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Reactive blending of poly(ethylene terephthalate) and bisphenol-A polycarbonate: effect of various catalysts and mixing time on the extent of exchange reactions

Maurizio Fiorini*
Dipartimento di Discipline Economico-Aziendali, Università di Bologna, Piazza Scaravilli, ZIG0126 Bologna, Italy

and Francesco Pilati
Dipartimento di Chimica, Università di Modena, Via Campi 183, I-G1100 Modena, Italy

and Corrado Berti and Maurizio Toselli
Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, Viale Risorgimento Z, I-G0136 Bologna, Italy

and Vladimir Ignatov
Industrie ILPEA S.p.A., Viale dell Industria 37, I-21023 Malgesso (Va), Italy
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The catalytic activity towards exchange reactions in poly(ethylene terephthalate) (PET)–bisphenol-A polycarbonate (PC) reactive blending was compared for various lanthanide compounds (based on europium, cerium, samarium, terbium and erbium), and for titanium- and calcium/antimony-based catalysts. The effect of reaction time on the extent of reaction was studied by selective solubility tests coupled with ^{1}H n.m.r. and a selective degradation procedure for PC sequences was carried out to achieve information on the PET block length change. Each of the above methods can be used to get information on the reaction extent; however, a better understanding of the reaction mechanism is achieved by using more than just a single method. Titanium showed a higher catalytic activity; however, lanthanide catalysts, especially those based on samarium, europium and cerium, allowed the block length in the PC/PET block copolymers formed by exchange reactions during melt mixing to be controlled more easily, and at the same time they did not promote the side-reactions that occurred in the presence of titanium- or calcium/antimony-based catalysts. Copyright © 1996 Elsevier Science Ltd.

(Keywords: reactive blending; exchange reactions; lanthanides)

INTRODUCTION

Reactive blending is a very promising technology for preparing new polymeric materials starting from different polymers, when they can undergo chemical reactions in the molten state. This processing technology has some advantageous features: it is complementary towards polymerization processes, has high flexibility and versatility, requires lower capital investment and has a lower impact on the environment.

When different reactions can take place during the mixing, and the system is made even more complex by the immiscibility of the two polymers (so that reactions take place mainly at the interface), the control of the chemical structure, and therefore of the properties of the final products, requires a detailed knowledge of the reaction pathways. In the case of polycondensates, such as bisphenol-A polycarbonate (PC) and poly(ethylene terephthalate) (PET), the activity of a catalyst, either present as a residue from polymer synthesis or purposely added before blending, can be of paramount importance in determining the resulting chemical structure. From the same homopolymer blend composition, copolymers with chemical structure ranging from diblock copolymers with high molecular weight blocks to multiblock copolymers with shorter and shorter segments (and eventually random copolymers for the most active catalysts) can in principle be prepared.

We have recently reported[1] that new catalysts based on lanthanide compounds possess a wide range of catalytic activity towards the different reactions taking place during PET/PC reactive blending. In particular, we reported that for a definite time of mixing the various catalysts led to remarkable differences in the chemical structure of the products obtained after melt mixing; in this paper we extend the research above by considering

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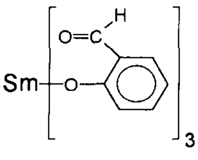
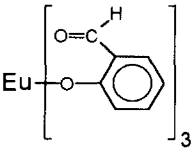
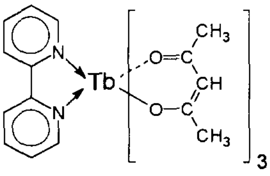
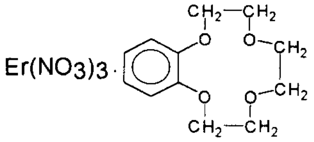
* To whom correspondence should be addressed

Table 1 Catalysts used for PC/PET reactive blending

Catalyst	Abbreviation
$Ti(OC_4H_9)_4$	$Ti(OBu)_4$
$Ca(OOCCH_3)_2 \cdot 2H_2O + Sb_2O_3$	Ca/Sb
	$Sm(L)_3$
	$Eu(L)_3$
$Ce(CH_3COO)_3 \cdot xH_2O$ $x = 4–6$ mol	$Ce(ac)_3$
	$Tb(acac)_3diPy$
	$Er(NO_3)_3$Benzo-12-Crown-4

the effect of mixing time on the chemical structure of the products obtained by reactive blending of PC and PET synthesized with various catalysts based on lanthanides (cerium, samarium, erbium, europium and terbium), titanium and calcium/antimony.

EXPERIMENTAL

Materials

PC (intrinsic viscosity 0.65 dl g^{-1} in chloroform at 30°C) was kindly supplied by EniChem. PET samples were prepared by us by reacting dimethyl terephthalate (DMT) and ethylene glycol (EG) in the presence of the various catalysts listed in *Table 1* at a molar concentration of 0.063 mol per 100 mol of DMT[2].

Catalysts used for PET synthesis are in part commercial products ($Ti(OBu)_4$, $Ca(CH_3COO)_2$, Sb_2O_3, $Ce(CH_3COO)_3$) purchased from Aldrich and used without further purification and in part known compounds[3] prepared according to the procedure previously described[2].

Melt mixing

A Brabender Plasticorder PL-2000 equipped with an electrically heated W-50 mixer was used for melt mixing. The mixer capacity was 50 ml and the total volume of polymers to be mixed was about 45 ml (based on the temperature of 270°C). PC/PET blend composition was fixed at 50/50 by weight for all the blends used in this study.

Polymer samples dried under vacuum at 140°C overnight were introduced in the preheated mixer at 270°C, and this temperature was held for the whole process. The mixer was closed with a gas cover, which allowed a stream of dry nitrogen to be maintained throughout the entire mixing. The rotor speed was set at 30 r.p.m. and kept constant for all samples. During the mixing, samples of 3–5 g were taken from the mixer at intervals and cooled in air.

Selective solubility fractionation and selective degradation

Selective solubility fractionation and selective degradation of PC sequences were carried out by the same procedure reported in a previous paper[1]. For the selective solubility tests, samples of 1 g (exactly weighed) taken from each blend were dissolved in dichloromethane–trifluoroacetic acid (96/4 v/v), then tetrahydrofuran was added slowly under stirring to precipitate the insoluble fraction. A solvent/non-solvent ratio equal to 1/3 was used in all the tests. After filtration, the insoluble fraction was dried under vacuum at 100°C.

The soluble fraction was recovered by evaporating the solvent mixture under reduced pressure. The selective degradation procedure was similar to one previously proposed[4], and it has been checked to assure that: (i) no bisphenol-A carbonate units were left in the PET residue and (ii) the effect on the molecular weight of neat PET was negligible.

Measurements

^1H n.m.r. spectra were recorded with a Varian Gemini 200 instrument; samples were dissolved in $CF_3COOD/CDCl_3$ 20/80 (v/v). Tetramethylsilane (TMS) was used as an internal standard to measure chemical shifts. Typical n.m.r. spectra have been reported previously[1]; in this study, we used the peaks at δ 8.1 (terephthalate protons from PET), 4.8 (methylene protons from PET), 7.1–7.3 (BPA (bisphenol A) aromatic protons from PC) and 1.7 (methyl protons from BPA) to determine the composition of soluble and insoluble fractions.

The intrinsic viscosity of PET fractions after selective degradation of PC segments was calculated from viscosity measurements of diluted solutions in phenol/1,1,2,2-tetrachloroethane (40/60, w/w) at 25°C using Ubblehode viscometers.

The molecular weight distribution of the residual PET after selective degradation was investigated by size exclusion chromatography (s.e.c.) carried out on samples dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol/dichloromethane (HFIP/DCM) 10/90 (v/v), and eluted with a solvent mixture HFIP/dichloromethane/chloroform 5/20/75 (w/w) at 0.6 ml min^{-1} and 25°C using a set of Polymer Labs Pigel columns (500, 10^3 and 10^4 Å) and a u.v. detector.

RESULTS AND DISCUSSION

In our previous paper[1] we reported that various lanthanide catalysts gave different products when PET and PC were melt mixed at 270°C for 20 min. Those data can be taken as evidence of different catalytic activity; however, to elucidate in more detail the process evolution in the presence of those catalysts, we extended

Table 2 Characterization data for PC/PET blends prepared with the titanium catalyst

Reaction time (min)	Soluble fraction (wt%)	PET in the soluble fraction (wt%)	$[\eta]$ of PET blocks after selective degradation (dl g^{-1})	PC in the insoluble fraction (wt%)	% of total PET found in the soluble fraction	% of total PC found in the insoluble fraction
0	50.0	0.0	0.90	0.0	0.0	0.0
5	33.2	5.5	0.13	28.1	3.7	37.5
10	30.1	36.6	0.10	43.4	21.8	61.3
20	100.0	50.0	0.09	ND	ND	ND
30	100.0	50.0	0.06	ND	ND	ND
60	100.0	50.0	ND	ND	ND	ND

ND, not detected

Table 3 Characterization data for PC/PET blends prepared with the samarium catalyst

Reaction time (min)	Soluble fraction (wt%)	PET in the soluble fraction (wt%)	$[\eta]$ of PET blocks after selective degradation (dl g^{-1})	PC in the insoluble fraction (wt%)	% of total PET found in the soluble fraction	% of total PC found in the insoluble fraction
0	50.0	0.0	0.80	0.0	0.0	0.0
10	45.8	6.9	0.44	12.3	6.2	13.6
20	19.9	26.7	0.22	44.1	10.6	70.7
30	19.1	41.9	0.15	44.9	15.2	76.6
60	46.2	32.7	0.13	42.9	32.9	42.6

Table 4 Characterization data for PC/PET blends prepared with the europium catalyst

Reaction time (min)	Soluble fraction (wt%)	PET in the soluble fraction (wt%)	$[\eta]$ of PET blocks after selective degradation (dl g^{-1})	PC in the insoluble fraction (wt%)	% of total PET found in the soluble fraction	% of total PC found in the insoluble fraction
0	50.0	0.0	0.74	0.0	0.0	0.0
10	49.9	3.5	0.51	6.6	3.6	6.4
20	28.3	11.0	0.30	33.7	6.2	48.9
30	18.9	20.5	0.20	41.4	7.5	69.1
60	70.8	47.7	0.13	39.4	65.6	23.7

Table 5 Characterization data for PC/PET blends prepared with the cerium catalyst

Reaction time (min)	Soluble fraction (wt%)	PET in the soluble fraction (wt%)	$[\eta]$ of PET blocks after selective degradation (dl g^{-1})	PC in the insoluble fraction (wt%)	% of total PET found in the soluble fraction	% of total PC found in the insoluble fraction
0	50.0	0.0	0.80	0.0	0.0	0.0
10	49.6	2.9	0.60	6.9	3.0	6.8
20	29.0	7.3	0.47	31.7	4.2	45.6
30	23.1	20.8	0.23	41.7	9.7	63.7
60	21.8	31.3	0.15	43.2	13.3	69.3

the study to different reaction times. The catalyst formula and abbreviations are reported in *Table 1*. The catalyst concentration was the same for all the tests performed (0.063 mol% based on the PET repeating unit); for calcium/antimony system, the concentration was 0.063 mol% for each metal.

Three indicators of the extent of exchange reactions were used for each blend sample: (i) the amount of soluble fraction after the selective solubility tests described in the experimental part; (ii) the chemical composition of soluble and insoluble fractions obtained according to (i); and (iii) the intrinsic viscosity and s.e.c. curves of PET blocks remaining after the selective degradation of PC sequences. The data are reported in *Tables 2–8*.

Effect of catalyst and reaction time on the relative amount of the soluble fraction

In the absence of any exchange reaction, the soluble weight fraction for a 50/50 blend composition remains constant at 50 wt%, since only PC is soluble under the experimental conditions for the selective solubility test (see the Experimental section earlier). The effectiveness of the separation method was confirmed for PET/PC blends prepared both at low temperature from solutions and at high temperature by melt mixing in the presence of di-*n*-octadecylphosphite (DNOP), a good catalyst inhibitor[1,5,6]. In both cases, the insoluble fraction was found to be 50% by weight and it contained only PET.

In contrast, when exchange reactions take place, a progressive shift towards larger amounts of the soluble or insoluble fraction is expected[1,4] because the block copolymers resulting from exchange reactions have a different solubility due to the dominance of PC or PET blocks. In other words, this means that PET blocks are present in the soluble fraction when the solubility of PC blocks prevails, and that PC blocks are present in the insoluble fraction when the prevailing effect is the insolubilitity of PET blocks.

An increase of the overall soluble fraction is also

Table 6 Characterization data for PC/PET blends prepared with the erbium catalyst

Reaction time (min)	Soluble fraction (wt%)	PET in the soluble fraction (wt%)	$[\eta]$ of PET blocks after selective degradation (dl g^{-1})	PC in the insoluble fraction (wt%)	% of total PET found in the soluble fraction	% of total PC found in the insoluble fraction
0	50.0	0.0	0.79	0.0	0.0	0.0
10	49.2	2.5	0.50	5.1	2.5	5.2
20	43.4	4.1	0.42	15.6	3.6	17.5
30	30.3	7.9	0.34	33.6	4.9	45.6
60	19.0	14.2	0.24	40.3	5.3	66.7

Table 7 Characterization data for PC/PET blends prepared with the calcium/antimony catalyst

Reaction time (min)	Soluble fraction (wt%)	PET in the soluble fraction (wt%)	$[\eta]$ of PET blocks after selective degradation (dl g^{-1})	PC in the insoluble fraction (wt%)	% of total PET found in the soluble fraction	% of total PC found in the insoluble fraction
0	50.0	0.0	0.82	0.0	0.0	0.0
4	40.6	4.9	ND	14.2	3.8	17.9
10	40.8	4.1	0.17	16.0	3.2	19.4
20	35.5	5.8	0.15	37.3	4.8	41.8
30	27.0	12.2	0.11	35.3	6.5	52.0
60	19.9	29.8	0.11	43.3	11.6	71.3

ND, not detected

Table 8 Characterization data for PC/PET blends prepared with the terbium catalyst

Reaction time (min)	Soluble fraction (wt%)	PET in the soluble fraction (wt%)	$[\eta]$ of PET blocks after selective degradation (dl g^{-1})	PC in the insoluble fraction (wt%)	% of total PET found in the soluble fraction	% of total PC found in the insoluble fraction
0	50.0	0.0	0.69	0.0	0.0	0.0
10	49.4	ND	0.46	ND	ND	ND
20	50.7	ND	0.63	ND	ND	ND
30	49.5	ND	0.70	ND	ND	ND
60	44.2	3.8	0.68	14.1	3.4	15.7

ND, not detected

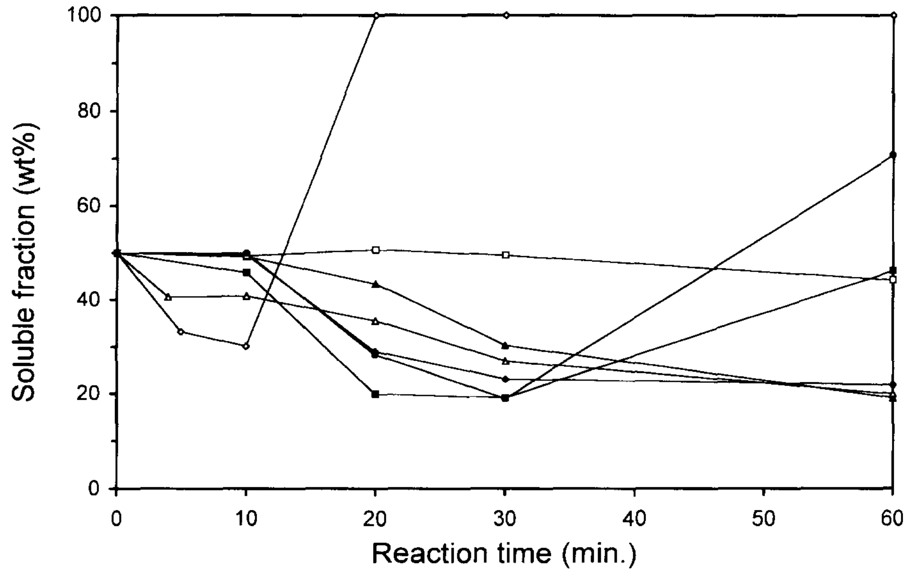


Figure 1 Change of the percentage of the soluble fraction as a function of time for different catalysts (■, Sm; ◆, Ce; ▲, Er; □, Tb; ◇, Ti; △, Ca/Sb; ●, Eu)

expected as a consequence of a progressive shortening of the average block length.

Figure 1 shows the data relative to the change of the soluble weight fraction with time for various catalysts. The initial decrease of the soluble fraction means that the effect of PET prevails on the effect of PC blocks, making part of the PC insoluble. The initial slope of these curves can be taken as an indicator of the activity of the catalyst towards exchange reactions. Based on these data, the terbium derivative appears to be the least active one,

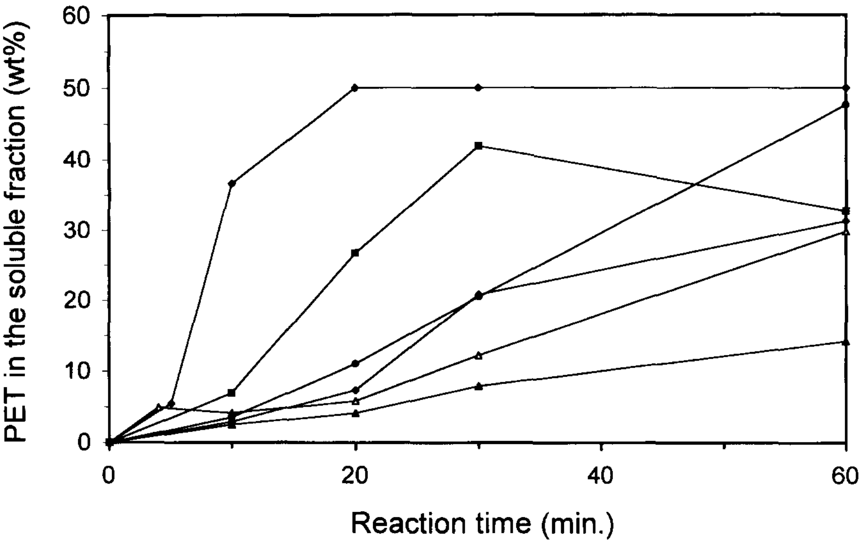


Figure 2 Change in composition of the soluble fraction as a function of time for different catalysts (■, Sm; ◆, Ce; ▲, Er; ◇, Ti; △, Ca/Sb; ●, Eu)

because solubility changes very slowly with time and even after blending for 60 min the soluble fraction is still 44.2%. In contrast, the titanium catalyst is very active, and within 20 min all the blend becomes soluble.

The other catalysts have activity levels intermediate between those described above for the terbium and titanium catalysts. Within the reaction time span considered in our investigation, the solubility for the europium and samarium catalysts reached a minimum and started to increase again. For all the other catalysts, the amount of the soluble fraction keeps on decreasing throughout the reaction time considered. From these curves, it clearly appears that examination of solubility data for different catalysts at just one fixed reaction time can be misleading; due to a minimum present in some curves, we can observe the same amount of soluble fractions at different reaction times (*Figure 1*).

Composition of soluble and insoluble fractions

Further support for the exchange reactions reported above can be obtained by analysing the composition of the soluble and insoluble fractions by ^{1}H n.m.r. The data are collected in *Tables 2–8* for the different catalysts. Again, the terbium catalyst clearly appears to be the least active one; after 60 min just 3.4% of the total PET was detected in the soluble fraction and 15.7% of the total PC in the insoluble one.

The titanium catalyst, in contrast, is so active that within 10 min, 61.3% of the total PC was found in the insoluble fraction and 21.8% of PET in the soluble fraction. It is interesting to observe that there was a sharp change in the composition of the two fractions after 5 and 10 min of reaction, even if the weight fractions were very similar (33.2 and 30.1%, respectively). In fact, as shown in *Table 2*, the PET content in the soluble fraction increases from 5.5 to 36.6%, in the interval of 5–10 min, and the PC content in the insoluble fraction changes from 28.1 to 43.4%.

Although it is the most active catalyst among those investigated in this study, the titanium cata-lyst leads, however, to a significant increase in the rate of two competitive side-reactions: the formation of cyclic ethylene carbonate (EC) and the formation of aromatic–aliphatic ether linkages via the decarboxylation of aromatic–aliphatic carbonate moieties formed by direct ester–carbonate exchange reactions[7].

For all the other catalysts, signals attributable to side-reaction products were barely detectable in the n.m.r. spectra, even for mixing times longer than 60 min.

It is clear that the composition analysis adds information and can contribute to a better definition of the order of catalytic activity. In *Figure 2* the amount of PET contained in the soluble fraction as a function of reaction time is reported and the different curve profiles can be considered as an indicator of the catalytic activity of the various metal compounds. The titanium catalyst clearly appears to be the most active, as the curve is very steep, and after just 20 min, PET accounts for 50% of the soluble fraction (all the blend is soluble). Samarium follows titanium in decreasing catalytic activity order; however, europium, which has a catalytic activity lower than samarium at short reaction times, yields a higher percentage of soluble PET at longer reaction times (60 min). Cerium and calcium/antimony have similar intermediate catalytic activity, while erbium and terbium are much less active.

The results reported in *Tables 2–8* also show that the amount of PC in the insoluble fractions changes, increasing more rapidly than the amount of PET in the soluble fractions; however, the differences in composition at different reaction times for the various catalysts are smaller and therefore ordering the catalytic activity by using the composition of the insoluble fractions is less effective.

Molecular weight of PET blocks

Further progress in the understanding of the reaction mechanism and catalytic behaviour of the various catalysts can be derived from knowledge of the change in the average block lengths with the mixing time. Usually this is a very difficult task for block copolymers because spectroscopic methods are almost ineffective when the molecular weight is relatively high. For PC/PET block copolymers a characterization procedure has been developed[1,4], in which PC blocks are degraded selectively leaving PET blocks almost unaffected. This procedure allowed us to get information on the average length of

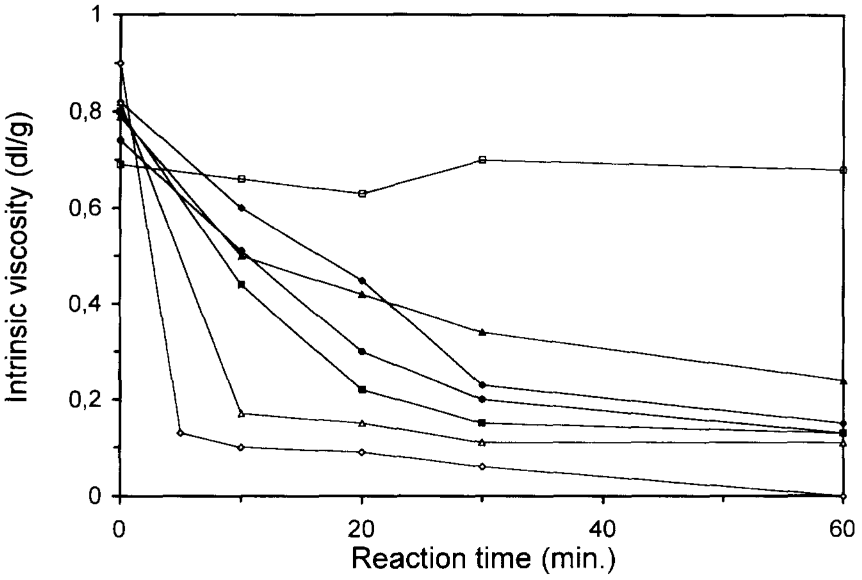


Figure 3 Decrease of the intrinsic viscosity of PET blocks, after selective degradation, as a function of reaction time for different catalysts (■, Sm; ◆, Ce; ▲, Er; □, Tb; ◇, Ti; ▲, Ca/Sb; ●, Eu)

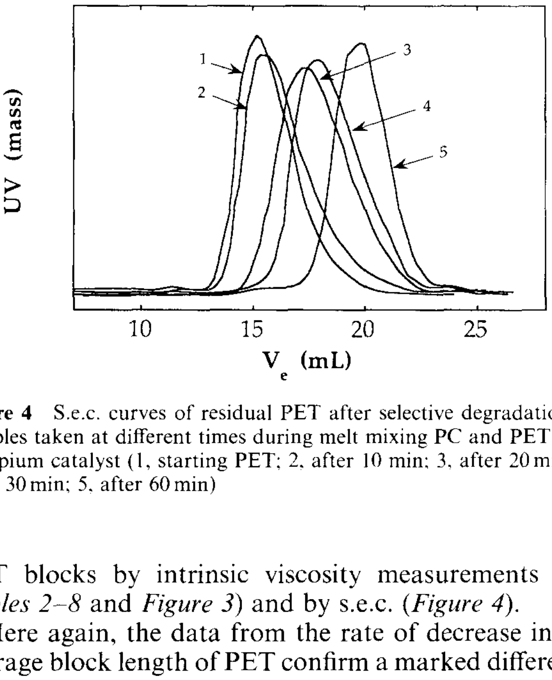


Figure 4 S.e.c. curves of residual PET after selective degradation of samples taken at different times during melt mixing PC and PET with europium catalyst (1, starting PET; 2, after 10 min; 3, after 20 min; 4, after 30 min; 5, after 60 min)

PET blocks by intrinsic viscosity measurements (see *Tables 2–8* and *Figure 3*) and by s.e.c. (*Figure 4*).

Here again, the data from the rate of decrease in the average block length of PET confirm a marked difference in the catalytic activity among the metal compounds studied in this work. In particular, the intrinsic viscosity of PET synthesized with the terbium catalyst practically does not change after mixing with PC for 60 min; this confirms the very low activity of this catalyst in PET–PC exchange reactions. In contrast, the titanium catalyst induces a sharp decrease in the block length (after just 10 min, the intrinsic viscosity drops from 0.9 to 0.1 dl g^{-1}); this fact is further evidence that the titanium compound is the most active of the catalysts studied in this work.

We observed a sharp decrease of the decrease of the intrinsic viscosity also for calcium/antimony catalytic system; this appears in contrast to the above reported experimental evidence and suggests that the overall mechanism is different from the other catalysts. This result can be explained by the high degradation rate measured for PET samples in the presence of the calcium/antimony catalyst[3,8]; the observed fast decrease of the intrinsic viscosity of PET segments can be mainly attributed to degradation rather than exchange reactions.

All the other lanthanide compounds were found to possess intermediate catalytic activity, in that the PET block length decreased at a lower rate, compared to the titanium and calcium/antimony catalysts, but still showing an appreciable activity towards exchange reactions. In some respects, the slower rate of decrease of the average block length of PET makes lanthanide catalysts quite interesting for PET/PC reactive blending because they allow the block length of the block copolymers to be controlled more easily and undesirable side-reactions to be avoided.

The effect of different catalysts on the molecular weight distribution was also investigated by s.e.c. As an example, *Figure 4* reports the s.e.c. curves obtained for PET residues (europium catalyst) remaining after selective degradation of samples taken at different reaction times, along with the curve for the starting PET prepared with the same catalyst. As was expected, a progressive shift towards higher retention volumes (V_e) with increasing mixing time was observed, whereas the peak shape remains similar to that of the starting PET. Finally, it has to be noted that while for the titanium and lanthanide catalysts the molecular weights distribution of the residual PET after selective degradation was unimodal, for the calcium/antimony catalyst, broader trimodal peaks were found[1], giving further evidence of a stronger PET degradation activity for this catalytic system.

CONCLUSIONS

The properties of materials prepared by reactive blending PET with PC can depend strongly on the reactions taking place during melt blending. As several reactions are possible and they take place mainly at the interface between two immiscible polymer melts (in particular at short reaction times), the selective activity of the catalyst towards exchange and degradation reactions and the solubility of the catalyst within the different polymer phases may be key factors for the process. Within this framework, the choice of the right catalyst becomes very important as it allows materials with the desired properties to be prepared. In order to obtain correct information about the catalytic activity, several investigative methods have to be used. In fact, the results of our study show that a single method of investigation can lead to misleading conclusions, and that a deeper insight in the reaction mechanism can be inferred by analysing the data obtained from different indicators.

From the results of this study, lanthanide catalysts seem to offer several advantages with respect to traditional catalysts such as titanium or calcium/antimony compounds. In fact, lanthanide catalysts are still quite active towards exchange reactions (more active than calcium/antimony compounds) but do not catalyse side-reactions, as titanium catalysts do. They do not give rise to discoloration in the final blends and the block length in PC/PET block copolymers can be more easily controlled. For these reasons, lanthanide catalysts can be considered as very promising catalysts for industrial-scale applications of PC/PET reactive blending.

REFERENCES

1 Fiorini, M., Berti, C., Ignatov, V., Toselli, M. and Pilati, F. *J. Appl. Polym. Sci.* 1995, **55,** 1157

2 Ignatov, V., Pilati, F., Berti, C., Tartari, V., Carraro, C., Nadali, G., Fiorini, M. and Toselli, M. *J. Appl. Polym. Sci.* 1995, **58,** 771

3 'Gmelin Hanbuch der Anorganischen Chemie, Coordination Compounds of Sc, Y, La to Lu,' (Ed. W. Hoffman) 8th edn, Vols D1–D4, Springer-Verlag, Berlin, 1980–1986

4 Pilati, F., Marianucci, E. and Berti, C. *J. Appl. Polym. Sci.* 1985, **30,** 1267

5 Delimoy, D., Bailly, C., Devaux, J. and Legras, R. *Polym. Eng. Sci.* 1988, **28,** 104

6 Kollodge, J. K. and Porter, R. S. *Macromolecules* 1995, **28,** 4097

7 Berti, C., Bonora, V., Pilati, F. and Fiorini, M. *Makromol. Chem.* 1992, **193,** 1665

8 Zimmermann, H. in 'Polyesterfasern, Chemie und Technologie' (Ed. H. Ludewig), 2nd edn, Akademie Verlag, Berlin, 1975, Ch. 4