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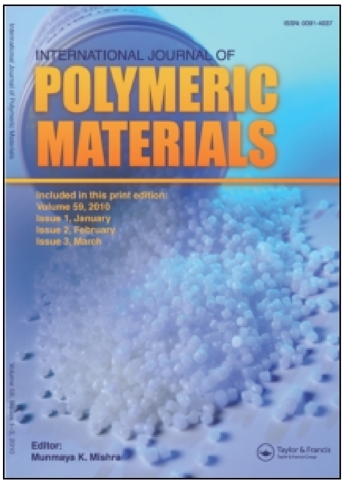

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Changes in Properties of PET/PC Blend by Catalyst and Time

Patricia S. C. Pereira[a]; Luis C. Mendes[a]; Rosário E. R. Abrigo[a]
[a] Instituto de Macromoléculas Professora Eloisa Mano (IMA), Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Rio de Janeiro, Brazil

To cite this Article Pereira, Patricia S. C. , Mendes, Luis C. and Abrigo, Rosário E. R.(2008) 'Changes in Properties of PET/PC Blend by Catalyst and Time', International Journal of Polymeric Materials, 57: 5, 494 — 505
To link to this Article: DOI: 10.1080/00914030701816045
URL: http://dx.doi.org/10.1080/00914030701816045

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International Journal of Polymeric Materials, 57:494–505, 2008

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030701816045

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Patricia S. C. Pereira
Luis C. Mendes
Rosário E. R. Abrigo
Instituto de Macromoléculas Professora Eloisa Mano (IMA),
Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia,
Rio de Janeiro, Brazil

The effects of the catalyst and residence time on poly(ethylene terephthalate)/polycarbonate blends (PET/PC) were studied. The T_g *increased, while the* T_m *decreased with catalyst content and residence time as a consequence of exchange reactions during the processing. The extent of these reactions also influenced the crystal size of PET. Additionally, impact and tension properties were influenced by the level of transesterification reactions. The best value of impact was* $89{,}7 \pm 0{,}9\,J \cdot m$ *for the PET/PC blend which contained* 75×10^{-3} *wt% of catalyst and 10 min of residence time, which represents a fourfold increase over the neat PET. Concerning elastic modulus, the best value was 60% higher than plain PET due to a higher amount of PC chains inserted in the PET. The melt flow index showed that the presence of PC enhanced the thermal stability of PET due to the formation of PET/PC copolymers.*

Keywords: cobalt III acetylacetonate, flow property, mechanical properties, PET/PC reactive blending, phase behavior

Received 7 October 2007; in final form 15 October 2007.

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

Address correspondence to Luis C. Mendes, Instituto de Macromoléculas Professora Eloisa Mano (IMA), Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco J, P.O.Box 68525, Avenida Horácio Macedo, 2030 21941-598, Rio de Janeiro, Brazil. E-mail: lcmendes@ima.ufrj.br

INTRODUCTION

Both poly (ethylene terephthalate) (PET) and polycarbonate (PC) are engineering plastics. Commercially, PET is the most successful member of the thermoplastic polyester family, showing relatively low toughness and high resistance to common solvents. Conversely, PC has high impact strength but poor solvent resistance. Due to their intrinsic strengths and weaknesses they have been studied as special materials mainly by blending them [1,2]. Similar to polyamides, PET and PC contain reactive functional groups able to produce exchange reactions during the mixing of the polymers in the molten state [1–4].

The reactive blending of PET and PC has provided a successful route for producing new materials with combined properties [5–10]. When both are blended in the molten state, PET and PC can have exchange reactions, mainly transesterification, forming block and/or random copolymer. The phase behavior and morphology of the final product are greatly dependent on the type of copolymer [11–13].

An ambiguous discussion on the miscibility of PET/PC blends can be found in the current literature, which considers that the system ranges from completely miscible at any composition to completely immiscible [14–16]. Nassar et al. have reported that the morphology was dependent on the composition. In the range of 70–90 wt% of PET, the molten PET/PC was homogeneous and the material showed a single glass transition temperature (T_g), while compositions below that range presented two T_g. They concluded that the PET-rich blend is completely miscible in the amorphous phase, whereas the PC-rich one is divided into two amorphous phases [14]. Hanrahan and coworkers have found only one glass transition temperature (T_g) in compounds containing 60–70 wt% of PET, whereas two values of T_g were observed below this range [15]. The disagreement could be attributed to the degree of esterification/transesterification reaction that occurs between PET and PC during the melting process. In the first stage of the mixing, the exchange reaction between carboxyl groups of PET and carbonates of PC generates block copolymer. When the reaction proceeds for a longer time, random copolymer is produced. The resultant copolymers can affect the blend's homogeneity as an emulsifying agent [17–21].

There is hardly any work on mechanical properties of PET/PC blend. Kong and collaborators have prepared a PET/PC 50/50 blend with and without a catalyst [22]. They have pointed out that the products have shown poor mechanical properties. Conversely, Fraise and coworkers, using recycled PET and PC, have achieved high values of impact and tension properties in their blended products [23].

Mendes and collaborators have prepared blends of PET/PC using cobalt acetylacetonate as an external catalyst and concluded that the residence time and type and amount of catalyst influenced the thermal properties and composition of the resultant copolymers [24,25].

The aim of the present paper is to evaluate the effect of the cobalt catalyst and its processing time as factors affecting the phase behavior, mechanical, thermal and flow properties of PET/PC reactive blending. According to our findings, the best properties were reached at 10 min and 75×10^{-3} wt% of catalyst concentration.

EXPERIMENTAL PART

Materials

PET and PC were supplied by Braskem and GE Plastics South America, respectively. According to the supplier, PET intrinsic viscosity and density were $0.80 \pm 0.02\,\mathrm{dl \cdot g^{-1}}$ and $1.39\,\mathrm{g \cdot cm^{-3}}$, respectively. The PC MFI and density were respectively 2.5 g /10 min and $1.2\,\mathrm{g\,cm^{-3}}$, as showed in the technical sheet. The commercial cobalt III acetylacetonate was produced by J.T. Baker Chemical Co.

Blending

PET/PC (50/50 wt%) blends were prepared in Haake Reomix 600 internal mixer at 270°C, 60 rpm, at different processing times (5–20 min) and catalyst concentrations (6.25–75×10^{-3} wt%). Before processing, the polymers had been dried for 16 h at 120°C to remove water to prevent hydrolysis in the molten state. After blending, the material was ground to make its handling easier. The neat PET and PC were processed during 10 min without catalyst and were considered as reference materials.

Thermal Analysis

The thermal analysis was carried out in a Perkin-Elmer differential scanning calorimeter (DSC-7), calibrated by high purity standards. The samples were initially heated from 40°C to 280°C/min at a heating rate of 20°C/min in a nitrogen atmosphere, kept for 2 min and then cooled down to 40°C at the same rate. A second heating cycle was then carried out up to 280°C at 10°C/min. Finally the sample was cooled to 30°C at 10°C/min. The glass transition temperature (T_g), melting temperature (T_m) and enthalpy of fusion (ΔH_m) were measured during the second scan. 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 ($136\,J \cdot g^{-1}$) [25]. The thermal parameters of the homopolymers and blends are listed in Table 1, Figures 1 and 2.

Wide Angle X-ray Scattering (WAXS)

WAXS measurements were performed by a Miniflex Rigaku diffractometer (40 kV, 30 mA) with a copper X-ray tube (CuKα, wavelength $\lambda = 1.5418$ Å), using a compression 0.5 mm film. The film was prepared in a Carver press, at 275°C, during 1 min, under pressure of 2.7 MPa. Finally, the pressure was released and the material cooled to 25°C. The WAXS data were collected step-by-step mode of 0.05° from 5 to 35° in 2θ. Bragg's equation was used to calculate the crystal parameters. The crystallite size (L_{hkl}) was calculated using the Scherrer equation [26,27].

Mechanical Properties

The tensile properties were determined according to ASTM D 638 using injection-molded specimens (IV type) prepared in Ray-Ban injection machine model RR 3400. The injection temperature, pressure, mold temperature and injection time were 280°C, 6.5 bar, 40°C and 3 min, respectively. The tension test was performed in EMIC DL

TABLE 1 Impact Resistance, Crystal Size and Crystallinity of PET, PC and Blends

			Crystal size (L_{hkl})			
Samples	Processing time (min)	Catalyst (wt%)	L_{001}	L_{010}	Impact energy (J/m)	X_c (%)
PET	10	–	52.4	118.2	19.2 ± 0.7	36
PET/PC	10	–	53.3	119.9	34.7 ± 1.9	28
PET/PC	5	50×10^{-3}	34.1	82.0	26.9 ± 2.5	23
PET/PC	10	50×10^{-3}	24.3	67.4	40.7 ± 1.3	22
PET/PC	20	50×10^{-3}	Nd	Nd	22.1 ± 0.9	19
PET/PC	10	6.25×10^{-3}	41.6	104.5	35.1 ± 1.5	29
PET/PC	10	12.5×10^{-3}	39.9	104.4	37.0 ± 3.6	26
PET/PC	10	25×10^{-3}	44.2	120.0	38.5 ± 2.8	23
PET/PC	10	50×10^{-3}	24.3	67.4	40.7 ± 1.3	22
PET/PC	10	75×10^{-3}	48.2	125.6	89.7 ± 0.9	13

Nd: Not defined.

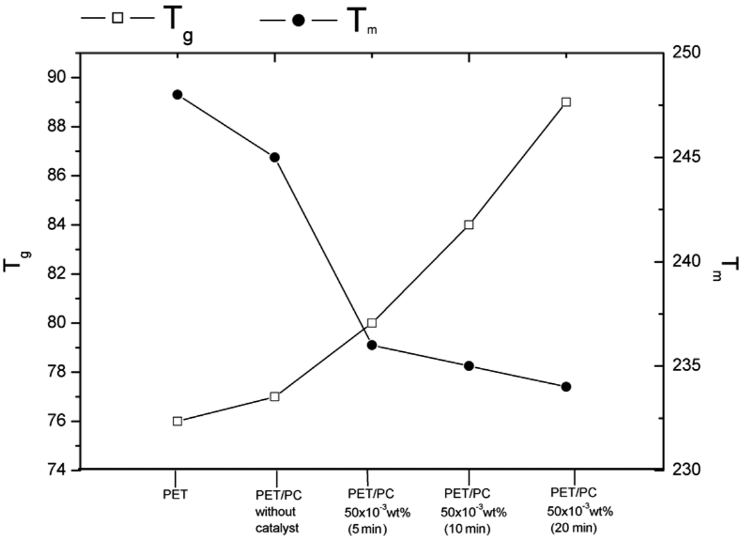

FIGURE 1 Effect of time on T_g and T_m.

equipment at the testing speed of 10 mm/min, distance between grips 55 mm and gauge length 30 mm. The result was the average value of five specimens. The Izod impact test took place following the

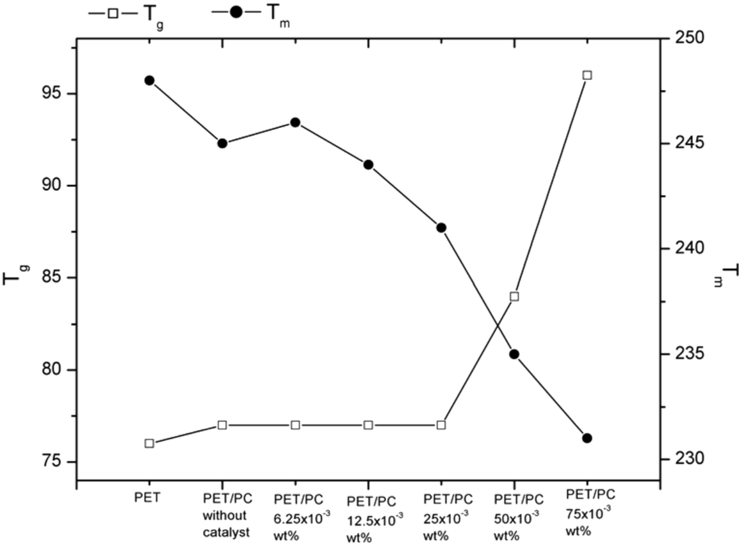

FIGURE 2 Effect of catalyst content on T_g and T_m.

ASTM D 256 using a Ceast Resil Impactor. The injected specimens were molded as described above. The result was the average of seven specimens.

Melt Flow Index (MFI)

The melt flow index was determined by Dynisco Polymer Test. The procedure described in ASTM D 1238 followed the test conditions for PET: 285°C and 2.16 kg. The result was the average of three determinations.

RESULTS AND DISCUSSION

Wide Angle X-ray Scattering (WAXS)

The WAXS was used to evaluate the modifications in the amorphous and crystalline structure of PET, PC and blends. The X-ray diffractograms of PET, PC and blends as a function of processing time and catalyst concentration are shown in Figures 3–4. In Figure 3, as expected [28], the WAXS curve of PET presented three crystalline planes *a*, *b* and *c*, $2\theta = 25.9$, 17.2, 14.3, respectively, as was shown in a previous paper [25]. The WAXS curve of PC exhibited an amorphous halo, typical of that homopolymer. The X-ray diffractograms curve

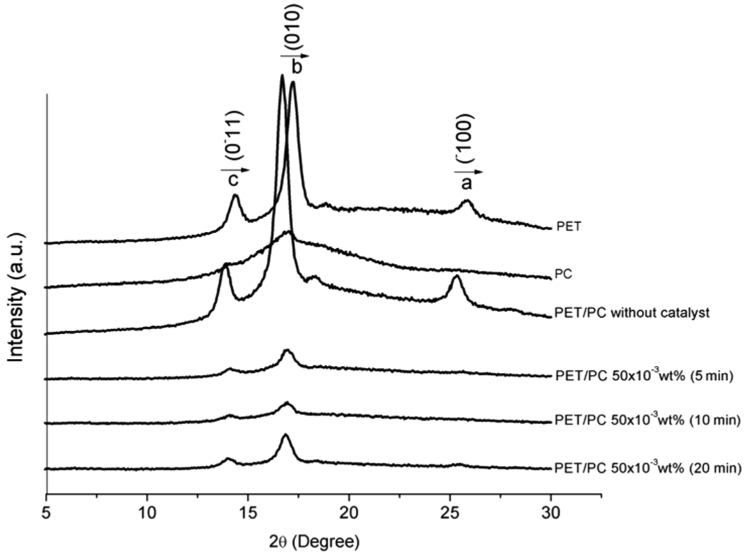

FIGURE 3 WAXS curves of PET, PC and blends processing time.

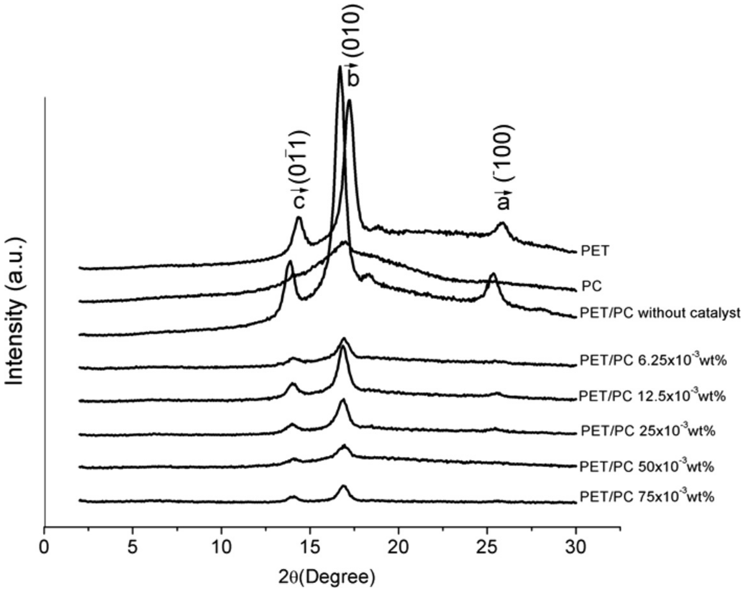

FIGURE 4 WAXS curves of PET, PC and blends catalyst content.

of the blend without a catalyst was similar to PET, but the crystalline plane *b* was slightly displaced to a lower angle due to the presence of PC. In the WAXS curves of catalyzed blends, the peaks related to crystalline planes reduced their intensities at any processing time (Figure 3). Specifically, the crystalline plane *a*, related to Miller index (100) tended to disappear in all processing times [26]. The content of the transesterification reaction increased with the residence time, meaning that more PC fragments were inserted in the PET chain. The presence of the PC unit broke the sequence of terephthalic acid-ethylene glycol (repeat unit) along the PET chain leading to the formation of copolymer and consequently the decrease of PET crystallinity. The planes of the WAXS diffractogram have the tendency to show only an amorphous halo in a completely miscible system.

Considering the processing time of 10 min and varying the catalyst content (Figure 4), the WAXS curves are similar to those shown in Figure 3. However, the influence of the catalyst is striking. It was noted that in the presence of any catalyst content the PET crystalline parameters were altered. Crystalline peak intensities also decreased and plane *a* disappeared as well. Independent of the amount of cobalt catalyst, all blends still retained the crystallinity. Such results indicate that catalyst and residence time play an important role in transesterification reactions which change PET crystalline parameters and crystallinity.

Both time and catalyst content are important for the extent of transesterification reaction. At a certain residence time, the blend needs a large amount of catalyst to attain a high level of exchange reactions. Similarly, a long period of reaction is necessary to achieve a high extent of transesterification reaction with a constant amount of catalyst. The formation of block copolymer or random copolymer depends on the residence time and catalyst content.

Thermal Properties (DSC)

The variation of PET T_g and T_m with processing time and catalyst amount is shown in Figures 1 and 2. The T_g increased gradually, while the T_m decreased abruptly attaining a value close to 235°C independent of the residence time. When catalyst content was considered, the behavior was a little different. The T_g practically remained unchanged up to 25×10^{-3} wt% of catalyst and then grew at higher concentrations. The upper value of T_g (98°C) is close to 101°C, which represents the theoretical value of T_g for a miscible system, calculated according to Fox's equation [29]. The T_m was continuously reduced with catalyst content. The changes in these thermal parameters arose from transesterification reactions mainly at catalyst concentration over 25×10^{-3} wt%. As mentioned in the WAXS section, the processing time and catalyst content influence the extent of transesterification reaction. During the mixing process, exchange reactions occur, which play an important role in the final product. This extent controls the production of block or random copolymer and affects the miscibility of the system and consequently, the values of T_g and T_m.

Impact Resistance

Table 1 shows the impact values of the materials related to PET crystal size and degree of crystallinity (X_c). The impact of the noncatalyzed blend increased. The same happened in blends with 50×10^{-3} wt% of catalyst concentration at different residence times. With respect to catalyst content, the impact attained values around 40 J · m up to 50×10^{-3} wt%. Above that amount, the best value of impact was 90 J · m, which represents a fourfold increase over the neat PET. In this work, the crystal size seems not to be an impact control parameter. The determining factor of impact resistance is the insertion of PC in the PET chain which is controlled by the residence time and catalyst content, leading as a consequence to a drop of PET crystallinity.

Tension Properties

The tension properties of the materials are presented in Table 2. The tension properties of noncatalyzed blends were similar to PET except for stress at break, which increased. The time effect was different for each mechanical parameter. The yield parameters were the same as those found for PET. The elastic modulus and stress at break rose while the elongation at break went down. Considering the catalyst content, it was observed that yield parameters were similar to PET except for 75×10^{-3} wt%. The elastic modulus and stress at break increased, but elongation at break was reduced. In the plot of elastic modulus vs. PET degree of crystallinity (Figure 5), it was noticed that the modulus grew despite the fact X_c decreased. A decrease in modulus with the decreasing of PET crystallinity was expected. This disagreement could be explained by the formation of PET and PC block/random copolymers. As can be seen in Table 2, the elastic modulus of PC is approximately seven times higher than that of the PET. Therefore, the insertion of PC units in the PET chain compensates the loss of PET crystallinity and can raise the modulus of the final product.

Melt Flow Index (MFI)

The MFI results are listed in Table 3. At to 10 min of processing, it was noticed that catalyzed blends showed MFI in the same order of magnitude as PC. Above that time the MFI increased twofold. With regard to the catalyst concentration, firstly the blend showed a

TABLE 2 Tensile Properties of PET, PC and Blends

Samples	Processing time (min)	Catalyst (wt%)	Elongation at break (%)	Stress at break (MPa)	Elastic modulus (MPa)
PC [30]	–	–	160	67	2350
PET	10	–	287 ± 21	19.4 ± 9.8	347 ± 22
PET/PC	10	–	309 ± 18	38.0 ± 1.7	352 ± 43
PET/PC	5	50×10^{-3}	261 ± 15	31.9 ± 16.2	435 ± 59
PET/PC	10	50×10^{-3}	218 ± 60	31.4 ± 5.1	554 ± 47
PET/PC	20	50×10^{-3}	71 ± 13	26.2 ± 4.4	480 ± 63
PET/PC	10	6.25×0^{-3}	304 ± 35	36.6 ± 3.7	359 ± 14
PET/PC	10	12.5×10^{-3}	302 ± 33	36.5 ± 3.3	362 ± 36
PET/PC	10	25×10^{-3}	232 ± 73	28.6 ± 3.5	376 ± 33
PET/PC	10	50×10^{-3}	218 ± 60	31.4 ± 5.1	554 ± 24
PET/PC	10	75×10^{-3}	65 ± 12	22.7 ± 10.4	499 ± 19

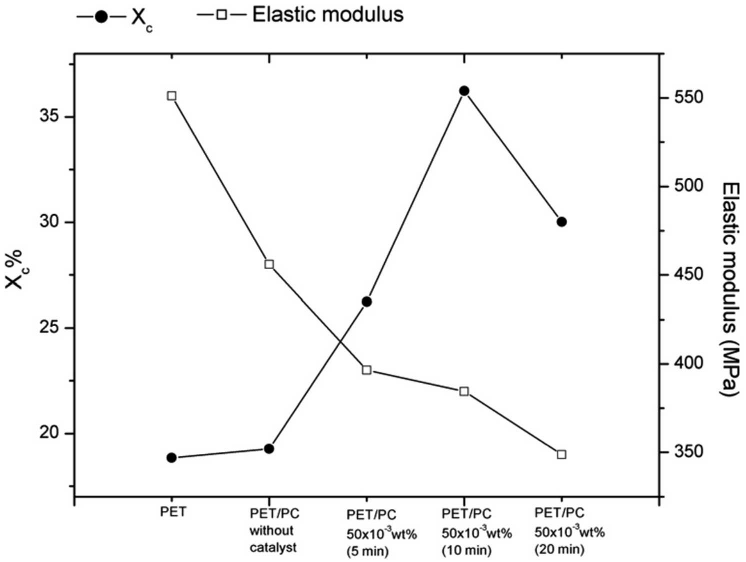

FIGURE 5 Effect of processing time on elastic modulus and X_c.

tendency to increase MFI but, with 50×10^{-3} wt% of catalyst, an inflection point arose and then a new increase was noticed. At residence time below 10 min, the PC enhanced the PET thermal stability, due to exchange reactions generating block and/or random copolymers. The PET degradation reactions were more prominent than the exchange reactions. At 75×10^{-3} wt% catalyst concentration, there was a competition between transesterification and PET degradation

TABLE 3 MFI of PET, PC and Blends

Samples	Processing time (min)	Catalyst (mass%)	MFI g/10 min
PET	10	–	187
PC	10	–	77
PET/PC	5	50×10^{-3}	82
PET/PC	10	50×10^{-3}	95
PET/PC	20	50×10^{-3}	161
PET/PC	10	12.5×10^{-3}	129
PET/PC	10	25×10^{-3}	293
PET/PC	10	50×10^{-3}	95
PET/PC	10	75×10^{-3}	182

reactions; the exchange reactions were more effective, leading to a material with better mechanical properties.

CONCLUSIONS

In this study, the effect of processing time and catalyst concentration was evaluated in PET/PC reactive blending. The WAXS and DSC analysis showed that an extended exchange reaction produced a copolymer with different T_g, T_m and crystal parameters. The elastic modulus, tensile and impact strength were improved due to the formation of PET/PC copolymers. The flow property indicated that the best material was achieved at 75×10^{-3} wt% of catalyst content and 10 min of processing. Both time and catalyst content were important to the extent of transesterification reaction. This extent controls the production of block or random copolymer, the miscibility of the system and consequently the properties of the final products.

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