1 and 10.8 g/10 min, respectively, were used. Each PC and the catalyst showed significant influence on calorimetric properties, thermal stability and WAXS patterns of the blends. Regarding to TG/DTG, the blends degraded in two steps which were attributed to PET rich phase and PC one and permit to infer that a partially miscible blends were produced.

Keywords Cobalt acetylacetonate II · Flow property · MFR · PET/PC reactive blending

Introduction

Due to so many prominent properties, PET and PC have been used as engineering plastics. Its crystalline state provides PET excellent chemical and barrier properties but poor impact resistance. Conversely, amorphous PC possesses high impact toughness, excellent optical properties and good dimensional stability but low chemical resistance [1, 2]. In general, ease of processing, improvement of production cycle, toughness and dimensional stability are reached when a crystalline polymer is blended with an amorphous one. These characteristics have become PET/PC blend feasible for automotive, packaging applications and so on [3, 4]. Reactive blending has been performed as a route for producing PET/PC blend. In that system, the occurrence of chemical reactions in the molten state leads to a new material with combined properties [5, 6]. Although, miscibility of PET/PC blends has been studied exhaustively different results arose and most of them did not take into account the transesterification/esterification and side reactions during the processing. The extent of these reactions can affect the phase structure, mechanical and thermal properties of the blends and so on [7–13]. The progressive development of interchange reactions depends on the blending conditions which include temperature, processing time, melt viscosity ratio of polymers, catalyst and so on. Among these factors, there will be one or more which act remarkably and different levels of compatibility can be reached [5, 14–17].

The aim of this work was to investigate the effect of PC with different melt flow rates and cobalt catalyst as modifier agents of thermal and rheological properties of PET/PC reactive blending.

Experimental part

Materials

PET and PC were supplied by Mossi & Ghisolfi Group and GE Plastics South America, respectively. The PET's melt flow rate (33.0 g/10 min) and density (1.39 g cm^{-3}) were

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determined according to American Society for Testing and Materials, ASTM D 1238 and ASTM D 792, respectively. Two kinds of PC labeled PC1 (3.1 g/10 min) and PC2 (10.8 g/10 min) with density 1.2 g cm^{-3} were used. Commercial cobalt acetylacetonate II was produced by J.T. Baker Chemical Co. was used as catalyst.

Blending

PET/PC (80/20 wt%) blends, with and without catalyst, were prepared in a co-rotating twin-screw extruder (L/D = 36 and 22 mm of screw diameter) equipped with vacuum system at 190–255 °C and 150 rpm. Before processing, the catalyst was added to PC and all polymers were dried for 16 h at 120 °C to remove water. After blending, the material was grounded for easing its handling.

Thermal analysis

DSC experiments

Calorimetric measurements were carried out in a Perkin-Elmer differential scanning calorimeter (DSC-7). The sample was heated from 40 to 300 °C at heating rate of 10 °C min^{-1} (1st scan), under nitrogen atmosphere, kept for 2 min and then cooled up to 40 °C at maximum cooling rate (second scan). Both procedures were done in order to erase the thermal history. A second heating (third scan) was carried out in the same protocol of the first scan. Finally, the sample was cooled up to 40 °C at 10 °C min^{-1} of cooling rate (fourth scan). The glass transition temperature (T_g), melting temperature (T_m) and enthalpy of fusion (ΔH_m) were measured from the curves. The heating and cooling crystallization temperatures, respectively, T_{ch} and T_{cc}, were determined when it was possible. For each blend, the PET's degree of crystallization (X_c) was calculated from the ratio of PET endothermic peak area (ΔH_m) and the enthalpy of fusion of 100% crystalline PET (136 J g^{-1}) [18], taking into account the weight of PET in the blend.

TG experiments

The TG and DTG curves of degradation were obtained by Perkin Elmer TGA-7. The analysis was carried out from 30 to 700 °C, at 10 °C min^{-1}, under nitrogen atmosphere. The T_{onset} and T_{end} were determined.

Wide angle X-ray scattering (WAXS)

In order to evaluate the crystalline parameters of PET in blends, an X-ray diffractometer Miniflex Rigaku (40 kV, 30 mA) with copper X-ray tube (CuKα, wavelength $\lambda = 1.5418$ Å) was used. The angle 2θ was scanning from 5° to 35° and data were collected step-by-step at each 0.05°. The Bragg's equation was used for calculating the interplanar distances [19].

Melt flow rate (MFR)

The melt flow rate (MFR) was performed in a Dinateste plastometer, based on ASTM D 1238. For PET and blends, the test conditions were 260 °C and 1.2 kg. For each measure, 6 g of the material were loaded in the equipment.

Results and discussion

Differential scanning calorimetry (DSC)

The Fig. 1 shows the DSC curves of the second heating (third scan) of the materials. As expected, the PET's curve showed glass transition, crystallization and melting temperatures, T_g, T_{ch} and T_m, respectively, while the PC one showed only its T_g. In the blends' curves, T_g and T_{ch} of PET are shifted to higher temperature while the T_m decreased. The T_g of PC in the blends was not calculated because it was overlapped the T_{ch} of PET. Table 1 presents the thermal parameters of the homopolymers and blends concerning data of second heating (third scan) and the second cooling (fourth scan). The T_g and T_m of PET are in agreement with literature [7, 16, 20]. For all blends, with and without catalyst, the T_g of PET increased slightly. Although the T_g of PC not could be calculated, we can conclude that the blends formed a partially miscible

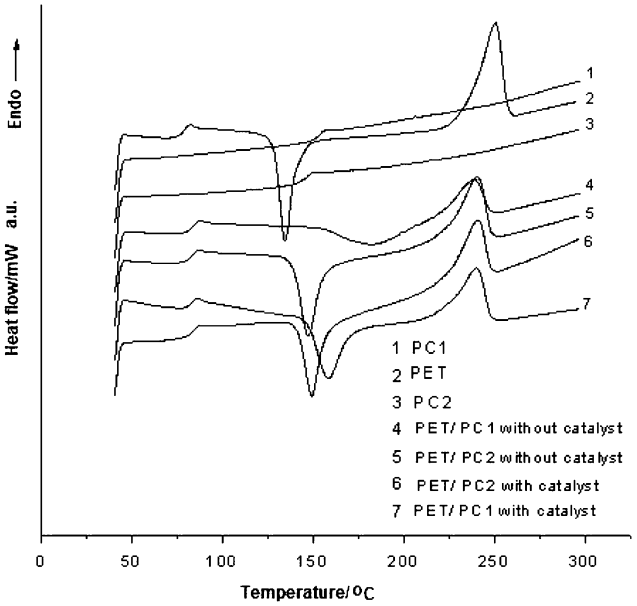

Fig. 1 DSC traces for PET, PC and PET/PC blends

Table 1 DSC parameters for PET, PC and PET/PC blends

Sample	T_g PET(°C)	T_g PC (°C)	T_{ch} (°C)	T_m (°C)	T_{cc} (°C)	X_c (%)
PET	79	–	135	250	184	40
PC_1	–	153	–	–	–	–
PC_2	–	145	–	–	–	–
PET/PC_1	84	–	181	238	–	15
PET/PC_2	83	–	147	240	151	22.5
PET/PC_1 with catalyst	85	–	179	239	–	22.5
PET/PC_2 with catalyst	83	–	149	240	153	22.5

systems because the T_g of blends ($\approx$83–84 °C) are too far those calculated by Fox's equation ($\approx$92 °C) [18]. The results of the 80/20 blend are in agreement with those reported by Mbarek and co-workers [21] although they have been prepared blends from recycled PET and PC. The T_{ch} of PET displaced to higher temperatures for both PC but there was not influence of the catalyst. The displacement was more noticeable for PC1 than PC2. In the molten state, PET/PC block copolymer was formed in some extent which was able to retard the PET's crystallization temperature as observed in the second heating in the DSC analysis. The shift of temperature was remarkable with PC1 which has the lowest MFR, that is, the higher molar mass. The PET's T_m was reduced regardless of the MFR of PCs and catalyst. The cold crystallization temperature (T_{cc}) was roughly dependent to PC's MFR. During the second cooling, PET's chains crystallized in the blends with PC2—possesses the lowest molar mass—because the PET portion in the block copolymer formed was still capable to crystallize regarding the size of block of PC and the rate of cooling. The effect of both PCs on the PET's degree of crystallinity of the blends was also observed. This parameter decreased at about 50% in the blends considering PET alone.

Thermogravimetry (TG) and derivative (DTG)

The TG curves of PET, PC and blends are shown in Fig. 2. The thermal curves of the homopolymers showed a single decay while the blends presented two-ones. As expected, PET showed lower thermal resistance than PC. The thermogravimetric curves of the blends are superposed and lay between homopolymer ones. Considering the DTG curves (Fig. 3) the blends degraded in two steps which were attributed to PET rich phase and PC one, respectively. A system with two phases was noticed by Zhang et al. [8] studying isothermal crystallization of PET/PC blend, without catalyst. Similar result was achieved by Kong et al. [4] in blends catalysed with lanthanum acetylacetonate.

In Table 2 are listed the degradation temperatures and residual matter of the materials. The T_{onset} and T_{end} of the blends were quite similar to those estimated for PET and PC homopolymers. These parameters seem to be regardless of the MFR and catalyst. For all materials, a carbonaceous residue was left due to incomplete burnt in nitrogen atmosphere. The same results were found in our previous articles [22–24] despite the blends have been processed in an internal mixer. The TG/DTG results indicated that

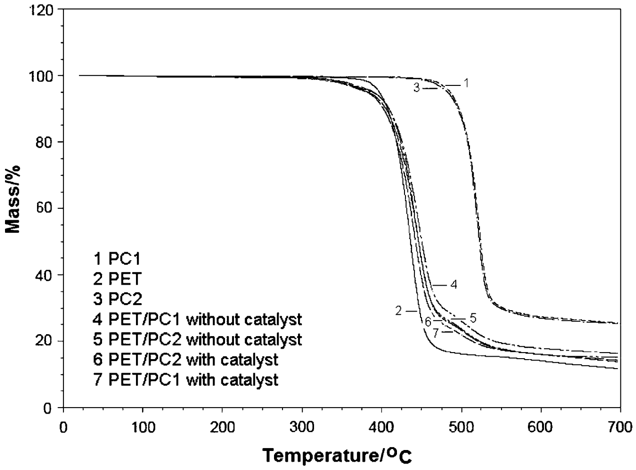

Fig. 2 TG curves of samples

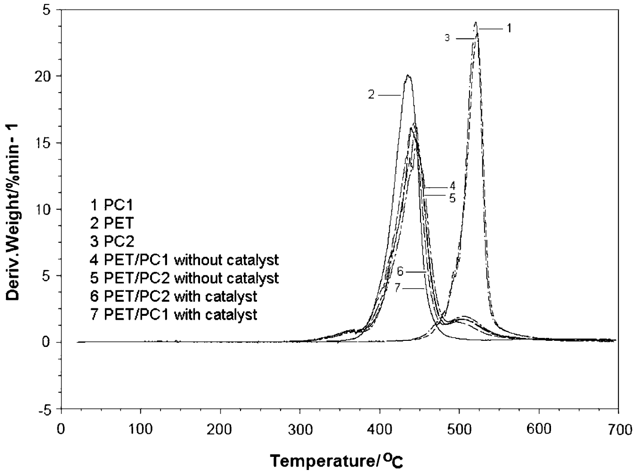

Fig. 3 DTG curves of samples

Table 2 Data taken from the TG curves for PET, PC and PET/PC blends

Sample	Degradation temperature/°C		Residue/%
	Start	End	
PET	411	475	12
PC_1	502	530	25
PC_2	502	530	25
PET/PC_1	416	545	15
PET/PC_2	412	535	14
PET/PC_1 with catalyst	415	535	16
PET/PC_2 with catalyst	411	525	14

partially miscible blends were achieved and corroborated the DSC ones.

Wide angle X-ray scattering (WAXS)

The WAXS was used to evaluate the modifications in the amorphous and crystalline structure of the materials (Fig. 4). As expected, the WAXS curve of PET presented three crystalline planes$\vec{a}$, $\vec{b}$ and $\vec{c}$, respectively, 25.7/17.0/14.1, associated to Bragg angles, as was shown in a previous work [22]. The PC diffractogram showed typical amorphous halo. The X-rays diffractrograms of non-catalysed blends seem to be independent to the MFR of PCs. Regarding the catalysed blends, the peaks of PET crystalline planes $\vec{a}$ and $\vec{c}$ disappeared whereas the $\vec{b}$ one showed less intensity specially for blend with PC1. These findings reveal the actions of different PCs and catalyst on the blends. The WAXS patterns indicated in some extent the occurrence of transesterification reaction between PET and PC in the molten state. The extent of that reaction was enough to produce block copolymer which altered PET's crystallization rate, crystal size and perfection. The results are in agreement with reduction of PET's T_m and degree of crystallinity showed in DSC analysis.

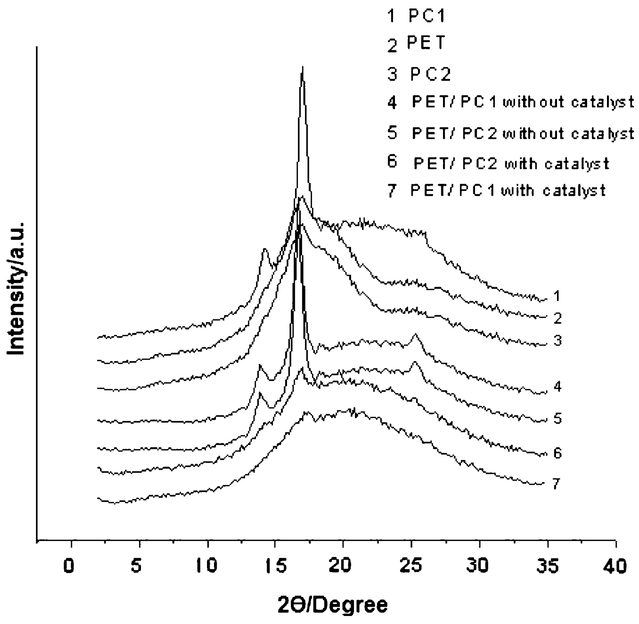

Fig. 4 WAXS curves for the homopolymers and blends

Table 3 MFI for the homopolymers and blends

Sample	MFI/g 10 min^{-1}
PET	33.0
PC_1	3.1
PC_2	10.8
PET/PC_1	5.0
PET/PC_2	4.7
PET/PC_1 with catalyst	2.4
PET/PC_2 with catalyst	2.6

Melt flow rate (MFR)

Table 3 shows MFR of neat polymers and their blends. All blends presented lower values of MFR than homopolymers. Again, the effects of PCs and catalyst on the blends are remarkable. For each pair of blends, the MFR were too close but for those catalysed, the MFR values are twice lower than non-catalysed ones. These results emphasize that there was a great interaction between the components in the molten state. Undoubtedly, the presence of cobalt catalyst had effectively an important role in the degree of transesterification of the catalysed material. Additionally, it must be into account some parameters such as residence time and temperature of processing. Garcia et al. [13] stated that the best residence time for non-catalysed PET/PC (70/30 wt%) blend must be lower than 3 min in order to avoiding degradation. Marchese et al. [20] studied the effect of the processing temperature on catalysed PET/PC (50/50 wt%) blend. In the interval of 240–250 °C, they observed no appreciable degradation of PET. The authors suggested that interchange reactions have been more prominent than degradation ones. In this work, we used processing conditions similar to those. So, we could conclude that PC, cobalt catalyst, adequate residence time and temperature all together have contributed to improving the PET's thermal stability.

Conclusions

The influence of PCs with different MFRs and cobalt catalyst in PET/PC blends was studied. Generally speaking, the presence of different PCs and catalyst affected the phase structure, thermal and rheological properties of the blends. Both DSC and TG/DTG results led to conclude that partially miscible blends were produced in the adopted processing conditions. The WAXS diffractograms of the catalysed blends showed different patterns when compared to those of the non-catalysed ones. In that analysis, the effect of the catalyst and PC1 on WAXS pattern was remarkable. The MFR of the blends decreased indicating strong interaction between blend's components in the molten state. Summarizing, the different PCs, cobalt catalyst, which speeded up the interchange reaction between PET and PC, plus the middle processing conditions, related to residence time and temperature, favored the changes in PET characteristics mainly the increase of its thermal stability.

Acknowledgements The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação Coordenação do Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Instituto Politécnico do Rio de Janeiro (IPRJ-UERJ) and Universidade Federal do Rio de Janeiro (UFRJ) for supporting this investigation.

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