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PET/PC blends and copolymers by one-step extrusion: 1. Chemical structure and physical properties of 50/50 blends

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Reactive blending of poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (PC) with a catalyst mechanically dispersed on polymers was performed by one-step extrusion for about 1 min at 275°C. The product appeared to be a transparent amorphous plastic with a single glass transition temperature. This approach provides a possibility to produce PET/PC block copolymers directly by extrusion of homopolymers or to create their compatible blends during one-step extrusion by varying the type and concentration of the catalyst. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Reactive blending proved to be a successful and low-cost way to produce compatible blends from initially immiscible polymers[1]. Block copolymers formed during reactive blending, because of interchain exchange reactions, play a role of compatibilizers. However, residues of catalysts in commercial PET (calcium acetate and antimony oxide) were found to be inefficient to promote fast exchange reactions in PET/PC blends[2]. On the contrary, residual amounts of Ti tetrabutoxide used for PET synthesis induce very rapid transesterification in the PET/PC melt[3], but it does not allow control of the chemical structure of resulting products and can also lead to severe degradation and discolouration effects.

New selective catalysts (lanthanide compounds) with intermediate activity towards exchange reactions were recently employed for PET synthesis and its further reactive blending with PC[4–8], although duration of the process performed in Brabender Plasticord 2000, was rather long (10–30 min).

The same catalysts, being dispersed mechanically on commercial PET or PC before their reactive blending, appeared to possess higher catalytic activity towards exchange reactions than the residues of lanthanide catalysts used for PET synthesis[9]. Recently, a new approach was developed on the basis of the results above: preparation of a 'dry blend' of commercial PET or PC with a catalyst provides a possibility to produce PET/PC block copolymers directly during one-step extrusion just for 1 min of the residence time in the extruder[10,11]. This argument will be considered in more detail in the present paper.

EXPERIMENTAL

Materials

PET ($[\eta] = 0.65\,\mathrm{dl\,g^{-1}}$ and $0.83\,\mathrm{dl\,g^{-1}}$ in 1,1′,2,2′-tetrachloroethane/phenol, 60/40 wt/wt, at 25°C) and PC in powder and in pellets ($[\eta] = 0.61\,\mathrm{dl\,g^{-1}}$ in the same solvent at 25°C) were commercial products supplied by EniChem S.p.A., Italy. Polymers before using were dried under vacuum overnight at 120°C. Samarium acetyl

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acetonate ($Sm(acac)_3 \cdot xH_2O$ ($x = 3$–4)) used as a catalyst was synthesized by standard technique from Sm trichloride and acetyl acetone[8].

Extrusion and injection moulding conditions

Fast reactive blending of PET and PC (50/50, wt/wt) was performed in a pilot plant twin-screw co-rotating extruder 'ICMA MC 33' ($D = 30$ mm; $L/D = 36$; 4–7 kg h^{-1}; 100–150 rpm) at 270–280°C in the extruder's head. The catalyst was initially dispersed on PET or PC pellets at a concentration of 0.011–0.066 mol% with respect to PET units or 0.015–0.09 wt% with respect to the final PET/PC blend. Duration of the extrusion under the above conditions was about 1 min.

The extruded product was cooled in water, pelletized and dried in a vacuum oven overnight at 120°C and extruded with commercial stabilizers ('Ultranox 626'* and 'Irganox 1010'†, 0.3 wt% of each of them with respect to the final product). The temperature of the second extrusion was variable in the range of 240–275°C, depending on the concentration of the catalyst employed; lower and upper temperatures were used for the PET/PC systems obtained with the catalyst (0.03–0.09%) and without it, respectively.

Injection moulding was performed in the injection moulder (Battenfeld, Unilog 4000 at temperatures of 245–275°C.

Measurements

Glass transition temperature (T_g) was measured by dynamic mechanical thermal analysis (d.m.t.a.) performed with a Polymer Lab. instrument (UK).

Crystallization (T_c) and melting (T_m) temperatures were calculated on the basis of thermograms of the first scanning of quenched samples obtained with a DSC 7 Perkin-Elmer instrument (50–300°C, 20°C min^{-1}, under nitrogen).

Melt rheology tests were performed according to a standard procedure ASTM D1238 with a CEAST instrument at 250–290°C (1.2 kg).

Micrographs were recorded by scanning electron microscopy (SEM) from the surface of the samples fractured in liquid nitrogen and covered with a conductive layer, using a Zeiss DSM 950 instrument.

^{1}H nuclear magnetic resonance (n.m.r.) spectra of the PET/PC block copolymers dissolved in $CDCl_3/CF_3COOD$ (85/15 wt/wt) were recorded with a Bruker AMX 300 instrument.

Solubility test of the samples ground to fine powder was performed in a Soxhlet apparatus with methylene chloride for 48 h.

Selective degradation of the PC fraction in PET/PC blends and copolymers was performed with piperidine in methylene chloride as described elsewhere[3]. This method provides a possibility to evaluate the length of PET segments in the blends and copolymers.

RESULTS AND DISCUSSION

As has been established[9], lanthanide compounds, being mixed with PET and PC just before their reactive blending in Brabender Plasticord 2000, induce much more rapid exchange reactions than the residues of the same catalysts in PET, remaining after its synthesis. This behaviour can be caused by the interfacial character of exchange reactions, occurring initially at the interface of the two immiscible polymers, where catalyst concentration is higher than the average concentration of the same amount of catalyst distributed homogeneously within the PET phase.

Since high intensity of melt mixing can promote interfacial exchange reactions, it was of interest to perform PET/PC reactive blending in the presence of the catalyst in a twin-screw extruder, which provides higher intensity of mixing and shear rate as compared with that of the Brabender apparatus.

The neat polymer blend of commercial PET and PC at the weight ratio of 50/50 produced by extrusion in a twin-screw extruder (see Experimental) was found to possess two distinct T_gs, corresponding to the PET and PC fractions (*Figure 1*, curve 3). There is only a small shift of PC transition peak from the initial value of 155°C (curve 1, neat PC) to 143°C, and a negligible shift of PET peak from 84 (curve 2) to 86°C. Meanwhile, extrusion of the PET/PC mixture in the presence of $Sm(acac)_3$ at the concentration of 0.045 wt% (0.033 mol% respect to PET) resulted in formation of a transparent product with a single T_g at 109°C (*Figure 1*, curve 4).

A slightly higher value was calculated by the widely used empirical Fox equation[12]

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

where W_{PET} and W_{PC} are the weight fractions of PET and PC, respectively. For $W_{PET} = W_{PC} = 0.5$ and initial values of $T_g^{PET} = 84°C$ and $T_g^{PC} = 155°C$ the calculated value of T_g is equal to 116.3°C.

Thus, the one-step extrusion of commercial PET and PC without any additional catalyst results in formation of a heterophasic blend with two distinct T_gs, whereas extrusion of the same polymers with the catalyst dispersed mechanically before blending results in formation of a transparent product with a single T_g.

Some other thermal and physicochemical characteristics

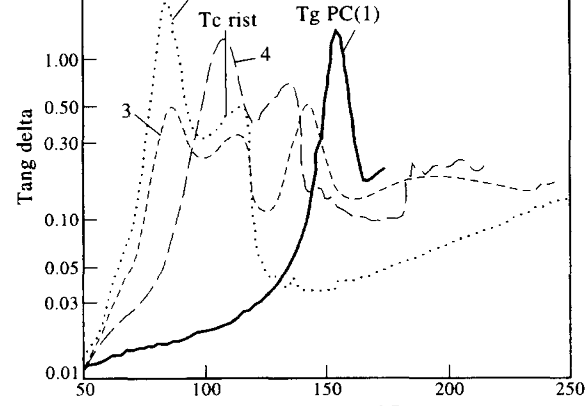

Figure 1 Data of d.m.t.a. of commercial PC (curve 1), PET (curve 2) and their blends (50/50, wt/wt) obtained by one-step extrusion without catalyst (curve 3), and in the presence of 0.045% of $Sm(acac)_3$ (curve 4)

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* 2,4,8,10-Tetraoxa-3,9-diphosphasopiro[5.5]undecane (commercial stabilizer)

† Benzenepropanoic acid derivatives (commercial antioxidant)

Table 1 Properties of the PET/PC (50/50 wt/wt) blends and copolymers obtained by extrusion in a twin-screw extruder for 1 min at 275°C and 100 rpm

	D.m.t.a.		D.s.c.				
Material	T_g (I) (°C)	T_g (II) (°C)	T_c (ΔH_c) (°C)(J g^{-1})	T_m (ΔH_m) (°C)(J g^{-1})	Solubility in CH_2Cl_2 (%)	$[\eta]^a$ of resulting blend (dl g^{-1})	$[\eta]^b$ of PET segments (dl g^{-1})
PET	84	–	135 (−19.73)	250 (20.81)	0	0.65^c	0.65
PC	–	155	–	–	100	0.61^c	–
PET/PC without catalyst	86	143	144 (−13.29)	249 (19.93)	48	0.60	0.60
PET/PC with 0.045% Sm(acac)$_3$	109	not observed	183 (− 7.13)	232 (6.93)	26	0.55	0.28

[a] Intrinsic viscosity of the resulting blends measured in 1,1,2,2-tetrachloroethane/phenol (60/40, wt/wt) at 25°C

[b] Intrinsic viscosity of PET segments after selective degradation of the PC fraction with piperidine measured in the same solvent as above at 25°C

[c] Intrinsic viscosity of starting polymers measured under the same conditions

of the PET/PC samples are presented in *Table 1*. According to the differential scanning calorimetry (d.s.c.) data obtained during the heating cycle (see Experimental), there is a slight shift of crystallization temperature of PET fraction from 135°C (neat PET) to 144°C in the PET/PC blend extruded without catalyst. Melting point is found the same as that of the neat PET (249–250°C). For the PET/PC system, extruded in presence of the catalyst, T_c is increased to 183°C, while the melting temperature is reduced to 232°C that allowed to mould the final product at a temperature 30°C lower than that of the same blend obtained without catalyst (see Experimental).

Data of solubility of the resulting blends in methylene chloride can be used for qualitative evaluation of the final polymer composition. As has been established[6–11], the initial solubility value of 50%, corresponding to the pure PC fraction, decreases with formation of PET/PC block copolymers during reactive blending, and then increases during further randomization of the block copolymers above. Since residues of catalysts in the commercial PET cannot promote exchange reactions in the PET/PC melt[2,3,7], the value of solubility of the neat PET/PC blend was close to 50%, which indicates the absence of chemical interactions in the polymer system during extrusion.

The solubility of the product obtained by extrusion of the PET/PC blend in the presence of the catalyst decreases significantly to 26%, which confirms formation of block copolymers. The resulting polymer system can be considered a PET/PC block copolymer with some content of starting homopolymers. It should be noted that the data of solubility test do not provide the possibility to calculate exactly the polymer composition of the resulting product, since PET/PC copolymers with shortened blocks become soluble in methylene chloride[3,7,9]. Combination of the solubility data, selective degradation of the PC fraction, and the n.m.r. technique can give a more detailed picture of polymer composition[6,7].

The value of intrinsic viscosity of the neat PET/PC blend (see *Table 1*) is very close to that of a simple mixture of homopolymers calculated on the basis of viscosities of starting polymers, according to additive principle for the viscosity of two polymers in solution

$$[\eta]_{PET/PC} = W_{PET}\,[\eta]_{PET} + W_{PC}\,[\eta]_{PC} \qquad (2)$$

For $W_{PET} = W_{PC} = 0.5$ the intrinsic viscosity of the simple polymer mixture is 0.60 dl g^{-1}, very close to the calculated value (0.63 dl g^{-1}). After reactive extrusion with the catalyst the value of intrinsic viscosity was found to be 0.55 dl g^{-1}, reflecting changes in the chemical structure of the product.

The method of selective degradation of PC moieties in PET/PC blends and copolymers with piperidine allows evaluation of the length of residual PET segments. A negligible decrease of viscosity from the initial value of 0.65 dl g^{-1} to 0.60 dl g^{-1}, corresponding to the PET fraction after selective degradation of PC in the neat PET/PC blend, just confirm the absence of exchange reactions during extrusion without catalyst. The much lower viscosity of residual PET in the PET/PC system extruded in the presence of the catalyst clearly indicates formation of block copolymers with PET blocks to be at least half the length as compared with the initial lengths of the PET macromolecules (see *Table 1*).

PET/PC samples extruded with and without the catalyst were also examined by a SEM technique. Thus, the micrograph of the fractured surface of the neat PET/PC blend presented in *Figure 2a* demonstrates biphasic character, whereas the micrograph of the sample extruded in the presence of Sm(acac)$_3$ revealed one polymer phase (*Figure 2b*).

Effect of catalyst concentration

All the results above were obtained at a catalyst concentration of 0.045%. In order to explore the influence of the concentration of Sm(acac)$_3$ on the properties of the resulting blends and block copolymers, extrusions of the PET/PC mixture (50/50, wt/wt) in the presence of 0.015, 0.03 and 0.09 wt% of the catalyst were performed.

As is seen from the data presented in *Figure 3*, even at the lowest catalyst concentration definite shifts of two T_gs were observed, although the product was still visually opaque. However, it becomes transparent at the catalyst concentration of 0.03%, when the sample still demonstrates two different T_gs. The temperature shifts in this case were more significant (from 86 to 97°C for PET, and from 155 to 129°C for the PC phase). A single value of T_g appears at a catalyst concentration of 0.045%. Further increase in the concentration does not lead to any change in T_g. Thus, the sample extruded with

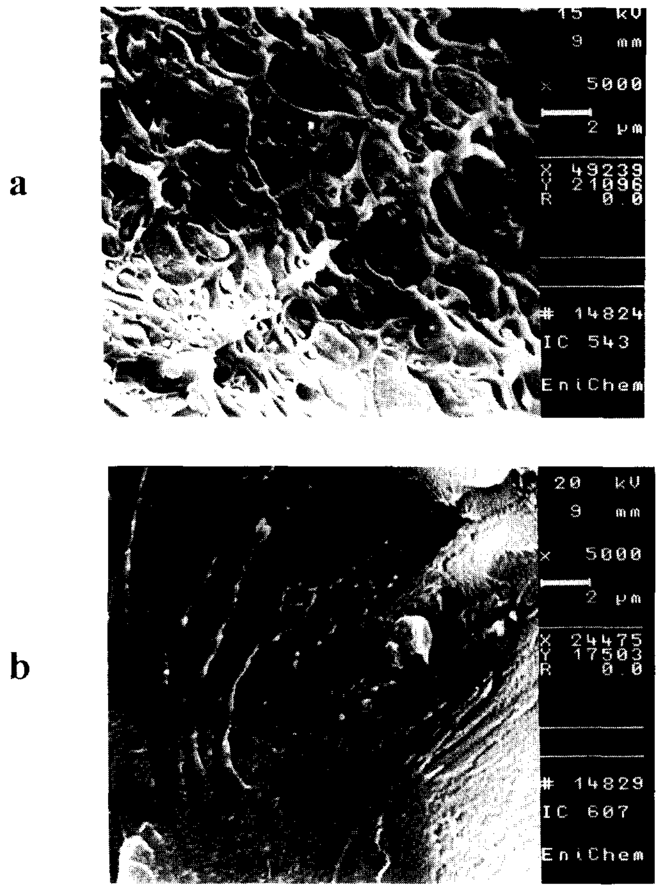

Figure 2 Micrographs of the PET/PC blends extruded without catalyst (a), and in the presence of 0.045% $Sm(acac)_3$ (b)

0.09% of $Sm(acac)_3$ has the same transition value as that of the sample with the catalyst concentration half as much.

The solubility curve (*Figure 4*) shows the same trend: the content of soluble fraction initially decreases with the increase of catalyst concentration and then remains equal with further increase of concentration. Formation of PET/PC block copolymers results in lower solubility of the final blend. A plateau on the solubility curve reflects different effects such as formation of block copolymers along with catalyst diffusion from the interface into the inner part of the polymer melt, saturation of the surface, etc. Only further increase of catalyst concentration would lead to formation of random copolymers with higher solubility[9].

Curves of crystallization and melting temperatures presented in *Figure 5* have the same plateau in the concentration range of 0.045–0.09%. The first parameter increases for about 50°C, while the melting point decreases for 18°C. As is mentioned above, the higher crystallization and lower melting temperatures of PET/PC block copolymers provide a possibility to perform their processing (extrusion and injection moulding) at a temperature 30–35°C lower than that needed for the neat PET/PC blend.

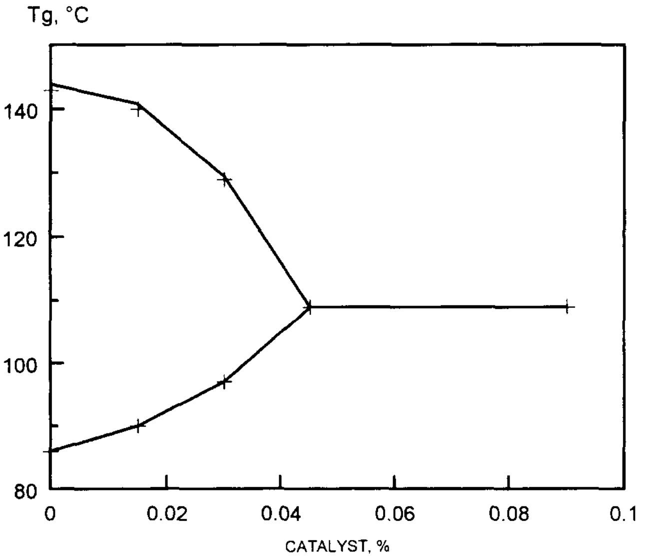

Figure 3 Dependence of the values of T_g on the concentration of the catalyst

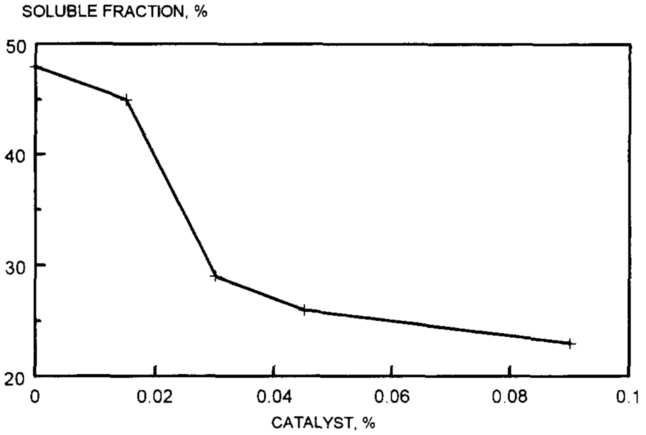

Figure 4 Influence of the catalyst concentration on the solubility of PET/PC blends and copolymers in methylene chloride

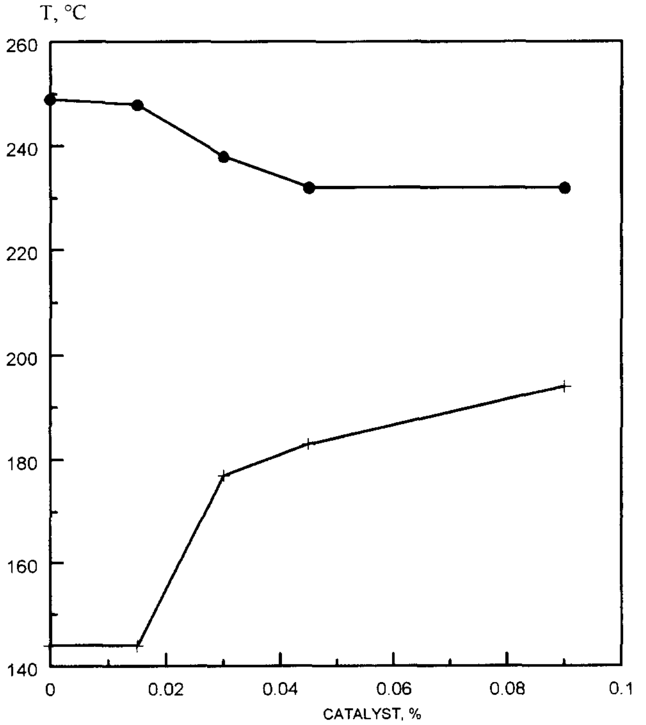

Figure 5 Data of crystallization (+) and melting temperatures (●) of PET/PC blends and copolymers obtained by one-step extrusion in the presence of various amounts of $Sm(acac)_3$

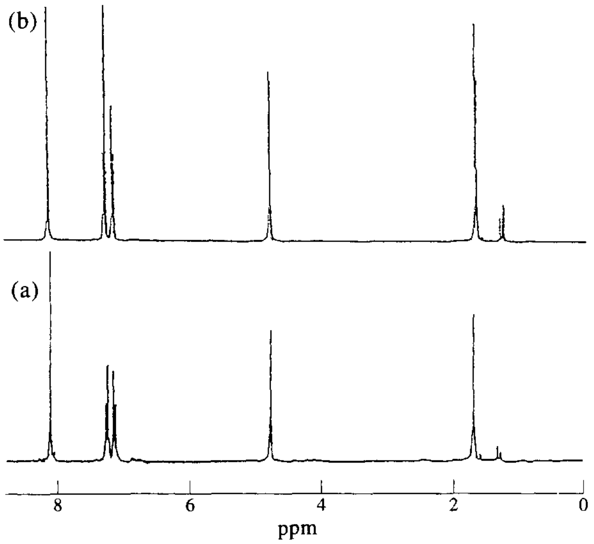

Figure 6 (a) ^{1}H n.m.r. spectrum of the PET/PC block copolymer obtained by extrusion with 0.09% of Sm(acac)$_3$ (CDCl$_3$/CF$_3$COOD, 85/15 wt/wt); (b) ^{1}H n.m.r. spectrum of unreacted PET/PC blend

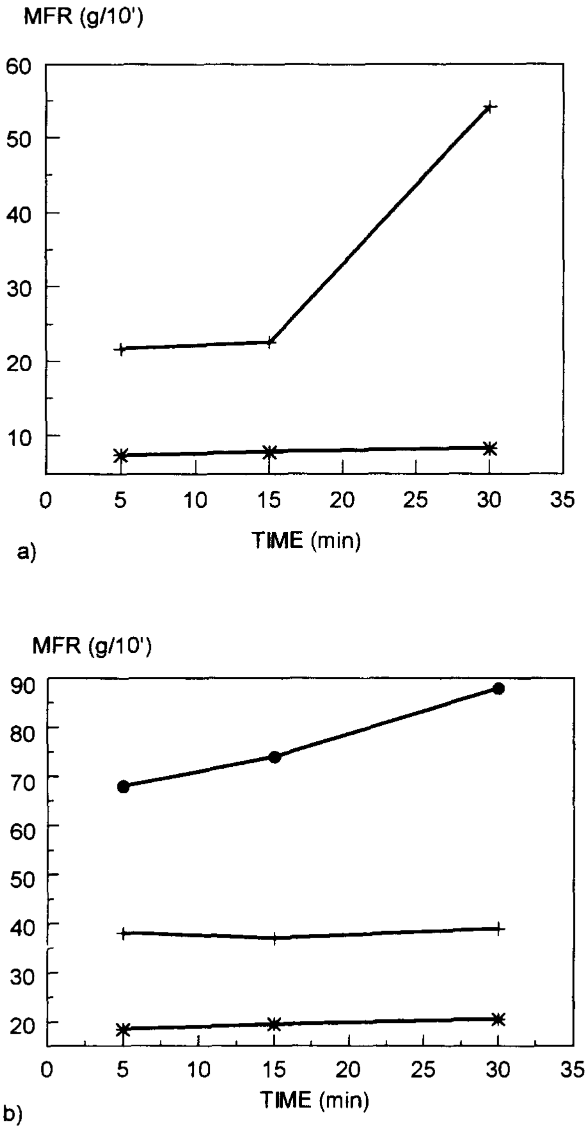

Figure 7 Melt rheology data at 250 (*), 270 (+), and 290°C (●) of the PET/PC samples obtained in the presence of 0.045% of Sm(acac)$_3$ (a) and stabilized with Ultranox 626 Irganox 1010 (b)

All the above results revealed that the optimal concentration of Sm(acac)$_3$ for production of PET/PC block copolymers by one-step extrusion lies in the range of 0.03–0.05%. Further increase in catalyst concentration does not significantly change the thermal and physicochemical characteristics of the product.

Selective character of catalyst

As has been established before[5–7,9], residues of lanthanide catalysts in PET, remaining after its synthesis, do not lead to side reactions during PET/PC reactive blending performed in Brabender as in case of Ti catalyst. The same behaviour of Sm catalyst was found when it was added to the polymers before their extrusion. The ^{1}H n.m.r. spectrum (*Figure 6a*), recorded for the PET/PC block copolymer obtained by extrusion with 0.09% of Sm(acac)$_3$ shows only signals corresponding to terephthalic protons (8.15 ppm), aromatic protons of bisphenol A (7.1–7.4 ppm), ethylene protons adjacent to ester groups (4.8 ppm), and methyl protons of bisphenol A (1.7 ppm). There are no signals of protons adjacent to aromatic ether groups formed by destruction of carbonate groups with elimination of carbon dioxide or signals of cyclic ethylene carbonate usually formed by degradation of unstable bisphenol-A-ethylene carbonate as in case of Ti catalyst[3,7,9]. The ^{1}H n.m.r. spectrum of unreacted PET/PC blend is given as a control (*Figure 6b*). Thus, lanthanides, being added to PET/PC mixture before reactive blending, do not almost cause side reactions unlike the Ti catalyst. Moreover, the use of titanium tetrabutoxide as a catalyst for PET/PC one-step extrusion failed, perhaps because of its immediate hydrolysis even before extrusion that makes Ti derivatives insoluble in the polymer melt, whereas the 'dry blend' of PET with Sm(acac)$_3$ was found to be much more stable towards hydrolysis.

Effect of stabilizers

Residues of the catalyst in PET/PC block copolymers were neutralized with commercial inhibitors used for Polyesters (Ultranox 626 and Irganox 1010, 0.3 wt% of each of them respect to the final product, see Experimental). In order to examine its processability, stabilized samples of PET/PC block copolymers, containing residues of Sm(acac)$_3$ (0.045%), were extruded repeatedly in a single-screw extruder Brabender at 250°C and 100 rpm. A negligible decrease in intrinsic viscosity of the samples extruded reveals their good thermal stability under the processing conditions.

Moreover, even non-stabilized samples appeared to be stable at 250°C, as it was established by melt rheology tests (*Figure 7a*). However, the value of the melt flow rate increases dramatically after 15 min of heating at 270°C that indicates both further exchange reactions and degradation processes. For stabilized samples this effect was observed only at 290°C, and it was not so strong (*Figure 7b*).

On the basis of the results above we can conclude that polymer materials based on PET/PC block copolymers obtained by one-step extrusion in the presence of the catalyst can be used for the further processing at 240–250°C without any stabilizer. For processing at elevated temperatures standard commercial antioxidants as Ultranox 626 and Irganox 1010 can be employed, in order to provide the required thermal stability.

Effect of the type of starting PET and PC

All the results above were obtained on commercial fibre-grade PET ($[\eta]=0.65\,\mathrm{dl\,g^{-1}}$). However, as has been established, bottle-grade PET ($[\eta]=0.83\,\mathrm{dl\,g^{-1}}$) and the bottles scrapped for recycling ($[\eta]=0.86\,\mathrm{dl\,g^{-1}}$), being extruded with PC, do not significantly change thermal and physicochemical properties of the samples as compared with those of the samples obtained with fibre-grade PET. This fact allows to extend the method above to other commercial types of PET and reveals a possibility for polymer recycling by one-step extrusion. This direction will be developed in our further work.

The PC used in most of our experiments was an unstabilized EniChem powder product. Other types of PC in powder and in pellets stabilized with standard antioxidants were employed as well. Preliminary data of one-step extrusion of PET (fibre- and bottle-grade) with various types of PC allow us to conclude that even stabilized commercial PC can be used for the process above, although to reach the same level of interchange reaction the catalyst needs to be raised by a factor of 1.5, depending on the type of stabilizers employed for PC.

All the results above allow us to conclude that the new innovative method of PET/PC reactive blending by one-step extrusion provides a possibility to produce a variety of new transparent polymer materials with a single T_g by varying the type and concentration of the catalyst and initial polymer composition.

Thermal and physicochemical properties of PET/PC blends and copolymers at various polymer compositions produced by one-step extrusion and effect of the catalyst nature will be published later.

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