

PET/PC blends and copolymers by one-step extrusion: 2. Influence of the initial polymer composition and type of catalyst

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One-step extrusion proved to be an innovative technique for the production of poly(ethylene terephthalate)/bisphenol A polycarbonate (PET/PC) compatible blends and copolymers by transesterification in the presence of a small amount of catalyst which was mechanically dispersed on the polymers before their extrusion. This method provides possibilities for producing a variety of polymeric materials with different thermal and physico-chemical properties by varying the initial polymer compositions, concentrations and type of catalyst. Copyright © 1996 Elsevier Science Ltd.

(Keywords: reactive blending; one-step extrusion; block copolymers)

INTRODUCTION

In our previous work^{1–3} we have reported some results for the synthesis of PET in the presence of various lanthanide compounds, where residues of the latter in the PET were found to possess intermediate activity towards exchange reactions during PET/PC reactive blending, although the duration of the process when performed in a Brabender Plasticord 2000 apparatus was rather long (10–30 min).

It was established that the same catalysts, when dispersed mechanically on commercial PET or PC before the reactive blending process, demonstrate higher catalytic activity towards exchange reactions than the equivalent residues of lanthanide catalysts found in the PET after its synthesis⁴. On the basis of these results an innovative technique for PET/PC reactive blending by one-step extrusion was developed^{5,6}. In this present work the influence of the initial

polymer compositions and type of catalyst employed are discussed.

EXPERIMENTAL

Materials

PET ($[\eta] = 0.65 \text{ dl g}^{-1}$ in 1,1,2,2-tetrachloroethane/phenol, 60/40 (wt/wt), at 25°C) and PC ($[\eta] = 0.61 \text{ dl g}^{-1}$ in the same solvent at 25°C) were commercial products supplied by EniChem SpA, Italy. Before using the polymers, they were dried under vacuum overnight at 120°C. Lanthanum acetyl acetonate ($\text{La}(\text{acac})_3 \cdot x\text{H}_2\text{O}$ ($x = 3-4$)) was purchased from Aldrich, while $\text{Sm}(\text{acac})_3 \cdot x\text{H}_2\text{O}$ ($x = 3-4$), $\text{Ca}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, and $\text{Pb}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ were synthesized by using standard techniques³.

Extrusion and injection moulding conditions

Reactive blending of the PET/PC system, using weight ratios of 30/70, 50/50 and 70/30, was performed in a pilot-plant ICMA MC 33 twin-screw extruder ($d = 30 \text{ mm}$; $l/d = 36$; $4-7 \text{ kg h}^{-1}$; 100–150 r.p.m.) with

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a temperature of 270–280°C in the extrusion head. The catalyst was initially dispersed on the PET pellets at a concentration of 0.033 or 0.066 mol% (with respect to PET, for all of the catalysts employed), or 0.024–0.09 wt% (with respect to the final product). The duration of the extrusion under the above conditions was ca. 1 min. The extruded products were stabilized with the commercial inhibitors 'Ultranox 626' (2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (as stabilizer)) and 'Irganox 1010' a mixture of benzenepropanoic acid derivatives (as antioxidant), both at concentrations of 0.3 wt% with respect to the final product, by additional extrusion or directly during the injection moulding stage.

Injection moulding was performed in a 'Battenfeld Unilog 4000' machine at temperatures of 245–250°C (for samples obtained in the presence of La, Sm and Pb acetyl acetonates) and 275°C (for the neat PET/PC blends and those obtained with Ca and Zn acetyl acetonates).

Measurements

The glass transition temperatures (T_g s) were measured by dynamic mechanical thermal analysis (d.m.t.a.) using a Polymer Laboratories (UK) instrument.

The crystallization and melting temperatures (T_c and T_m , respectively) were calculated from the thermograms of the first scanning of quenched samples, obtained with a Perkin-Elmer DSC-7 instrument (50–300°C, 20°C min⁻¹, under nitrogen).

Solubility tests of the samples (ground to fine powders) were carried out in a Soxhlet apparatus with methylene chloride for 48 h.

Selective degradation of the PC fraction in the PET/PC blends and copolymers was performed with piperidine in methylene chloride, as described elsewhere². This method provides a way to destroy the PC moieties and also recover the PET segments from the PET/PC blends and copolymers.

RESULTS AND DISCUSSION

Effect of initial polymer composition

As reported in our previous work⁶, PET/PC block copolymers at an initial weight ratio of 50/50 were produced by one-step extrusion in a pilot plant twin-screw extruder for less than 1 min in the presence of Sm(acac)₃ (0.045 wt% with respect to the final product). The catalyst employed was active enough to induce interchain exchange reactions in the PET/PC melt during the extrusion process. In order to explore the effect of the initial polymer composition, PET/PC blends and copolymers were also prepared at initial weight ratios of 70/30 and 30/70 by one-step extrusion without a catalyst being present and with 0.045 wt% of Sm(acac)₃ dispersed initially on the PET pellets.

The data obtained from d.m.t.a. presented in Figure 1 reveal negligible shifts of the transition temperatures of the PET and PC fractions in the neat blends extruded without catalyst, while extrusion of the same blends in the presence of the catalyst results in formation of block copolymers with a single T_g , which is regulated by the initial polymer composition. The values of the T_g were close to those calculated by the

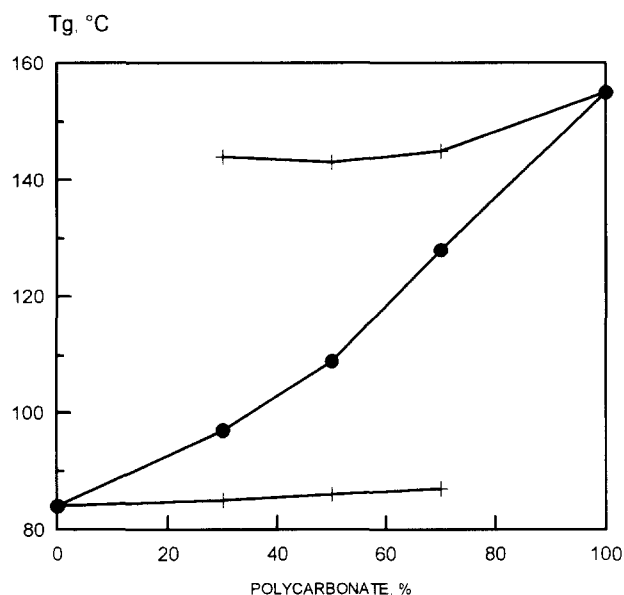


Figure 1 Influence of PET/PC initial composition on the value of T_g of the resulting blends obtained by extrusion without catalyst (+), and for copolymers produced in the presence of 0.045 wt% Sm(acac)₃ (●)

empirical Fox equation⁷:

$$1/T_g = W_{\text{PET}}/T_g^{(\text{PET})} + W_{\text{PC}}/T_g^{(\text{PC})} \quad (1)$$

where W_{PET} and W_{PC} are the weight fractions of PET and PC, respectively. For $W_{\text{PET}} = 0.7$, $W_{\text{PC}} = 0.3$ and initial values of $T_g^{(\text{PET})}$ and $T_g^{(\text{PC})}$ of 84 and 155°C, respectively, the calculated value of T_g was equal to 103°C (versus 97°C measured by d.m.t.a.). For a weight ratio of PET/PC of 30/70, the calculated transition value (131°C) was also slightly higher than the experimental one (126°C). It should be noted that the same curve of T_g versus PET content was presented by Suzuki *et al.*⁸, with the difference being that the PET/PC copolymers were obtained by reactive blending for 42–137 h at 270°C, while the one-step extrusion method in the presence of the catalyst provides the same results for times less than 1 min.

The values of the intrinsic viscosity of the neat PET/PC blend at various initial compositions were very close to those found for simple mixtures of homopolymers (Figure 2, curve 1). As reported previously⁶, slightly lower values of the viscosity of the PET/PC block copolymers obtained in the presence of the catalyst (Figure 2, curve 2) can be explained by certain conformational peculiarities of the block copolymers when compared with those of the starting homopolymers.

Data for the intrinsic viscosity of PET segments after selective degradation of the PC moieties in the PET/PC blends and copolymers confirm the absence of exchange reactions in the neat PET/PC blends extruded without catalyst (Figure 3, curve 1), while the reduced values of the intrinsic viscosity of the residual PET in the product obtained in the presence of the catalyst indicate the formation of block copolymers with the PET blocks gradually shortened with a decrease in the initial PET/PC weight ratio (Figure 3, curve 2).

The values obtained for the soluble fractions of the neat blends in methylene chloride (Figure 4, curve 1) correspond exactly to the PC weight fraction, which just

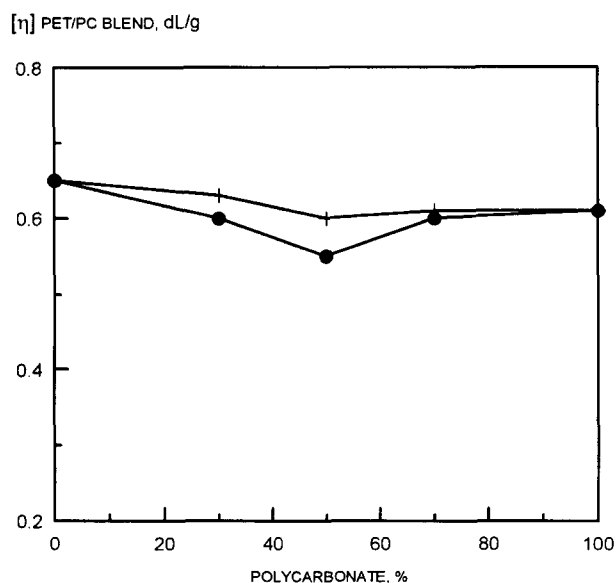


Figure 2 Intrinsic viscosity data (tetrachloroethane/phenol, 60/40 (wt/wt), 25°C) for PET/PC blends obtained without catalyst (+, curve 1), and for copolymers produced with 0.045 wt% $\text{Sm}(\text{acac})_3$ (●, curve 2)

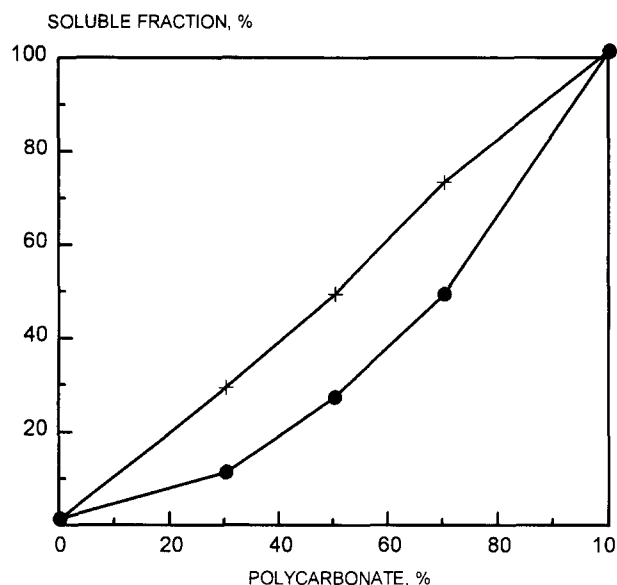


Figure 4 Solubility data (in methylene chloride) for PET/PC blends and copolymers obtained by extrusion without catalyst (+, curve 1), and in the presence of 0.045 wt% $\text{Sm}(\text{acac})_3$ (●, curve 2)

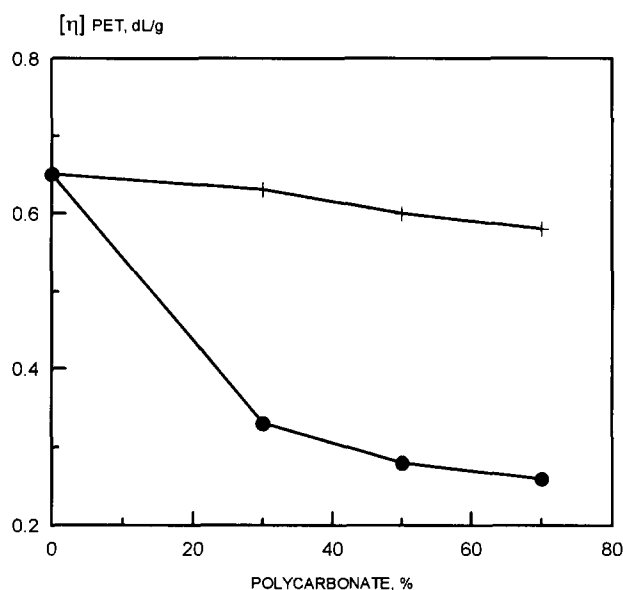


Figure 3 Intrinsic viscosity data (tetrachloroethane/phenol, 60/40 (wt/wt) 25°C) for PET segments after selective degradation of the PC fraction in the PET/PC blends obtained without catalyst (+, curve 1), and for copolymers produced with 0.045 wt% $\text{Sm}(\text{acac})_3$ (●, curve 2)

confirms the absence of any exchange reaction during the extrusion process. The negative slope of the solubility curve of the samples obtained in the presence of the catalyst indicates the progressive formation of the PET/PC block copolymers, which reduces the initial content of the non-reacted PC fraction (Figure 4, curve 2).

According to the data obtained by differential scanning calorimetry (d.s.c.), crystallization and melting temperatures of the PET phase in the PET/PC blends obtained without catalyst do not essentially change (curves 1 in Figures 5 and 6, respectively). For the PET/PC system extruded in the presence of the catalyst, the values of the crystallization temperature increase for the samples with higher PC content, while the values of

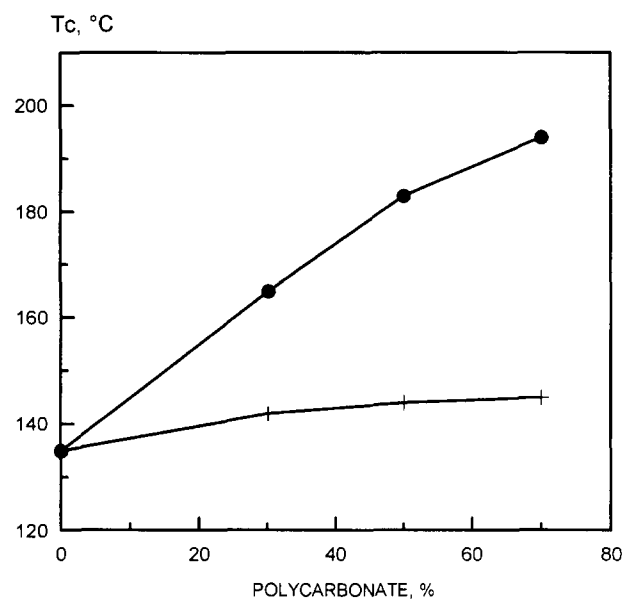


Figure 5 D.s.c. data of the products obtained by one-step extrusion; values of T_c of the neat PET/PC blends (+, curve 1) and of copolymers obtained in the presence of 0.045 wt% $\text{Sm}(\text{acac})_3$ (●, curve 2)

T_m decrease (curves 2 in Figures 5 and 6, respectively). The lower melting temperatures provide an opportunity to carry out polymer processing of the PET/PC block copolymers at temperatures at least 30–35°C lower than those of the neat PET/PC blends. The enhanced values of T_c , on the other hand, result in a higher stability of the transparency of the product.

Effect of the nature of the catalyst

Along with $\text{Sm}(\text{acac})_3$, other catalysts were tested in the PET/PC one-step extrusion process. Some of the results obtained are presented in Table 1. In order to evaluate the catalytic activity of the various metals, only one type of ligand (acetyl acetonate) was used, since it provided a good solubility of the catalysts in the PET/PC

Table 1 Properties of PET/PC (50/50 (wt/wt)) blends and copolymers obtained by one-step extrusion in a twin-screw extruder in the presence of various catalysts (0.033 or 0.066 mol% with respect to PET)

Catalyst (mol% (wt%))	$T_g(I)^a$ (°C)	$T_g(II)^a$ (°C)	T_c^b (°C)	T_m^b (°C)	Solubility in CH ₂ Cl ₂ (%)	$[\eta]$ of resulting blend ^c (dl g ⁻¹)	$[\eta]$ of PET segments ^d (dl g ⁻¹)
Without catalyst	86	143	144	249	48	0.60	0.60
Sm(acac) ₃ 0.033 (0.045)	109	^e	183	232	26	0.55	0.28
Sm(acac) ₃ 0.066 (0.09)	109	- ^e	194	232	23	0.59	0.22
La(acac) ₃ 0.033 (0.044)	111	- ^e	189	236	24	0.58	0.30
Pb(acac) ₂ 0.033 (0.039)	111	- ^e	^e	^e	23	0.59	0.17
Ca(acac) ₂ 0.033 (0.024)	87	143	143	250	49	0.60	0.63
Ca(acac) ₂ 0.066 (0.048)	88	140	170	243	44	0.6	0.43
Zn(acac) ₂ 0.033 (0.026)	88	146	145	250	48	0.61	0.46
Zn(acac) ₂ 0.066 (0.052)	89.5	137.5	166	243	45	0.60	0.43

^a Results obtained from d.m.t.a

^b Results obtained from d.s.c.

^c Intrinsic viscosity of the final product (tetrachloroethane/phenol, 60/40 (wt/wt), 25°C)

^d Intrinsic viscosity of PET segments after selective degradation of PC moieties in the final product (tetrachloroethane/phenol, 60/40 (wt/wt), 25°C)

^e Not observed

melt, unlike acetates, oxalates, tartrates and phthalates of the lanthanide metals⁴. All catalysts were introduced in the same way, i.e. as 'dry blend' with the PET pellets. The extruded products were stabilized by additional extrusion with standard stabilizers (see Experimental

section) at 240°C (for the samples obtained with Sm, La and Pb acetyl acetonates) and 275°C (for all other samples).

The data presented in the table reveal that La has the same catalytic activity as Sm (all parameters of the samples are almost identical). Pb(acac)₂ proved to be the most active catalyst. When using double the concentration of Sm(acac)₃, the d.s.c. results obtained for this sample show peaks for the crystallization and melting temperatures at 194 and 232°C, respectively, while the sample extruded with 0.033 mol% of Pb(acac)₂ has neither crystallization nor melting temperatures, which indicates a higher degree of conversion of the exchange reactions in this case. As a consequence, the PET/PC copolymers have a more random structure, as can be clearly seen from the values of the T_c , T_m and intrinsic viscosity of the PET segments after selective degradation of the PC fraction.

The acetyl acetonates of Ca and Zn were not active enough to form PET/PC block copolymers even at double the catalyst concentrations. Samples extruded with these catalysts display two transition peaks and a solubility in methylene chloride which is close to 50%. However, at double the catalyst concentrations rather significant shifts of T_c and T_m were observed when compared with the values recorded for the neat PET/PC blends (see Table 1). These catalysts can be obviously used for PET/PC reactive blending at higher concentrations or at longer time of extrusion, but they would hardly provide formation of PET/PC block copolymers by the one-step fast extrusion process.

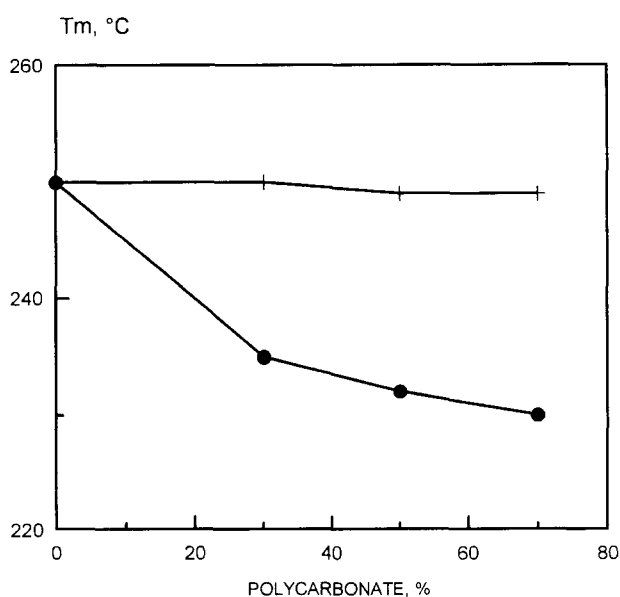


Figure 6 D.s.c. data of the resulting products obtained by one-step extrusion; values of T_m of the neat PET/PC blends (+, curve 1), and of copolymers obtained in the presence of 0.045 wt% Sm(acac)₃ (●, curve 2)

All of the results above confirm that the method of one-step extrusion in the presence of a specific catalyst provides a means of producing a variety of polymer materials based on PET/PC blends and copolymers with different thermal and physico-chemical properties by varying the initial polymer compositions, concentration and type of catalyst. The results obtained from physico-mechanical measurements on these materials will be presented in future publications.

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