Study of the Reactions Occurring during Melt Mixing of Poly(ethylene Terephthalate) and Polycarbonate

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Synopsis

In this work the reactions taking place during melt mixing of bisphenol-A polycarbonate (PC) with poly(ethylene terephthalate) (PET) were studied by selective degradation of PC sequences, solubility tests, and IR spectroscopy. It was found that exchange reactions between PC and PET took place, contrary to what has been previously suggested by other authors. Kinetic constants were evaluated from intrinsic viscosity measurements of PET blocks. The reaction rate was slow when only the Sb catalyst (residues of the PET polymerization) were present, but it was significantly accelerated by the addition of $Ti(OBu)_4$. In the presence of the latter catalyst, other side reactions, leading to discoloration and gas evolution, took place.

INTRODUCTION

There has been considerable commercial interest in blends of various polyesters with bisphenol-A polycarbonate (PC) as some polyesters have shown varying degrees of partial miscibility with PC[1-3] when examined for their transitional behavior by thermal analysis and dynamic mechanical testing.

These systems experience a variety of chemical reactions during high-temperature melt blending. Interchange reactions involving chain end groups, ester groups, and carbonate groups are possible in principle at the high temperatures required for melt mixing of polyesters and PC.

Of course, if interchange reactions occur during processing or mixing, this will affect the chemical structure of the final product. In the limit case of a very high degree of interchange reactions, the final product would be a random copolymer.

While a series of in-depth investigations of physical properties and thermal behavior have been performed for systems, such as poly(butylene terephthalate) (PBT) with PC,[1] poly(ethylene terephthalate) (PET) with PC,[2] and copoly(cyclohexanedimethanol(iso/tere)phthalate (PcHIT) with PC,[3-5] the chemical reactions occurring during melt mixing have been thoroughly investigated only for PcHIT/PC[6] and PBT/PC.[7]

The paper[2] and the patents[8-12] which have considered blends obtained from PET and PC studied this system only for its thermal and mechanical properties.

In their paper, Nassar et al.[2] arrived at the conclusion that PET is partially miscible with PC and, without proof, that no significant reactions occur during the mixing process.

The main aim of our work was to investigate the chemical structure of blends obtained by melt mixing of PET and PC to determine whether reactions take place.

Since it has been reported in previous papers[6,7] that catalysts, like titanium alcoxide, may play a relevant role in determining the rate of the interchange reactions, we studied the chemical structures resulting when Ti(OBu)$_4$ was added to, or omitted from, the PET/PC system.

Selective degradation of PC groups, achieved by a chemical attack with piperidine, was performed on blend samples to evaluate any change in the mean length of PET blocks due to interchange reactions.

EXPERIMENTAL

Products

PET and PC were commercial products and had the following characteristics:

—PET had an intrinsic viscosity of 0.565 dL/g in phenol/1,1,2,2-tetrachloroethane (P/TCE) (60/40 w/w) at 30.0°C and contained Sb catalyst, as residues of polymerization, in an unspecified amount.

—PC had an intrinsic viscosity of 0.745 dL/g in chloroform at 30.0°C.

All the other products used were reagent grade and were used as supplied. 2,2-bis(4-piperidinocarbonyloxyphenyl)propane (1) and 2-(4-hydroxyphenyl)-2-(4-piperidinocarbonyloxyphenyl)propane (2) were separated by elution with benzene/acetone (9:1), on an alumina column, from the degradation products of the chemical attack of piperidine on PC. They were characterized by IR spectroscopy, ^{1}H-NMR, elemental analysis, and mass spectroscopy. Their melting points, uncorrected, were 174–176°C and 155°C, respectively.

Melt Mixing

Twelve hundred grams of a 50/50 (w/w) composition of bisphenol-A polycarbonate and PET powders, previously dried at 130°C for 4 h, were introduced into a preheated 1.8-L stainless-steel batch reactor. The temperature dropped immediately, but returned to 275°C in about 15 min. The mixing was done, in an N$_2$ atmosphere, by a paddle agitator driven at 60 rpm. Samples were taken at various times from the bottom of the reactor. In a second type of run, Ti(OBu)$_4$ [0.13 g of Ti(OBu)$_4$/kg of mixture] was added to the 50/50 PET/PC mixture.

Solubility Tests

About 1 g of blend was added to 25 mL of methylene chloride and was agitated at room temperature overnight. The soluble fraction was separated from the insoluble one by filtration with 0.2 μm FG Millipore filters. Tests performed on unreacted mixtures of PET and PC showed that PC was quantitatively separated from PET with this procedure.

Selective Degradation of Polycarbonate Groups

The selective degradation of PC was achieved by reacting piperidine (0.01 mmol) in CH_2Cl_2 (25 mL) with a mixture of PC and PET (about 1 g, 50/50 w/w) for 1 h at room temperature. In fact, after this treatment, the 1780 cm^{-1} band of carbonate disappeared completely while a band at 1710 cm^{-1} (typical of urethane group) appeared in the soluble fraction. In addition, the insoluble fraction showed an IR spectra identical to that of pure PET, and, furthermore, the intrinsic viscosity of the residue was exactly the same as the initial PET. From these results we can conclude that in the above reaction conditions, only the carbonate groups are subjected to the chemical attack of piperidine and, furthermore, this reaction is quantitative.

Characterizations

The viscosities were measured at 30.0°C with an Ubbelhode viscometer. The intrinsic viscosity was obtained from measurements for each sample at four different concentrations. IR spectra were recorded on a Perkin-Elmer 257 Spectrometer. Hplc separation of the degradation products of PC after the chemical attack with piperidine was achieved with a Perkin-Elmer Series 2 instrument by eluting with CH_3OH/H_2O (68/32 v/v) at 1 mL/min using an ODS-HC Sil-X-1 0.26×25 cm column thermostated at 40°C and a UV detector (at 254 nm).

RESULTS AND DISCUSSION

Preparation of Blends

The blends were obtained by melt-mixing PET and PC at 275°C in a closed reactor (with a volume of about 1 L remaining over the molten polymers), as described in more detail in the experimental part.

Runs were performed both with and without $Ti(OBu)_4$ added to the polymers. In both cases a progressive decrease in the signal of the strain-gage mounted on the driving shaft was recorded.

When titanium tetrabutoxide was added to the polymers [0.13 g/(kg of polymer)] a strong increase of the internal pressure (from 1 to about 5 bars) and a progressive discoloration of the blend (from white to yellow) were observed. However, only a slight increase in the internal pressure and no discoloration were observed when $Ti(OBu)_4$ was not added to the polymers. As we found, in a separate test performed on PC plus $Ti(OBu)_4$, that no gas was evolved, the increase in the internal pressure can be ascribed, according to Devaux et al.,[7] to the carbon dioxide formed via the side reaction following acidolysis of PC (see below). The rate of carbon dioxide evolution is enhanced in the presence of Ti catalyst since it increases the rate of the thermal degradation of PET[13,14] and, consequently, the rate of formation of carboxyl end groups in PET. The discoloration of the blend (from white to yellow) can be explained according to Smith et al.[6] In fact they showed that yellow byproducts are formed in the presence of Ti catalyst and phenol groups, and we, too, observed discoloration from yellow to brown by heating PC in the presence of a relatively large amount of $Ti(OBu)_4$. The greater number

of phenol end groups formed in the presence of Ti catalyst as a consequence of the faster acidolysis reaction explains the discoloration observed in our case when Ti(OBu)$_4$ was added.

Solubility Tests

In Figure 1 the weight fraction of the blend soluble in CH$_2$Cl$_2$ are reported vs. mixing time for runs performed with and without the addition of Ti(OBu)$_4$ to the PET/PC mixture.

The blends obtained in the presence of Ti catalyst initially showed a sharp decrease in the soluble weight fraction compared to the value of 0.5 expected if no reaction takes place, followed by a sharp increase in the soluble weight fraction up to complete solubility.

For blends obtained without the addition of Ti(OBu)$_4$ we observed in 2 h an initial slow decrease, followed by a slow increase, of the soluble weight fraction.

The decrease of the soluble weight fraction from the initial value of 0.5 can be explained only as a consequence of interchange reactions between PET and PC leading to macromolecules, which contain PC sequences in addition to PET sequences, which are no longer soluble in CH$_2$Cl$_2$.

The subsequent increase of the soluble weight fraction must be ascribed to the increased relative weight of PC sequences and to the shorter sequences of PET.

Therefore, from Figure 1 one can deduce that Ti(OBu)$_4$ is a much more effective catalyst for interchange reactions than Sb catalyst.

This conclusion is also supported by the IR investigation of the soluble and insoluble fractions.

The IR spectra of the soluble fractions showed in the 1700–1800 cm^{-1} range, practically the carbonate band only (1780 cm^{-1}) for the first sample, whereas, for subsequent samples, a progressive increase of the ester band (1720 cm^{-1}) with respect to the carbonate band was observed. This means that increasing amounts of PET sequences were made soluble in CH$_2$Cl$_2$ by reaction between PC and PET. For the completely soluble blend samples, the ester band was always slightly higher than that for carbonate.
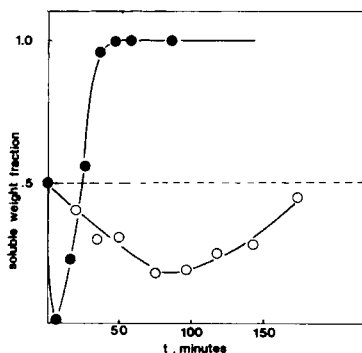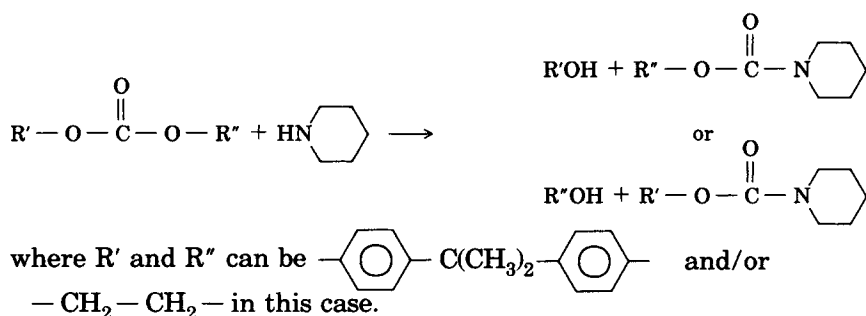

Fig. 1.   Soluble weight fraction (in CH$_2$Cl$_2$) vs. time for blends obtained by melt-mixing PET and PC in the presence (●) or in the absence (○) of Ti(OBu)$_4$.

The IR spectra of the insoluble fractions showed the bands for both ester and carbonate as expected from the weight fraction data, the former being always higher than the latter and increasingly so in time.

Selective Degradation of Blends

For more insight into the interchange reactions involved during melt mixing, we performed a selective degradation of the carbonate groups of the blends. This was achieved by reacting blend samples with a CH_2Cl_2 solution of piperidine. More experimental details about the chemical attack are given in the experimental part.

The reaction between piperidine and carbonate groups gives urethanes according to the general equation

$$R' - O - \overset{\overset{\displaystyle O}{\|}}{C} - O - R'' + HN\!\!\!\bigcirc \longrightarrow \quad \begin{array}{l} R'OH + R'' - O - \overset{\overset{\displaystyle O}{\|}}{C} - N\!\!\!\bigcirc \\[2mm] \text{or} \\ R''OH + R' - O - \overset{\overset{\displaystyle O}{\|}}{C} - N\!\!\!\bigcirc \end{array}$$

where R' and R'' can be $-\!\!\bigcirc\!\!- C(CH_3)_2 \bigcirc\!\!-$ and/or $- CH_2 - CH_2 -$ in this case.

Indeed in the IR spectra of the degradation products of PC and of PET/PC blends no traces of the 1780 cm^{-1} carbonate band were found and only bisphenol-A and the compounds 2,2-bis(4-piperidinocarbonyloxyphenyl)propane (**1**) and 2-(4-hydroxyphenyl)-2-(4-piperidinocarbonyloxyphenyl)propane (**2**) and the cyclic trimer of PET were identified by Hplc. Moreover, nearly constant ratios of (1/2) = 0.5 and (bisphenol-A/1) = 1 were found as expected from a random chemical attack on the carbonate groups.

Since it was previously verified that in these reaction conditions the intrinsic viscosity of pure PET remains unchanged, whereas carbonate groups are completely decomposed, this method can be used to isolate PET blocks from macromolecules containing chemically bonded PET and PC sequences. In fact all the fractions, insoluble in CH_2Cl_2 after this chemical attack, showed only the ester band (1720 cm^{-1}) in the 1700–1800 cm^{-1} region of their IR spectra, confirming that they contain PET sequences only.

The intrinsic viscosity of these insoluble fractions are reported in Figure 2; they were used to obtain the mean length of the PET sequences with the aid of the following Mark–Houwink equation[15]:

$$[\eta] = 7.61 \times 10^{-4} \, \overline{M}_n^{0.67} \tag{1}$$

From this figure it can be seen that the samples taken during the run performed without the addition of Ti(OBu)$_4$ gave, for about the first hour, intrinsic viscosities which were higher than those of the initial PET. We
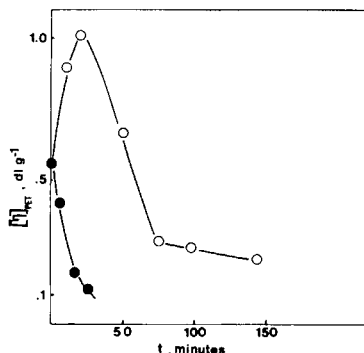
Fig. 2. Intrinsic viscosity vs. time for PET blocks after a chemical attack with piperidine of blends obtained in the presence (●) or in the absence (○) of Ti(OBu)$_4$.

can suggest two different explanations for this anomalous result: (i) ethanediol may react with PC during melt mixing and, in the absence of exchange reactions between PET and PC, its consumption may shift the chemical equilibrium in PET towards higher molecular weights; (ii) only the chain-end groups of PET react with PC, leading to short PC sequences connecting two or more PET macromolecules by chemical bonds. These short PC sequences might be shielded from piperidine attack by PET blocks.

An analysis of the PET intrinsic viscosities after piperidine attack lead us to favor the second hypothesis.
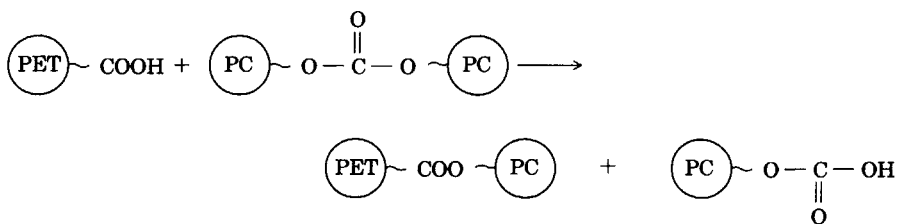
Interchange Reactions between PET and PC

The main interchange reactions which may take place, at the beginning, between PET and PC are the following:
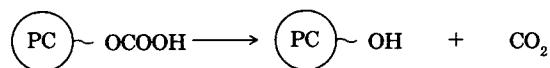
(I) Reaction between hydroxyl end groups of PET with carbonate groups of PC (alcoholysis):
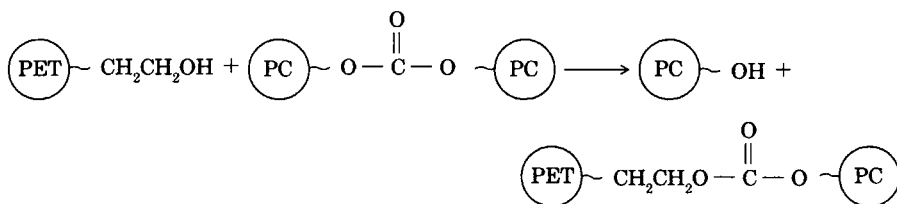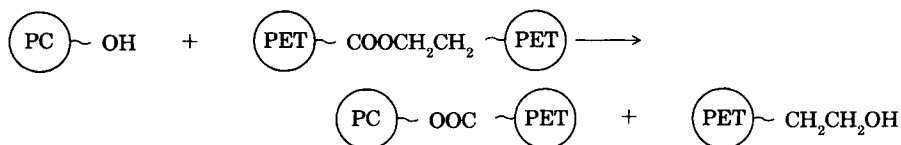

(II) Reaction between carboxyl end-groups of PET with carbonate groups of PC (acidolysis):
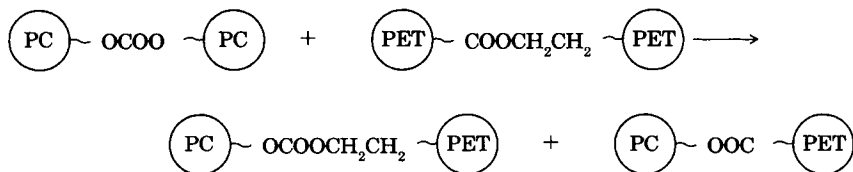
(III) ~OCOOH end groups formed in this reaction undergo a degradation according to the following reaction[7]:

$$\text{(PC)}\!-\!OCOOH \longrightarrow \text{(PC)}\!-\!OH \;+\; CO_2$$

(IV) Reaction between phenol end groups of PC with ester groups of PET (alcoholysis),

$$\text{(PC)}\!-\!OH \;+\; \text{(PET)}\!-\!COOCH_2CH_2\!-\!\text{(PET)} \longrightarrow$$

$$\text{(PC)}\!-\!OOC\!-\!\text{(PET)} \;+\; \text{(PET)}\!-\!CH_2CH_2OH$$

(V) Reaction between ester and carbonate groups (esterolysis),

$$\text{(PC)}\!-\!OCOO\!-\!\text{(PC)} \;+\; \text{(PET)}\!-\!COOCH_2CH_2\!-\!\text{(PET)} \longrightarrow$$

$$\text{(PC)}\!-\!OCOOCH_2CH_2\!-\!\text{(PET)} \;+\; \text{(PC)}\!-\!OOC\!-\!\text{(PET)}$$

The main question which must be answered is which of these reactions actually take place. Very little information is available about these reactions, and, furthermore, in this case the reactions take place in a medium which changes from heterogeneous to homogeneous.

The above results of the solubility tests and selective degradation runs clearly show that some of the above chemical reactions between PET and PC took place during melt mixing. The only reaction which can explain the evolution of gas is the side reaction III following acidolysis (II); this obviously means that reaction II takes place. On the other hand, the decrease of the intrinsic viscosity of PET blocks much faster than that predicted by thermal degradation only,[13,14] particularly when Ti(OBu)$_4$ was added, means that the ester bonds must be involved in the reaction with PC, i.e., reaction IV, V, or both must take place.

Additional insight in this regard can be achieved only by a separate study on model molecules.

This kind of study on systems similar to ours has been done by Devaux et al.[7] Their results can be assumed to be valid in our case also.

They found that reaction IV did not take place in to a significant extent, and, therefore, the decrease in the length of PET blocks in our case must be attributed to reaction V. From the above discussion only reaction V and thermal degradation can be responsible for cleavage of ester bonds. Each cleavage of the ester bonds gives a new, distinct PET block. According to Nassar et al.[2] our system consists, at the beginning, of two amorphous phases which apparently contain both components. We can reasonably suppose

that reaction V takes place with the same kinetic constant k_V in the two phases. In this hypothesis the correct equation for the increase in the number of PET blocks is the following:

$$(dN_{PET}/dt) = k_V(C'_{est}C'_{carb} + C''_{est}C''_{carb}) + k_{deg}C_{est} \tag{2a}$$

where C'_{est} and C'_{carb} are concentrations of ester groups and carbonate groups in one phase, C''_{est} and C''_{carb} the concentrations in the other phase, and C_{est} the concentration of ester groups in the whole blend. The relative amount and the compositions of the two phases are not known. However, the 50/50 (w/w) blend we used is not far from those found to be homogeneous[2] (60–70% by wt of PET), and we can reasonably suppose that the term in parentheses in eq. (2a) is not significantly different from that derived for a homogeneous system and reported below:

$$\frac{dN_{PET}}{dt} = k_V C_{est} C_{carb} + k_{deg} C_{est} \tag{2b}$$

where N_{PET}, C_{est}, and C_{carb} are the moles of PET blocks of ester and of carbonate groups in a kg of the whole blend, respectively. Since C_{est} and C_{carb} can be reasonably assumed to be constant, eq. (2b) can be integrated to give

$$N_{PET} = N^0_{PET} + (k_V C^0_{est} C^0_{carb} + k_{deg} C^0_{est})(t - t^0) \tag{3}$$

where k_V, C^0_{est}, and C^0_{carb} are the kinetic constant of reaction V, initial concentrations of ester and carbonate groups referred to a kg of blend, and k_{deg} is the kinetic constant of the thermal degradation of PET.

N_{PET} can be evaluated using eq. (1) with the intrinsic viscosity values obtained from the residue after the chemical attack with piperidine of the blend samples.

Plotting N_{PET} vs. time a linear plot was in fact obtained (see Fig. 3): from the beginning, for the Ti-containing system, and after an initial period of anomalous behavior for systems containing only Sb as catalysts.
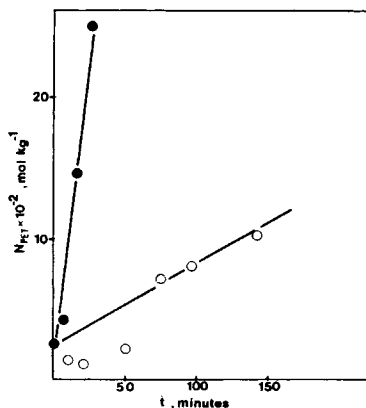

Fig. 3.   Number of PET blocks (mol/kg blends) vs. time in the presence (●) or in the absence (○) of Ti(OBu)₄.

From the slopes, using $k_{deg} = 5.4 \times 10^{-5}(min^{-1})$,[13] we obtained $k_V = 9.9 \times 10^{-4}$ (kg/mol · min) for titanium catalyzed reactions and $k_V = 2.6 \times 10^{-5}$ (kg/mol · min) in the absence of titanium catalyst. The result for the Ti-catalyzed reaction is similar to that reported by Devaux et al.[7] for the PBT/PC system at 250°C ($k_V = 2.2 \times 10^{-3}$ kg/mol · min).

The k_V value in the absence of Ti catalyst is of the same order of magnitude as the uncatalized reaction, studied by model molecules for the system PBT/PC[7]; this partially justifies the conclusion that no reaction takes place as suggested by Nassar et al.[2] In fact, for a short time of melt mixing (as used by those authors) only a small degree of reaction is to be expected if the titanium catalyst is not added as was the case for their studies.

CONCLUSIONS

The above experimental results show conclusively that when PET and PC are melt-mixed, they undergo chemical reactions, which lead to changes in the chemical structure of the polymers.

This finding modifies a previously reported conclusion.[2] The chemical structure of the final blend is strongly dependent both on the melt-mixing time and on the kind of interchange catalyst added to the polymers. Titanium alcoxide catalyst gives fast exchange reactions which involve ester and carbonate groups (esterolysis) and carbonate groups and end groups of PET (alcoholysis and acidolysis), but, at the same time, side reactions take place, leading to discoloration and gas evolution.

Without the addition of titanium alcoxide (i.e., when only Sb catalyst is present) the exchange reaction between ester and carbonate groups procede at a much lower rate (practically the same as the uncatalyzed reaction[7]), but neither discoloration nor gas evolution takes place to a significant extent.

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