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Reactions induced by triphenyl phosphite addition during melt mixing of poly(ethylene terephthalate)/poly(butylene terephthalate) blends: influence of phosphite structure and polyester chain-end concentration

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The addition of phosphite during melt processing of polyester leads to the creation of two different types of linkages: ester bonds and bonds including phosphorus atoms. The influence of different parameters on these reactions has been investigated. Experiments carried out with different grades of poly(ethylene terephthalate) show that variables such as total concentration of reactive end-groups and hydroxyl/carboxyl chain-end ratio control not only the number but also the nature of the reactions that occur. The addition of different phosphites also reveals the influence of the nature and structure of the organic groups attached to the phosphorus atom on the reaction with polyester chain ends. Finally, the mechanisms described for polyester/phosphite systems are successfully applied to acrylic polymers, broadening the scope for application of these reactions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); triphenyl phosphite; reactive processing)

INTRODUCTION

The influence of triphenyl phosphite (TPP) addition during melt mixing of poly(ethylene terephthalate) (PET) or poly(ethylene terephthalate)/poly(butylene terephthalate) (PET/PBT) blends has been investigated previously[1-4]. Torque measurements during polyester processing and corresponding intrinsic viscosity values have confirmed the occurrence of chain extension[1,2]. Detailed chromatographic investigation has confirmed the molecular-weight increase[3]. Moreover, the dual nature of the reaction mechanism has been highlighted[2,3], and schemes deduced from model-compound study[4] have been applied successfully to polymers. In addition to ester bond creation, the formation of a linkage including phosphorus atoms has been verified by chromatography and elemental analysis. The high sensitivity of this new link to water, phosphorus by-products and phenolic solvents at high temperature explains the instability observed under specific conditions[3].

All the previously reported experiments concerning the reaction mechanisms involved one PET material or PET/PBT blends[2,3]. In this paper, the extension to other grades of polyester enables analysis of the influence of new parameters, such as the total concentration of reactive chain ends or the ratio between hydroxyl and carboxyl end-group concentrations. The addition of different phosphites is investigated in order to highlight the influence of the nature of the organic groups attached to the phosphorus atom on the chain-extension mechanisms occurring on reaction with polyester end-groups. Finally, these reactions are extended to other polymers (acrylics) possessing chain ends of similar nature.

EXPERIMENTAL

Materials

1,1,2,2,-Tetrachloroethane (TCE) (Aldrich, 99%) was distilled before use. Phenol (Janssen, 99%), benzoyl chloride (Aldrich, 99%), triphenyl phosphite (TPP) (Janssen, 99⁺%), di-n-octadecyl phosphite (Janssen, 95%), triphenyl phosphate (Janssen, 99⁺%) and tributyl phosphite (Janssen, 95%) were used as received. Diphenyl phosphite (DPP) (Janssen) was also used as received. The presence within DPP of large amounts

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Table 1 Concentration of different types of polyester chain ends, determined on polyesters as received, and ratio between hydroxyl and carboxyl end-groups

	[-OH] (eq. g/10^6 g)	[-COOH] (eq. g/10^6 g)	[phenyl groups] (eq. g/10^6 g)	[-OH]/[-COOH]
PET	68	38	–	1.8
PETOH1	36	45	25	0.8
PETOH2	108	22	–	4.9

of phenol and TPP impurities was confirmed by h.p.l.c. and ^{31}P n.m.r. analyses[4].

Bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite (BTBP) (Ultranox® 626) and distearyl pentaerythritol diphosphite (DPD) (Weston® 618F) were supplied by GE Specialty Chemicals.

Two samples of end-functional acrylic polymers (R8860/76, hydroxyl end functional; and R8567/247, carboxyl end functional) were supplied by ICI. These acrylic polymers were prepared by chain transfer of linear acrylic polymers by the appropriate chain-transfer agents, i.e. thioethanol and thiolactic acid. The monomeric composition of the two polymers is identical and they contain methyl methacrylate and butyl acrylate in the ratio 48.16/51.84. Each polymer chain possesses only one reactive end-group with a hydroxyl or carboxyl nature, respectively. Calculated value of the glass temperature is 0°C.

Poly(butylene terephthalate) (PBT) was Celanese 2000 supplied by Hoechst Celanese. Poly(ethylene terephthalate) (PET) was B73L supplied by ICI. Some PET B73L was modified in order to reduce the concentration of hydroxyl chain ends. This modified PET, the preparation of which is described below, will be referred to as PETOH1 in this paper. Another grade of PET used in this work was Bx2954 supplied by ICI. This is characterized by a high concentration of hydroxyl end-groups and will be referred to later in this work as PETOH2. Concentrations of chain ends and ratio between hydroxyl and carboxyl end-groups were measured by infra-red spectroscopy[2] for the different grades of PET. They are displayed in *Table 1*.

Preparation of PETOH1. Functionalization of PET can be achieved by reaction between acid chloride and hydroxyl chain ends of the polyester[5]. In the present work, addition of benzoyl chloride was used to reduce the concentration of hydroxyl end-groups by formation of unreactive phenyl chain ends (*Scheme 1*). The concentration of carboxyl end-groups is not significantly modified by this treatment.

In a round-bottomed flask, benzoyl chloride (0.60 g) was dissolved in 250 ml tetrachloroethane. In another flask, 25 g of PET were dissolved in 200 ml boiling tetrachloroethane. Conditions of reaction must be anhydrous. Pyridine (0.34 g) was present in the two
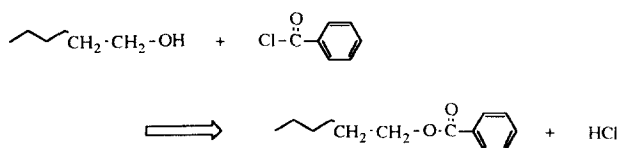
solutions. Its total amount was stoichiometrically equivalent to the amount of acid chloride used. After PET dissolution, the temperature is reduced to 100°C and the two solutions are mixed together. After 1 h reaction at this temperature, the polyester is precipitated in distilled acetone and washed by refluxing distilled acetone in a Soxhlet-type apparatus for 60 h. This purification eliminates excess acid chloride and also benzoic acid created by reaction with traces of water present in the solution.

Concentrations of hydroxyl and carboxyl chain ends in this modified PET were measured by infra-red spectroscopy (*Table 1*).

Processing conditions

PET or PET/PBT 75/25 (w/w) blends, previously dried overnight at 120°C under vacuum, were kneaded in a Brabender Plastograph equipped with an electrically heated mixing device, W50EH. The mixing speed used was 30 rotations per minute. The temperature was regulated in the range 275–280°C. The atmosphere was controlled by blowing nitrogen above the mixing chamber. Temperature and torque were continuously recorded during the mixing process.

Different phosphite quantities were added to the polyesters. Phosphite concentrations are always reported in amount of additive per weight of base polymer. In all Brabender experiments, the polymers were mixed for 5 min in order to get a homogeneous polyester melt before adding the phosphite. The zero time corresponds to the introduction of the phosphite into the mixer, a reference sample being withdrawn just before. Other samples were withdrawn for analysis after different mixing times ranging from 1 to 35 min.

These samples, previously frozen in liquid nitrogen, were finely ground in a crushing mill from IKA. The polyester purification from phosphite reaction by-products was carried out by extraction with distilled acetone for 72 h in a Soxhlet-type apparatus, followed by drying overnight at 120°C under vacuum.

Gel permeation chromatography

Gel permeation chromatography was performed at 50°C with a 60/40 (w/w) phenol/tetrachloroethane eluent using a Waters 150C high-temperature chromatograph with a refractive-index detector. Two Shodex columns from Showa Denko (ref. AT-80M/S) and one Ultra-styragel column (500 Å from Waters) were used in series. The flow was 0.5 ml min^{-1}.

Polyester samples for g.p.c. analysis were purified from reaction by-products and dried before dissolution. The concentrations were 8 to 10 mg of polymer dissolved at room temperature in 2 ml of the same batch of solvent as the eluent phase. Approximately 120 μl were injected. The run time was fixed to 90 min. The eluent solvent was

Scheme 1 Functionalization of PET by reaction between hydroxyl end-groups and benzoyl chloride

maintained in a thermostatic bath at 30°C in order to prevent phenol crystallization.

The results were analysed on a Digital Micro Vax 2000 computer. The chromatograph was calibrated with 12 polystyrene standards supplied by Waters and ranging from 1250 to 2 700 000 g mol^{-1}. Molecular-weight values are therefore expressed in polystyrene equivalents (PS g mol^{-1}). The precision inherent to chromatographic measurements is better than 10%.

After conditioning the chromatographic columns for 15 days with the eluent phase at 50°C, the retention time stability of the polystyrene standards was verified. Nevertheless, new PS calibrations were conducted regularly in order to observe any modification of the system. Very good molecular-weight reproducibility with time was observed. It was also verified that the polyester holding time in solution in phenol/tetrachloroethane at 50°C does not have any influence on the measured molecular weight.

Phosphorus elemental analysis

Some 0.5 g of the samples were heated in 5 ml of concentrated sulfuric acid, followed by oxidation/heating with hydrogen peroxide until a clear solution is obtained. The solution is then diluted to 50 ml with purified water. This method of sample preparation is often referred to as wet oxidation.

Phosphorus is determined by inductively coupled plasma optical emission spectrometry (i.c.p.-o.e.s.) using a Perkin-Elmer Plasma II instrument. The instrument was calibrated using solutions containing 0, 10, 20 and 30 ppm P in 10% (v/v) sulfuric acid. The P concentrations were calculated from the emission intensities of the samples. The relative standard deviation of the measurement is typically 1% for three replicates.

Experiments carried out with acrylic polymers

Reactions between stoichiometric ratios of acrylic polymers and triphenyl phosphite (TPP) were carried out without solvent in a four-necked round-bottomed 50 ml flask fitted with nitrogen inlet, reflux condenser with a CaCl$_2$ tube and magnetic stirrer. The reactor was heated to 210°C in a regulated silicone oil bath. Small samples were removed periodically (after 10, 20, 30, 60, 120 and 240 min) and held under inert atmosphere in order to monitor the progress of the reaction. Some samples were submitted to reflux with distilled water for 37 h in a Soxhlet-type apparatus and dried afterwards at 120°C under vacuum overnight.

Gel permeation chromatography was performed at 25°C with a system consisting of a Waters Associates chromatography pump, a Millipore-Waters sample injector model 712 Wisp and a Millipore-Waters differential refractometer model 410. Five ultrastyragel columns (10^6, 10^5, 10^4 and 500 Å) were used in series. Tetrahydrofuran is a high-performance liquid-chromatography solvent (Lab-Scan). The polymer concentrations were 6 to 8 mg of polymer dissolved at room temperature in 2 ml of solvent. Approximately 50 μl were injected. The flow was 0.8 ml min^{-1}. The run time was fixed to 80 min. The results were analysed on a Digital Micro Vax 2000 computer. The chromatograph was calibrated with 16 polystyrene standards ranging from 580 to 2 890 000 g mol^{-1}. Molecular-weight values are therefore expressed in polystyrene equivalents (PS g mol^{-1}). The precision inherent to chromatographic measurements is better than 10%.

RESULTS

Influence of triphenyl phosphite addition in different grades of PET

The three grades of poly(ethylene terephthalate) considered in this study differ both by the total concentration of reactive chain ends and by the ratio between hydroxyl and carboxyl end-groups (*Table 1*).

Brabender processing. During polymer processing in the Brabender Plastograph, the torques recorded throughout the experiment are representative of the melt viscosity in the system. The evolution of torque for different grades of PET during mixing with 2% triphenyl phosphite is presented in *Figure 1*.

By taking into account the possible evaporation of some phosphite during mixing, the 2% TPP quantity corresponds for 'standard' PET to a stoichiometric amount of phosphite molecules and polyester chains, as previously described[2]. The triphenyl phosphite addition induced a very large torque increase, greater than
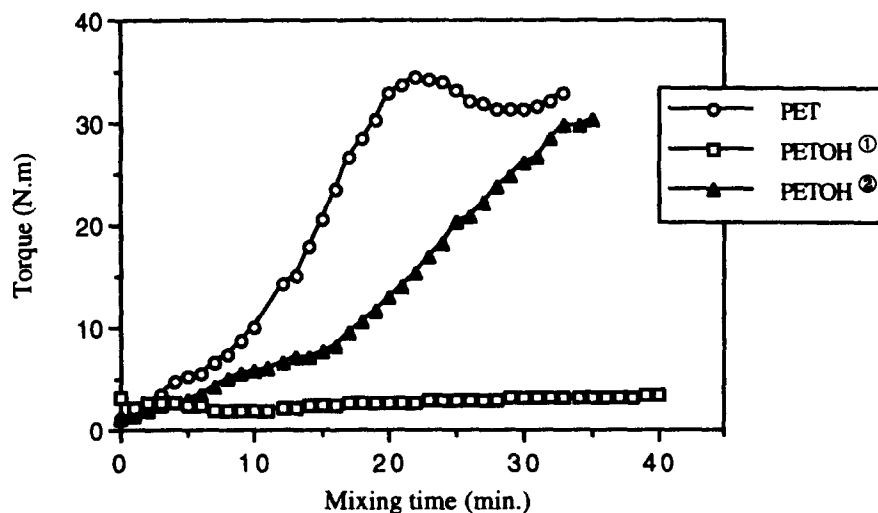

Figure 1 Torque *versus* mixing time for different grades of PET with addition of 2% TPP
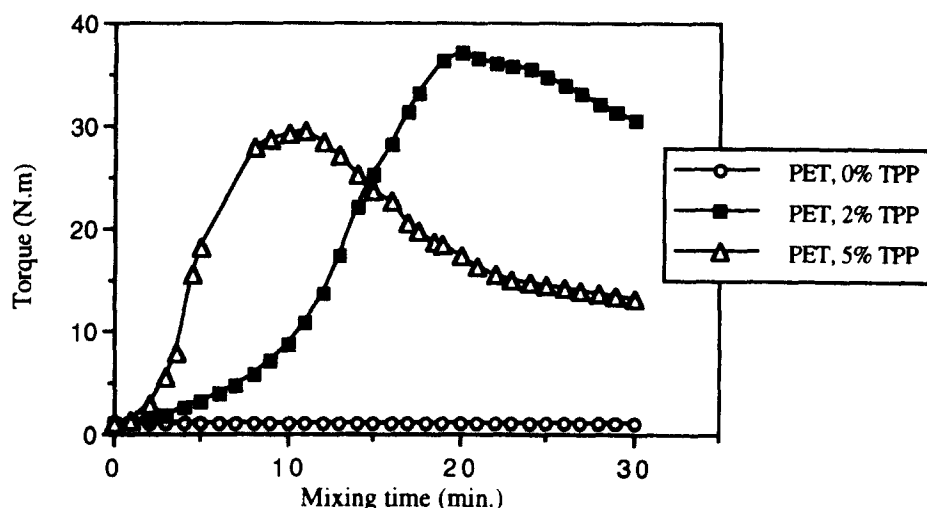
Figure 2 Torque *versus* mixing time for PET with addition of 0%, 2% or 5% TPP
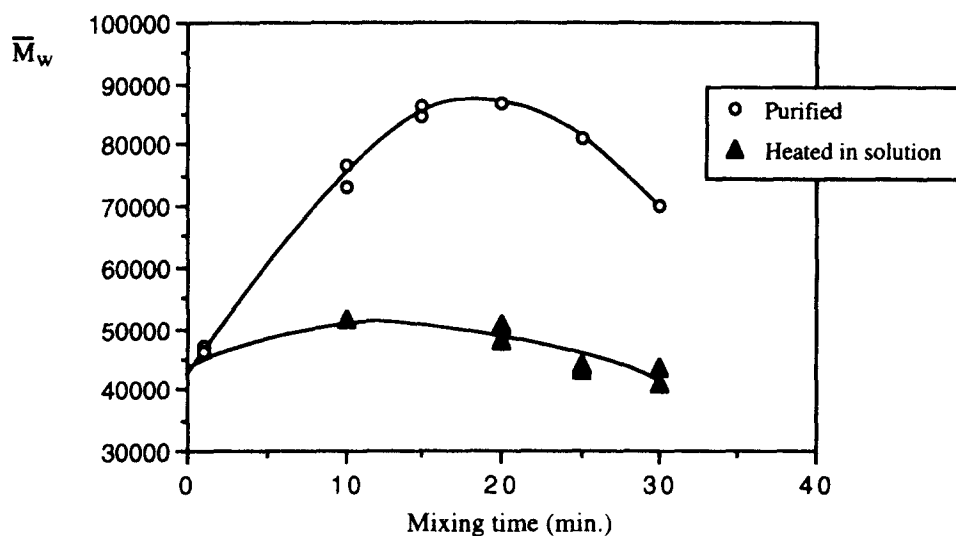

Figure 3 Weight-average molecular weight *versus* mixing time for PET with addition of 2% TPP, purified by acetone washing, before (O) and after heating for 15 h (▲) at 120°C in a phenol/TCE 60/40 solution

one order of magnitude. The maximum torque was observed after 15 to 20 min of mixing. After this value was attained, a steady decrease was observed at longer mixing times. It must also be noted that, during the torque increase up to high values, measurements revealed a progressive appearance of instabilities and oscillations and average values were calculated. This effect can be correlated with the formation of a high-viscosity polymer. The polyester melt progressively adopts an elastic behaviour and it therefore becomes meaningless still to consider the torque measurements as purely significant of viscous flow for that part of the curves. Moreover, such observation does not deny the possibility of branching during polyester/TPP system processing.

A higher concentration of hydroxyl chain ends in PETOH2 resulted in a regular torque increase for more than 30 min after TPP addition, but at a lower rate than previously observed. The maximum values obtained were roughly equivalent. On the other hand, no significant increase of the torque values could be observed after triphenyl phosphite addition in PETOH1.

Differences were observed by varying TPP concentration (*Figure 2*). When stoichiometric amounts of phosphite (2%) were added, the torque maximum was observed after 15 to 20 min of mixing. As larger phosphite quantities were added, more rapid torque increase was observed. With a large phosphite excess (5%), the torque curve maximum occurred earlier (in approximately 10 min), but the observed maximum value was then lower.

Polyester molecular-weight values. Chromatographic measurements of molecular weight carried out on polyesters after reaction with phosphite were performed on purified samples. Immediately after processing, polyester/TPP systems were refluxed with acetone. This treatment is efficient in preventing any degradation caused by reaction by-products.

Evolution of polyester molecular weight during mixing with triphenyl phosphite is displayed in *Figures 3* to *5* for the different grades of PET. The molecular weight of the purified samples was measured before and after heating at 120°C in phenol/TCE 60/40 solution for
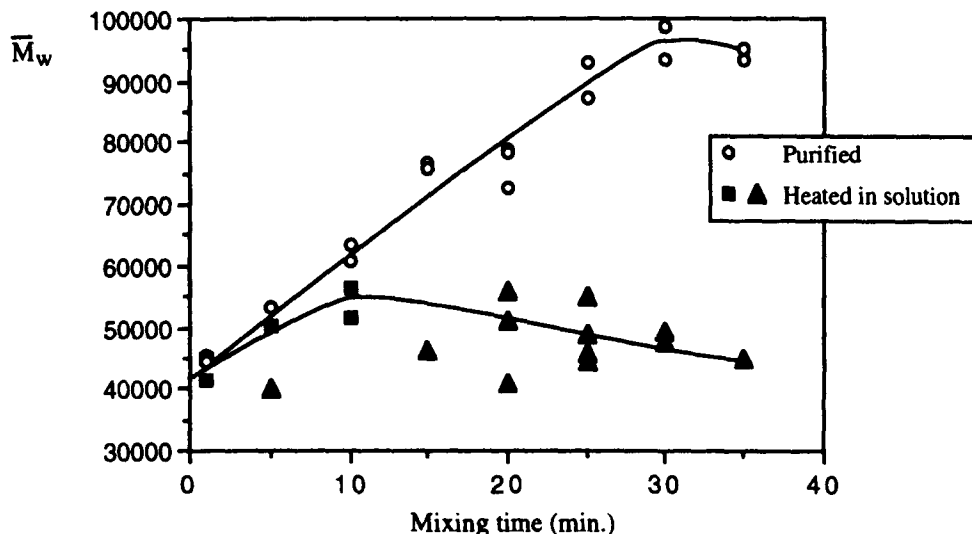
Figure 4 Weight-average molecular weight *versus* mixing time for PETOH2 with addition of 2% TPP, purified by acetone washing, before (O) and after heating at 120°C for 2 h (■) or 15 h (▲) in a phenol/TCE 60/40 solution
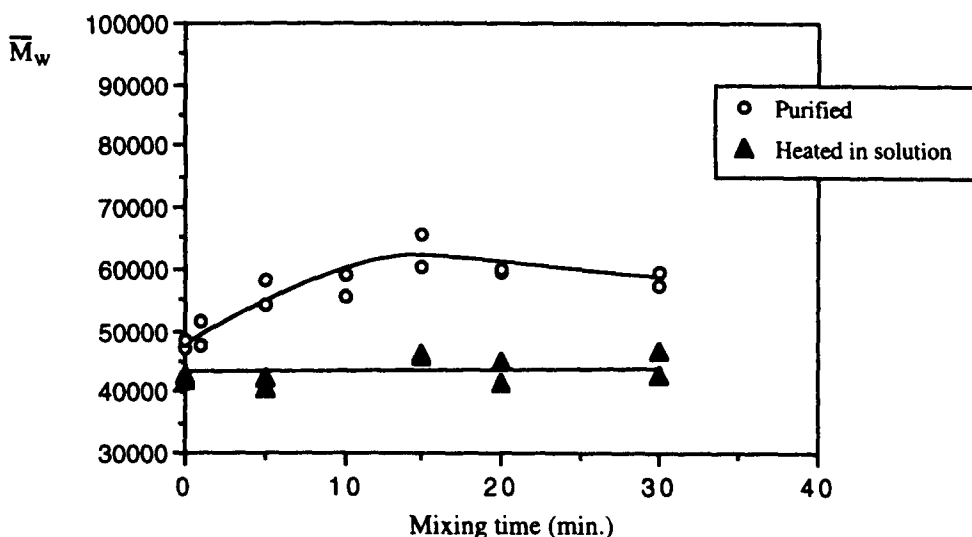

Figure 5 Weight-average molecular weight *versus* mixing time for PETOH1 with addition of 2% TPP, purified by acetone washing, before (O) and after heating for 15 h (▲) at 120°C in a phenol/TCE 60/40 solution

different times. Heating polyester/TPP systems at high temperature in the presence of phenolic solvents induces[2,3] the scission of the phosphorous-containing links created by the phosphite addition. By taking advantage of this efficient way to break the most reactive bonds, the molecular weights exclusively related to the presence of stable ester bonds can be measured. Previous results have shown that the degradation is rapid and can be assumed to be complete after 2 or 15 h at 120°C in solution.

For 'standard' PET (*Figure 3*), the triphenyl phosphite addition induced a large increase of the molecular weight. The molecular-weight values were doubled at maximum torque, i.e. 15 to 20 min after the phosphite addition. The highest molecular-weight values were observed for PETOH2, 30 min after triphenyl phosphite addition (*Figure 4*). Conversely, PETOH1 only showed a limited molecular-weight increase (*Figure 5*).

The formation of new ester bonds as a consequence of

TPP addition is shown by the slight molecular-weight increase measured in PET and PETOH2 after scission of the phosphorus links by heating in solution. On the other hand, this effect is not observed for PETOH1, where stable molecular-weight values were measured.

Phosphorus elemental analysis. The incorporation of phosphorus atoms into the polyester backbone after melt mixing with 2% triphenyl phosphite was measured for different PET grades. *Figure 6* displays the evolution *versus* time of the corresponding torque values. Samples (indicated by arrows) were withdrawn, purified from phosphite by-products by acetone refluxing and the amounts of bound phosphorus atoms were measured by elemental analysis. The results confirm that triphenyl phosphite reacts with all PET grades but that linked phosphorus amounts are not correlated with Brabender torque values.
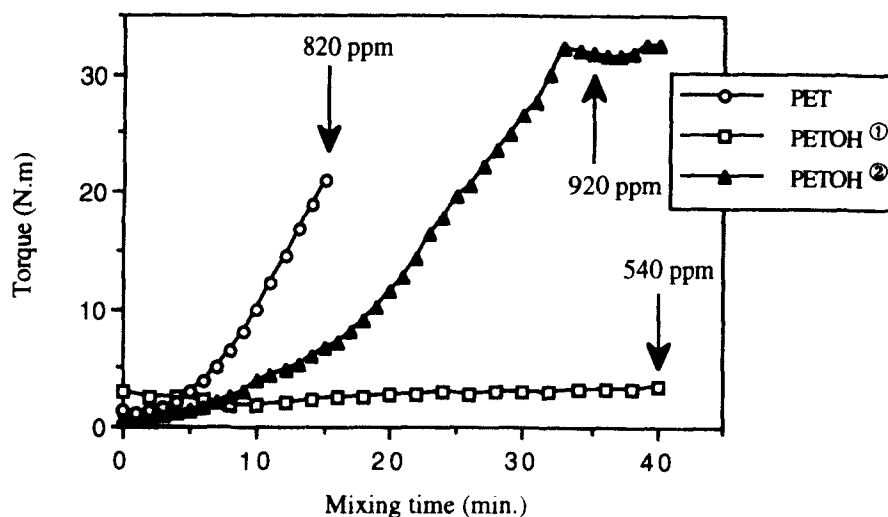
Figure 6 Torque *versus* mixing time for different grades of PET with an addition of 2% TPP and values of the linked phosphorus content measured by elemental analysis on samples withdrawn after different times (indicated by arrows) and purified by acetone refluxing
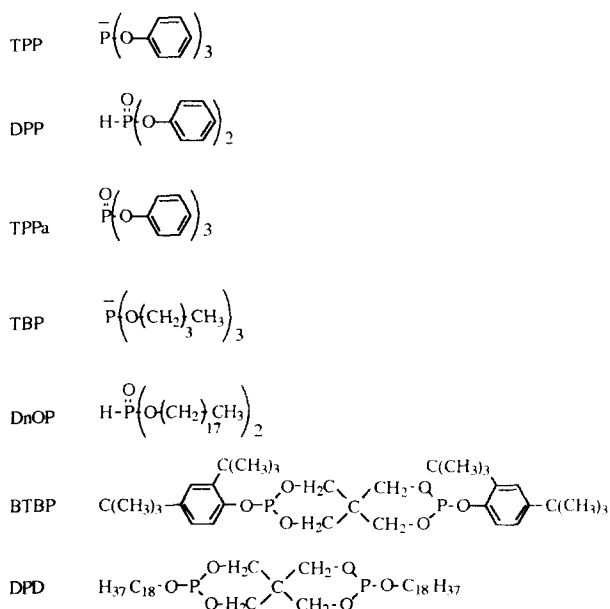

Figure 7 Structure of the different phosphorus compounds used

Action of different phosphites

The influence of the nature of the organic groups attached to the phosphorus atom has been investigated by following the evolution of torque values during melt mixing of PET/PBT systems with addition of different phosphite compounds. The phosphites considered in this study are displayed in *Figure 7*.

Addition of 2% diphenyl phosphite (DPP) to polyester blends induced a torque increase. However, by comparison with triphenyl phosphite, slower reaction rate and reduced values were obtained (*Figure 8*). On the contrary, the presence of 2% phenol or triphenyl phosphate (TPPa) did not modify the polyester behaviour. An immediate drop of the torque values down to zero was also observed as a consequence of di-n-octadecyl phosphite (DnOP) addition.

The amount of phosphite added has been deduced by considering the polyester number-average molecular weights (deduced from infra-red measurements[2]) after

5 min mixing in the Brabender, i.e. immediately before phosphite addition. By taking into account the possible evaporation of some phosphite during mixing, the quantities were calculated in order to promote a stoichiometric reaction with the polyester chains. The chosen values are thus 2% triphenyl phosphite (TPP)[2], 1.2% tributyl phosphite (TBP), 1.8% diphenyl phosphite (DPP), 3.6% bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite (BTBP) and 4.4% distearyl pentaerythritol diphosphite (DPD). Torque values measured during the experiments with these quantities of phosphites are compared in *Figure 9*.

While DPD addition caused a torque decrease, an increase was observed with DPP and BTBP. Reduced maxima and lower reaction rates (specially with BTBP) were measured by comparison with the observations realized after addition of 2% TPP. Oscillations appearing during processing had a greatly reduced magnitude.

By neglecting the presence of impurities in DPP, the addition of 1.8% diphenyl phosphite in the blends theoretically corresponds to an incorporation of 2338 ppm phosphorus in the polyesters. Sample purification by acetone refluxing has been proved to be an adequate procedure for the elimination of free phosphite by-products remaining trapped in the polymers[3]. The amount of phosphorus atoms chemically bonded to the polymer backbone after DPP addition was measured by elemental analysis on samples withdrawn after different mixing times and purified. Results are displayed in *Table 2*. The rapid incorporation of large amounts of phosphorus atoms in the polyester backbone is obvious.

The influence of tributyl phosphite (TBP) addition was observed in experiments carried out with PBT at 245°C. The lower boiling point of TBP prevents experiments at PET processing temperatures (274–280°C). The torque evolution following the addition of 1.2% TBP is displayed in *Figure 10*. Reaction between polyester and TBP induced a slow torque increase and oscillation phenomena were not observed. Measurements realized on samples withdrawn after 66 and 121 min reaction time both revealed the incorporation of 1100 ppm phosphorus into the polyester backbone. These amounts represent a
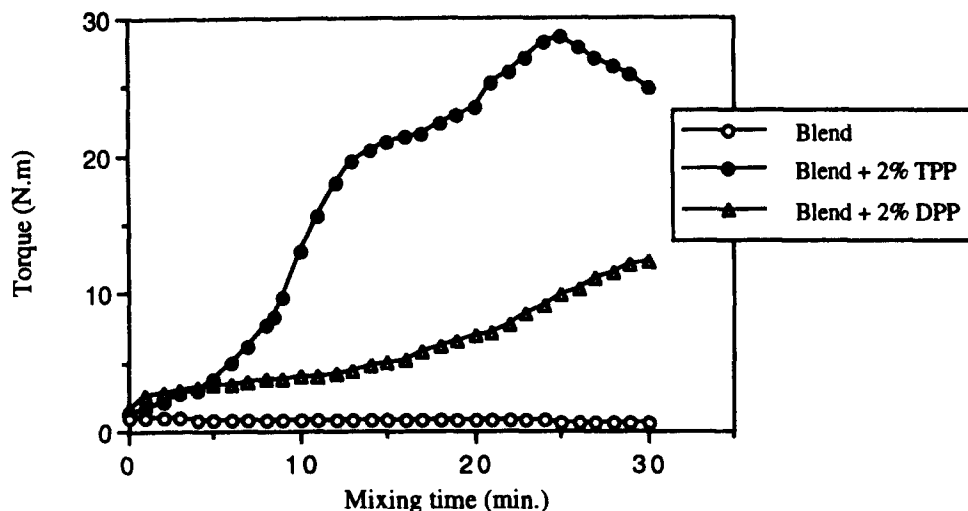
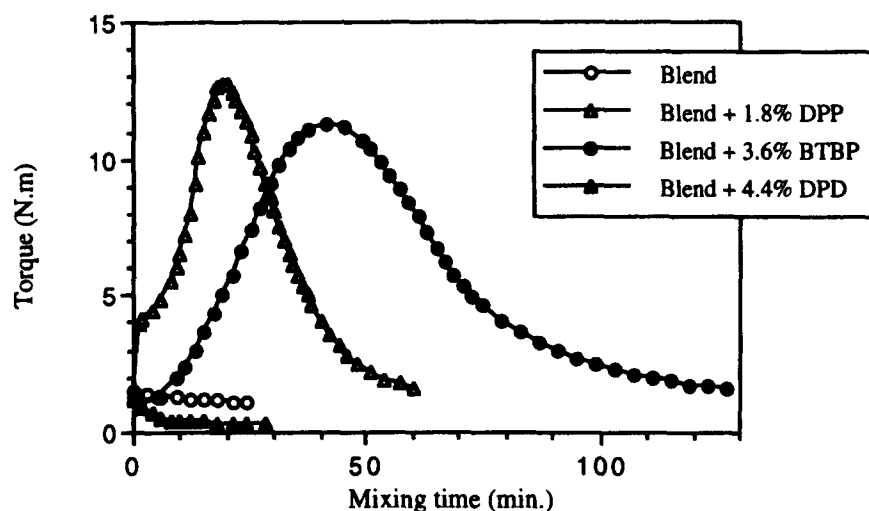**Figure 8** Torque *versus* mixing time for PET/PBT 75/25 blends alone and with addition of 2% TPP or 2% DPP

Figure 9 Torque *versus* mixing time for PET/PBT 75/25 blends alone and with addition of 1.8% diphenyl phosphite, 3.6% BTBP and 4.4% DPD

Table 2 Linked phosphorus content in PET/PBT 75/25 blends after reaction with 1.8% DPP. The polyester was withdrawn after different reaction times and purified by acetone washing

	5 min	20 min	30 min
1.8% DPP	1300 ppm	1600 ppm	1600 ppm

large proportion of the theoretical maximum values since the addition of 1.2% TBP represents the incorporation of 1467 ppm phosphorus in the polyester.

Extension to acrylic polymers

Weight-average $(\bar{M}_w)$ and Z-average $(\bar{M}_Z)$ molecular weights of acrylic polymers as received and of equimolar blends were measured and are displayed in *Table 3*. The chromatographic technique used gives reliable values for $\bar{M}_w$ and $\bar{M}_Z$. A very good molecular-weight reproducibility with time was observed for acrylic polymers containing no TPP. As anticipated, values of the equimolar blend were found to be intermediate between those of the components. Moreover, no appreciable molecular-weight change was measured after water reflux on polymers containing no TPP.

Reactions were carried out at 210°C between equimolar amounts of hydroxyl-ended acrylics, carboxyl-ended acrylics and triphenyl phosphite. The evolution of weight-average $(\bar{M}_w)$ and Z-average $(\bar{M}_Z)$ molecular weights of these polymers during reaction is displayed in *Figures 11* to *14*.

Measurements $(\bar{M}_w$ and $\bar{M}_Z)$ carried out on hydroxyl end-functional acrylic polymer after reaction with triphenyl phosphite highlight a molecular-weight increase (*Figures 11* and *12*). A subsequent reflux in water results in a large reduction of the polymer molecular weights towards the initial values.

Heating equimolar amounts of hydroxyl and carboxyl end-functional acrylics does not induce any molecular-weight modification, even after 4 h reaction at 210°C. On the other hand, an increase of $\bar{M}_w$ and $\bar{M}_Z$ values is clearly noticeable after stoichiometric TPP addition in this acrylic blend (*Figures 13* and *14*). Reflux in water results in a molecular-weight decrease, but the reduction is smaller (as observed with $\bar{M}_w$ measurements), and high values can still be observed in comparison with the unreacted blend.
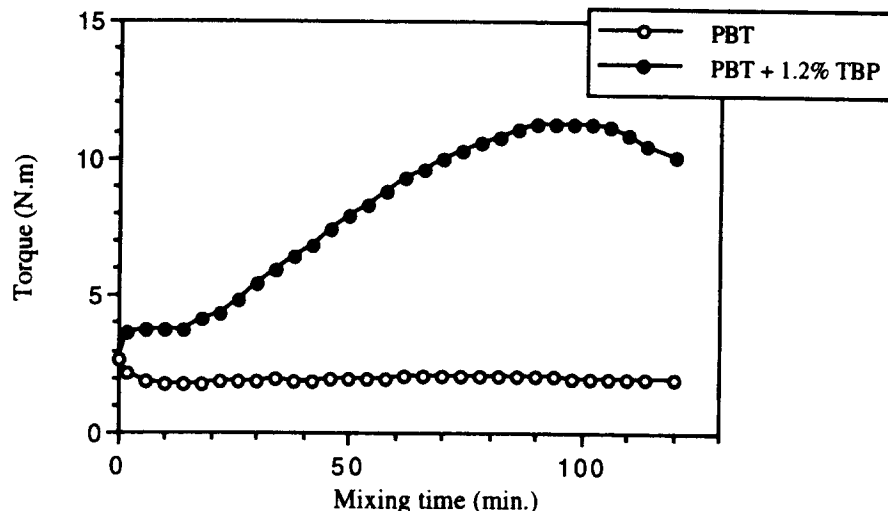
A molecular-weight decrease also results when

Figure 10 Torque *versus* mixing time for PBT alone and with addition of 1.2% TBP

Table 3 Weight-average and Z-average molecular weights (expressed in polysytrene equivalents) of hydroxyl and carboxyl end-functional acrylics as received, and of an equimolar blend made with them

	$\bar{M}_w$	$\bar{M}_z$
Acrylic –OH	5000	8200
Acrylic –COOH	6500	11400
Equimolar blend	5900	10200

samples withdrawn after reaction with phosphite are exposed to air moisture. The extent of this degradation is similar to that induced by water refluxing.

The water content of the hydroxyl end-functional acrylics was estimated by a thermogravimetric measurement of the polymer weight loss upon heating between 40 and 150°C. Under the storage conditions used, the water content represents 0.90% by weight of the acrylic polymer.

DISCUSSION

Detailed investigation of the changes induced by

triphenyl phosphite addition during polyester melt mixing has been achieved by a study with model molecules representative of hydroxyl and carboxyl polymer chain ends[4]. Reaction schemes deduced therefrom have been successfully applied to polymers[3].

Exchange between the phenoxy groups of the phosphite and polyester hydroxyl chain ends incorporates phosphorus (still in a reactive (P^{III}) state) into the polymer backbone. In the case of multiple substitutions, the phosphorus atom acts as a crosslink point between different polyester chains. Thus, the molecular weight increases and branching can occur. The temperature of reaction (280°C) favours phenol elimination and displaces the equilibrium in the desired way (*Scheme 2*).

Reaction between the carboxyl end-group and phosphite leads to ester bond formation and phosphonate release. If the reaction occurs with a phenoxy function of the phosphite molecule, phenyl ester is created at the polymer chain end (*Scheme 3*, pathway [2]). On the other hand, the reaction on a previously substituted site creates an ester bond as a new link between two polyester
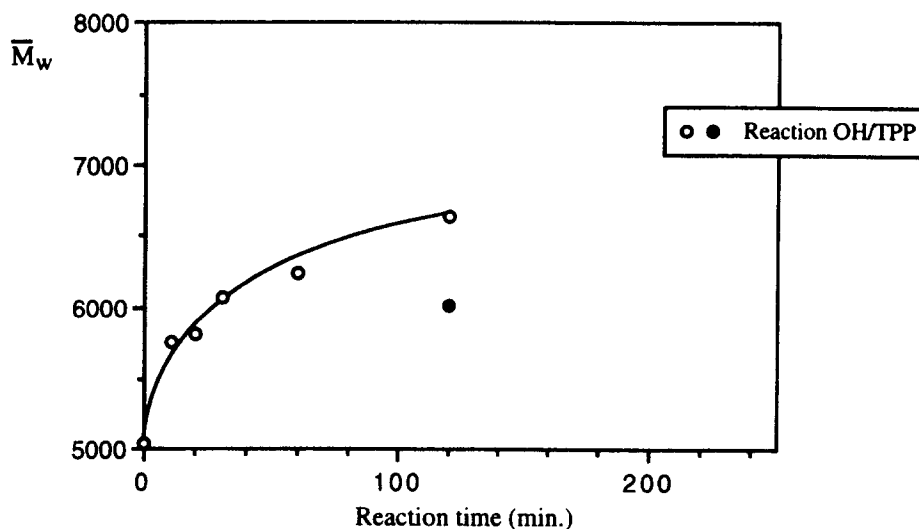

Figure 11 Weight-average molecular weight *versus* reaction time for equimolar amounts of hydroxyl-ended acrylics and triphenyl phosphite, before (O) and after (●) 37 h water reflux

Figure 12 *Z*-average molecular weight *versus* reaction time for equimolar amounts of hydroxyl-ended acrylics and triphenyl phosphite, before (O) and after (●) 37 h water reflux
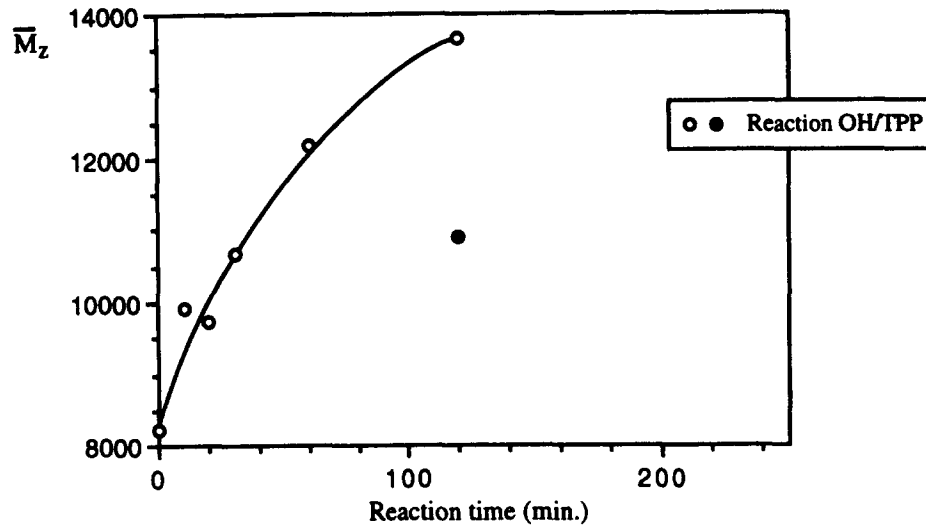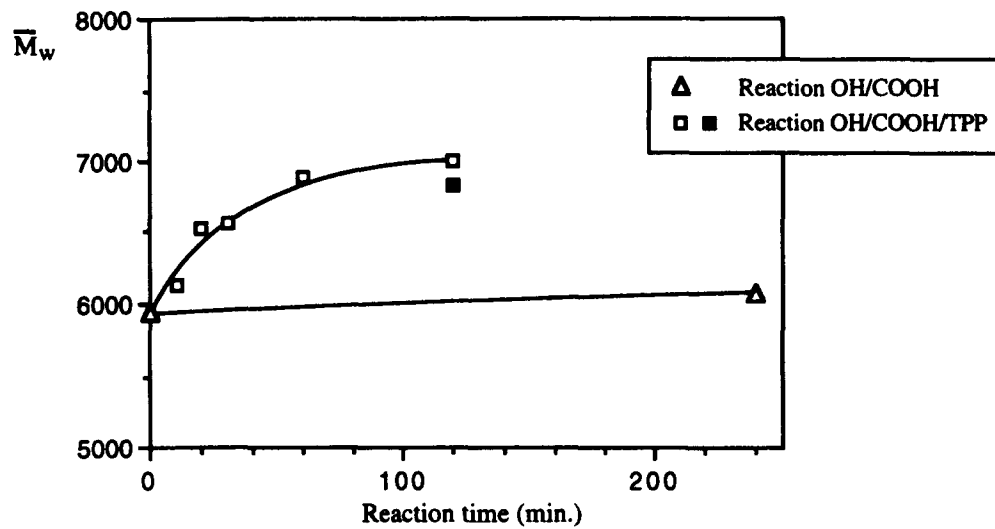

Figure 13 Weight-average molecular weight *versus* reaction time for equimolar amounts of hydroxyl-ended acrylics, carboxyl-ended acrylics and triphenyl phosphite, before (□) and after (■) 37 h water reflux. The reaction was also carried out between equimolar amounts of both acrylics, without TPP addition (△)

Figure 14 *Z*-average molecular weight *versus* reaction time for equimolar amounts of hydroxyl-ended acrylics, carboxyl-ended acrylics and triphenyl phosphite, before (□) and after (■) 37 h water reflux. The reaction was also carried out between equimolar amounts of both acrylics, without TPP addition (△)
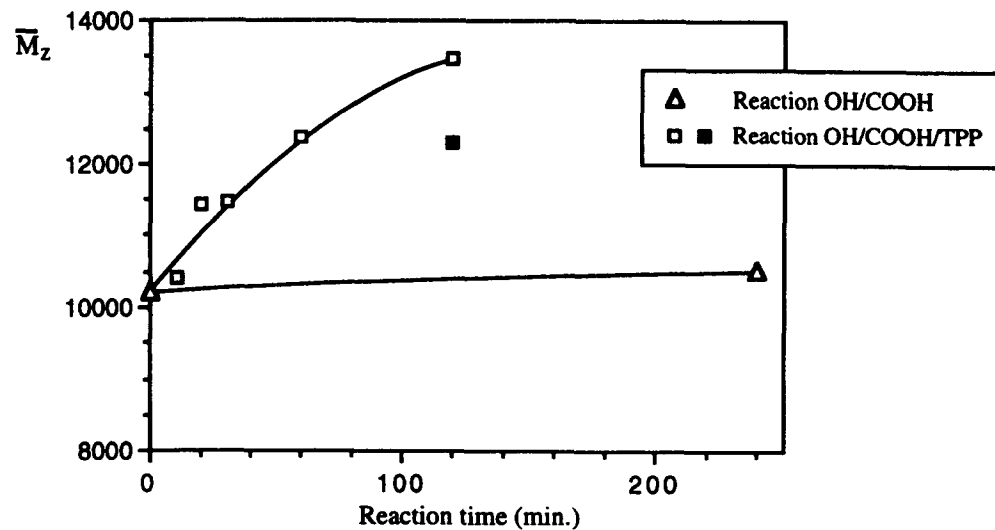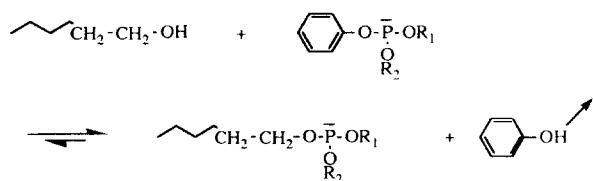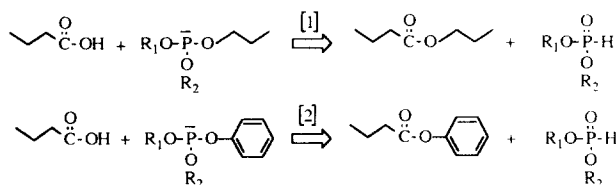
Scheme 2 Reaction mechanisms between polyester hydroxyl chain ends and phosphite (R_1 and R_2 are phenyl groups or polyester chains)

Scheme 3 Reaction mechanisms between polyester carboxyl chain ends and phosphite (R_1 and R_2 are phenyl groups or polyester chains)

Table 4 Molar ratio between the added triphenyl phosphite and the amount of hydroxyl and total reactive chain ends in the different grades, of PET, measured on the polyesters as received

	TPP/[−OH]	TPP/([−OH] + [−COOH])
PETOH2	0.60	0.50
PET	0.95	0.61
PETOH1	1.79	0.80

molecules. A molecular-weight increase can thus be observed. Using model molecules, this latter reaction pathway (*Scheme 3*, pathway [1]) has been shown to be favoured.

Large torque, viscosity and molecular-weight increases have fully confirmed the reality of chain-extension mechanisms. Correlation has been found between torque and molecular-weight values during the ascending part of the torque vs. time curves. Elemental analysis has proved the incorporation of significant quantities of phosphorus into the polymer chains after reaction with phosphite. The high reactivity of the phosphorus linkages towards water, phosphite by-products or phenolic solvents at high temperature has explained the occurrence of large molecular-weight decrease in specific conditions. After selective scissions of the phosphorus-containing bonds, a residual increase of the polyester molecular weight could still be observed. This has confirmed that the chemical reactions induced by the phosphite addition promote the formation of new ester bonds between polyester chain ends.

Influence of triphenyl phosphite addition in different grades of PET

A dual difference distinguishes the three grades of PET analysed in this study. In addition to the variations in hydroxyl/carboxyl chain-end ratio, the total concentration of end-groups able to react with triphenyl phosphite during melt mixing is also different. The values of these two parameters (measured on polyesters as received) exert an important influence on the behaviour of the polymer/TPP system. A high number of variables can, in fact, influence the polyester reactions: triphenyl phosphite amount, total number of reactive chain ends, chemical nature of these end-groups, etc. Relevant comparisons between the different experiments carried out are therefore difficult to achieve because of the crossed influence of many parameters.

Highest polyester torque values were reached after addition of stoichiometric phosphite amounts, while the presence of TPP in excess induced a faster increase of the torque (*Figure 2*). Similarly, a higher concentration of hydroxyl end-groups in PETOH2 corresponds to the

highest molecular-weight values but to a lower reaction rate (*Figures 3* and *4*). It could thus be concluded that the molar ratio between triphenyl phosphite and hydroxyl end-groups has a determining influence on the reaction rate in polyester/TPP systems (*Table 4*). However, the behaviour of PETOH1 obviously proves that such analysis is not satisfactory. The reason is that the considered variables control not only the number but also the nature of the chemical reactions occurring during processing.

For easier comparison with other PET grades, the effects of TPP addition in 'standard' PET will be considered as references for the incorporation of phosphorus atoms into the polymer backbone and creation of ester and phosphorus-containing linkages.

The higher concentration of reactive chain ends present in PETOH2 corresponds to a large increase of hydroxyl and a reduction of carboxyl end-groups (*Table 1*). After phosphite addition, similar amounts of linked phosphorus atoms were observed (*Figure 6*). The molecular-weight increase obtained was largely induced by the creation of a high number of phosphorus linkages—broken by heating in phenolic solution—rather than by the formation of new ester bonds (*Figure 4*).

The reduced concentration of reactive chain ends in PETOH1—only due to a decrease of hydroxyl end-groups—enabled no torque increase after TPP addition. Incorporation of significant amounts of phosphorus into the polyester backbone was nevertheless observed (*Figure 6*). A slight molecular-weight increase was noted and attributed to the formation of a few phosphorus-containing linkages. Reduced $\bar{M}_w$ values measured after heating samples in solution suggested that no new ester bonds were created (*Figure 5*).

Thus it appears that a decrease of the hydroxyl chain-end concentration ([−COOH] being constant) not only reduces the system reactivity but also greatly limits the formation of new ester bonds. The presence of significant amounts of hydroxyl groups is necessary to take full advantage of the positive TPP effect on the esterification process. However, the presence of both types of chain ends is necessary, and a too high value of the hydroxyl/carboxyl end-group ratio does not promote the creation of ester bonds but rather induces phosphorus link formation. A 'catalytic' action of the carboxyl chain ends favouring the ester formation can thus be suggested.

It is difficult to reach definitive conclusions concerning the precise influence of each parameter and the best processing conditions favouring creation of new ester bonds during polyester reactions with phosphite. It must indeed be considered that the values of the main parameters change continuously during processing.

As a matter of fact, it has previously been shown by elemental analysis that some phosphite evaporates during processing. Reproducibility of the amount of

linked phosphorus atoms is hardly obtained when stoichiometric TPP quantities are added[3]. Moreover, the concentrations of polyester chain ends are continuously modified, namely by hydrolysis or pyrolysis processes. Values measured on the polyesters as received or after 5 min mixing have been observed to differ already[2]. Reaction with phosphite also modifies the concentrations of reactive chain ends. The large end-group consumption after phosphite addition has furthermore been observed to induce a polyester reorganization. This point explains the torque and molecular-weight decreases observed at long processing times[3].

A highly systematic study would be necessary in order to highlight the exact influence of each fluctuating parameter on the number and nature of all reactions occurring during processing.

Action of different phosphites

Phosphites are used extensively in the stabilization of polymers against oxidative degradation during processing. The nature and structure of the organic groups attached to the phosphorus atom have been observed to have a large influence on the mechanism and efficiency of the antioxidant action of the phosphite[6-8]. Their action on chain-extension mechanisms occurring by reaction with polyester end-groups has been investigated here by analysing the torque evolution.

Triphenyl phosphate (TPPa) (P^V form) is produced by TPP (P^{III} form) oxidation. It did not induce any significant reaction in polyester blends. Diphenyl phosphite (DPP) is a by-product resulting from TPP hydrolysis or reaction with carboxyl end-groups[1,4,9]. Although it is mostly present in a stable phosphonate (P^V) form with two substituents per molecule (against three in TPP), its reactivity is illustrated by the rapidity of the reactions occurring with alcohols, as demonstrated on model molecules[1,4,10,11]. Phenol liberation was assumed to constitute the major driving force of this reaction. The torque increase measured after DPP addition in polyester blends and the incorporation of significant amounts of phosphorus atoms in the backbone fully confirm the extension of this mechanism on polymers and the creation of phosphorus-containing linkages between different polyester chains (*Scheme 4*).

A positive influence of DPP addition on promoting the formation of new ester linkages between polyester chains can also be envisaged. Further experiments are nevertheless necessary to prove the reality of the mechanism depicted in *Scheme 5*.

Different effects concerning the action of bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite (BTBP) have already been reported in the literature. Carduner *et al.* studied its influence on the inhibition of ester-exchange
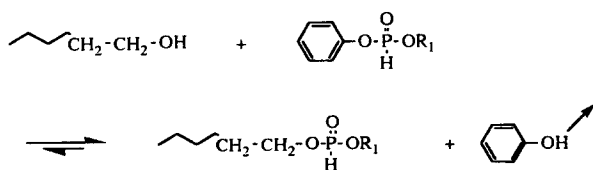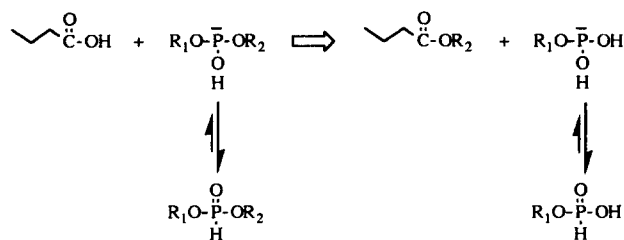
Scheme 5 Suggested reaction mechanism occurring between diphenyl phosphite and polyester carboxyl chain ends (R_1 and R_2 are phenyl groups or polyester chains)

reactions occurring in ternary polyester blends[12]. It was also described as efficient for controlling the amount of transesterification taking place during solid-state annealing of poly(ethylene terephthalate)/poly(ethylene naphthalene dicarboxylate) (PET/PEN) blends[13]. In this study, the addition of BTBP during polyester melt mixing was seen to induce an increase of the torque values (*Figure 9*). Similar observations were also realized for PET/polyester elastomer blends[14].

The reactivity of this compound is ensured by the presence of unshared pairs of electrons on phosphorus (P^{III}) atoms. Different points are able to explain the lower reaction rate and the limited torque values (by comparison with those measured after TPP addition). First, the presence of an amine stabilizer (1%) in Ultranox® 626 could influence the reaction rate and mechanism. Finally, the double functionality of the molecule and the presence of hindered phenyl substituents obviously contribute to the limited effect of BTBP addition.

The oscillations measured after DPP or BTBP addition during PET/PBT melt mixing were very reduced. This confirms that the occurrence of an elastic behaviour during polymer mixing is specially observable when high Brabender torque values are reached. Moreover, the relationship between the appearance of oscillations and polyester branch formation is not denied. No branching can be realized after addition of phosphites possessing only two reactive groups per molecule.

The addition of aliphatic phosphites such as di-n-octadecyl phosphite (DnOP) and distearyl pentaerythritol diphosphite (DPD) leads to a fast decrease of the polyester torque to very low values in a short period of time (*Figure 9*). A similar observation was also realized on PET/polyester elastomer blends[14]. An explanation could lie in the action of such a long-chain aliphatic phosphite as a lubricant in the Brabender mixing chamber. This artefact could thus falsify the torque value measurement and no valuable conclusion could thus be reached. This is only speculation, however.

Finally, the measurements carried out after tributyl phosphite addition to PBT confirm the importance of alcohol elimination as a driving force in the reaction between polyester and phosphite. As a matter of fact, in polyester/triphenyl phosphite systems, phenol results from substitution reactions between TPP and aliphatic hydroxyl end-groups. It can easily be taken off at processing temperatures. After addition of tributyl phosphite in PBT, the similar aliphatic nature of phosphite substituents and hydroxyl chain ends means that alcohol elimination constitutes the

Scheme 4 Reaction mechanism between polyester hydroxyl chain ends and diphenyl phosphite (R_1 is phenyl group or polyester chain)

only driving force of the reaction. The increase of the torque values and, more precisely, the incorporation of significant amounts of phosphorus atoms into the polyester backbone obviously show that reaction occurs between phosphite and polyester hydroxyl end-groups. This result definitively proves the essential importance of the easy alcohol elimination on the occurrence of reactions between phosphite and polyester chain ends.

Extension to acrylic polymers

The molecular-weight modifications measured by chromatography constitute a clear manifestation of the extended reactions induced by triphenyl phosphite addition in selectively end-functional acrylics.

The molecular-weight increase of hydroxyl-ended acrylics after triphenyl phosphite addition highlights the effects of reactions occurring exclusively between phosphite and hydroxyl groups, in the absence of carboxyl functions (*Figures 11* and *12*). This fully confirms the formation, between the polymer chains, of linkages different from ester bonds. The molecular-weight decrease induced by a water reflux clearly illustrates the high sensitivity of such linkages towards water. A simple exposure of the polymer to air moisture appears sufficient to induce a scission of a large proportion of these phosphorus containing links. All these bonds created by phosphite are nevertheless not broken since molecular weights do not decrease back to initial polymer values. This point questions the complete efficiency of the degradation procedure used, in the case of acrylic polymers.

The reactions resulting from TPP addition in equimolar amounts of hydroxyl and carboxyl end-functional polymers are also confirmed by the molecular-weight increase observed in *Figures 13* and *14*. Moreover, these chromatographic measurements also suggest that water reflux induces in this case only a limited decrease of the molecular-weight values. Although the procedure used cannot be accounted as fully efficient for breaking all bonds created in hydroxyl group/phosphite reaction, this limited molecular-weight decrease nevertheless supports the creation of new ester bonds (not influenced by a water reflux) as a consequence of the TPP addition in acrylic blends.

The large modifications induced by TPP addition are all the more remarkable because the experimental conditions are rather unfavourable. First, unlike the polyesters, the acrylic polymers studied here possess only one reactive chain end per molecule. Moreover, the reaction with phosphite has occurred despite the high water content measured in the acrylics (0.90% by weight at room temperature, greater than the theoretical amount sufficient to hydrolyse all TPP molecules to diphenyl phosphite).

The molecular-weight modifications measured are thus particularly illustrative of the high phosphite reactivity towards end-groups and the resulting chain extension. All these observations essentially confirm the reaction mechanism occurring between phosphite, hydroxyl and carboxyl chain ends, as deduced from investigations on polyesters. The promoting effect of triphenyl phosphite on the creation of new ester bonds is supported by the experiments conducted with acrylic

polymers. An extension of this mechanism can thus be envisaged for other polymers possessing hydroxyl and carboxyl end-groups.

CONCLUSION

The influence of different parameters on the polyester behaviour during processing with phosphites has been investigated. Experiments carried out with different PET grades show that variables such as total concentration of reactive end-groups and hydroxyl/carboxyl chain-end ratio control not only the number but also the nature of the reactions occurring. The presence of significant amounts of hydroxyl chain ends in the polyester is necessary to favour the creation of new ester bonds. On the other hand, a too high value of the hydroxyl/carboxyl end-group ratio promotes the formation of phosphorus-containing linkages. Thus, the presence of both types of chain ends appears necessary to take full advantage of the positive TPP effect on the esterification process.

Polyester processing with different types of phosphites illustrates the influence of the nature and structure of the organic groups attached to the phosphorus atom on the reaction with polyester chain ends. The reactivity of diphenyl phosphite, considered as a by-product of triphenyl phosphite reaction with the carboxyl end-group, is confirmed. The essential importance of an easy alcohol elimination (resulting from substitution reaction between phosphite and hydroxyl chain end) is also highlighted.

The mechanisms described in polyester/phosphite systems are confirmed by the successful extension to acrylic polymers. Despite the presence of only one reactive end-group per polymer chain, a molecular-weight increase is observed after reaction with triphenyl phosphite and the creation of two different natures of linkages is highlighted. Such observation enables the application of these mechanisms to other polymers possessing hydroxyl and carboxyl chain ends.

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