

Influence of covalently bound phosphorus-containing groups on the flammability of poly(vinyl alcohol), poly(ethylene-co-vinyl alcohol) and low-density polyethylene

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Poly(vinyl alcohol) and ethylene-vinyl alcohol copolymers have been phosphorylated with H_3PO_4 and H_3PO_3 . The phosphorylated samples possess pendent phosphate and phosphite groups and are significantly more flame retardant than the unmodified materials. The flame retardance arises in part from a condensed-phase mechanism involving dehydration, crosslinking and intumescent char formation, similar to that observed when certain phosphorus-based additives are used with poly(vinyl alcohol), cellulose and other highly hydroxylated polymers, and in part from a vapour-phase mechanism. Low-density polyethylene can also be rendered flame retardant to a certain extent by phosphonylation.

(Keywords: polyethylene; poly(vinyl alcohol); flame retardance)

INTRODUCTION

The main drawback of organic polymeric materials is, in many applications, their flammability. Burning polymers can give rise to toxic gases, especially carbon monoxide¹, and also to smokes that may hinder retreat from a fire. The increasing use of polymers in the home and in the work-place therefore means that making polymers more flame retardant is a matter of high priority.

Traditionally, flame retardation of polymers is achieved by using flame-retardant additives physically blended with the polymer. Still commonly used are halogenated flame retardants, which appear to function principally by reacting with radicals produced during combustion (mainly $H\cdot$ and $HO\cdot$), generating less-reactive halogen radicals². However, these reactions result in the release of toxic, corrosive, halogenous gases, such as hydrogen chloride. Consequently, the trend is now towards flame retardants with low or zero, halogen content. One of the most popular of these is aluminium hydroxide, which decomposes endothermically, releasing water vapour, thus diluting flammable gases and quenching the flames³. Increasing use is being made also of phosphorus-containing flame retardants. Flame retardation of organic polymers using phosphorus compounds is well established^{2,4}, and is particularly effective in polymers of high hydroxyl-group content, such as cellulose. In such polymers, phosphorus compounds appear to exert a flame-retarding effect through mainly a condensed-phase mechanism in which dehydration of the polymer is catalysed, followed by

crosslinking, leading ultimately to the production of a relatively incombustible, carbonaceous char⁵⁻⁹. The char insulates the underlying polymer from heat and oxygen, and water vapour from the dehydration reaction dilutes flammable gases and quenches the flame. Fewer toxic products are thus released into the atmosphere, and carbonaceous species are converted to char rather than released as smoke. However, a major disadvantage of all flame-retarding additives is that they may be lost in processing and during use of the polymer, and this may mean that high loadings are initially required.

Another way in which to reduce the flammability of polymers is chemically to bond the flame retardant to the polymer backbone, i.e. to use a reactive flame retardant. This gives the advantage of permanent attachment and can mean that smaller amounts of flame retardant are required, with consequently a much smaller influence upon the physical and mechanical properties of the polymer. Reactive flame retardants based on phosphorus, i.e. phosphorus-containing polyols, are currently used in the manufacture of polyurethane foams. Other examples in the literature include the use of vinyl and allyl phosphonates as comonomers in addition polymers, hydroxyalkyl phosphates and phosphonates as hydroxylated components in polyesterifications, and the addition of phosphines to unsaturated polymers¹⁰.

In this paper we report on the phosphorylation of poly(vinyl alcohol) and poly(ethylene-co-vinyl alcohol), the phosphonylation of low-density polyethylene, and the effects of these modifications upon the flammabilities of the polymers. Although the thermal degradation of phosphorylated poly(vinyl alcohol) has been extensively studied¹¹ and the phosphonylation of polyethylene has

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been previously described¹², there have until now been no systematic studies of these simple modifications upon the flammabilities of these polymers.

EXPERIMENTAL

Materials

Uncompounded samples of poly(vinyl alcohol) (PVOH), low-density polyethylene (LDPE), poly(ethylene-co-vinyl alcohol) (EVOH) and poly(ethylene-co-vinyl acetate) (EVAc) were obtained from the Aldrich Chemical Co., ICI Chemicals and Polymers Ltd, Attochem (France) and Bayer UK Ltd, respectively. The LDPE had a molecular weight of $2.0 \times 10^5 \text{ g mol}^{-1}$ (g.p.c. analysis by Rapra Technology Ltd) and was purified by refluxing with chlorobenzene and then cooling so that pure LDPE precipitated. The other polymers were used without purification. The poly(ethylene-co-vinyl alcohol) samples had specified vinyl alcohol (VOH) contents of 61 and 74 mol%, respectively, and the poly(ethylene-co-vinyl acetate) samples had specified vinyl acetate (VAc) contents of 12, 43 and 56 mol%. All reagents were obtained from the usual suppliers and were used after appropriate purifications.

Phosphorylation of PVOH

PVOH was phosphorylated with either H_3PO_3 or H_3PO_4 using both suspension and solution methods. The suspension method was adapted from the procedure of Nifant'ev *et al.*¹³. Approximately 24 g of finely powdered PVOH was placed in a mixture of 100 cm³ methanol and 15 g conc. H_3PO_3 in a round-bottomed flask. The methanol was then removed by rotary evaporation. To the PVOH was then added 100 ml of benzene and the mixture was heated for 3 h in a thermostatically controlled oil bath set at 80°C and was stirred rapidly throughout. The solid PVOH was then filtered off and washed with methanol and benzene and then dried to a constant weight in a vacuum oven at room temperature. A similar procedure was followed but using 21.1 g conc. H_3PO_4 instead of the H_3PO_3 so giving a similar concentration of phosphorus oxyacid in both cases.

Deionized water was chosen as a suitable medium for phosphorylations in solution since it enables the formation of phosphate ions, which react with protonated PVOH, forming a phosphate ester. Also, dehydration of PVOH is less likely when water is used as a solvent. Reactions were carried out in 5 litre flange-neck flasks, equipped with reflux condensers, thermometers and stirrers, on 30 g samples of polymer dissolved in aqueous solutions of H_3PO_4 , the concentrations of which ranged from 0.25 to 5.7 M. (The solutions of H_3PO_4 were made up after determining the exact concentration of the conc. H_3PO_4 using a method described by Belcher and Nutten¹⁴.) The mixtures were heated to 100°C using isomantles for periods of 100 min. The solutions were then left to cool to room temperature and the polymers recovered by precipitation in acetone. The precipitated polymers were filtered off, collected and then dried to constant weight.

Phosphorylation of EVOH

The three different grades of EVAc (12, 43 and 56 mol% VAc) were fully hydrolysed to EVOH by the following method. Approximately 30 g of EVAc were dissolved in 1.5 litres of n-butanol by refluxing (b.p. 116°C) with

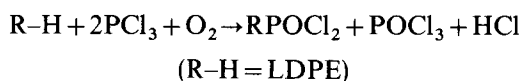
stirring in a 2 litre quickfit conical flask on a hot plate. Then 0.3 g of NaOH catalyst was added to the cooled mixture and the mixture was refluxed for 3 h, cooled, and then precipitated in water. The precipitated polymer was collected, filtered, washed with deionized water, and then dried to constant weight. These EVOH samples were then phosphorylated, along with the others, using the procedures outlined below.

First, 30 g EVOH (12 mol% VOH) were dissolved in 1 litre of tetrahydrofuran (THF) in a 2 litre conical flask by heating in a thermostatically controlled oil bath set at 100°C under reflux with stirring. After dissolution had occurred, H_3PO_4 was slowly added dropwise via the condenser so that the resultant acid concentration was 3.8 M (a higher concentration causes EVOH to precipitate). After 1 week, the solution was cooled and the polymer recovered by precipitation in deionized water and then dried to constant weight.

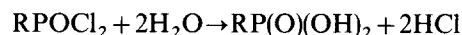
A slightly different procedure was followed for the other grades of EVOH (43, 56, 61 and 74 mol% VOH). Approximately 30 g of EVOH were added to 1.5 litres of a 50% w/v solution of H_3PO_4 in THF (corresponds to 4.56 M H_3PO_4) and the mixture was refluxed (b.p. 122°C) with stirring on a hot plate. As the reaction temperature was higher than that for the reaction with EVOH containing 12 mol% VOH, reaction times of only 2–4 h were necessary to achieve the desired levels of phosphorylation for these EVOH samples. The phosphorylated EVOH copolymers were precipitated in deionized water and were dried to constant weight.

Oxidative chlorophosphonylation of LDPE

The oxidative chlorophosphonylation of LDPE involves the direct reaction of the polymer with excess phosphorus trichloride in an atmosphere of oxygen:



The polymeric phosphonyl dichloride is then hydrolysed to give the polymeric phosphonic acid:



The reaction is of particular interest because it gives a product in which the phosphate unit is bonded directly to the carbon backbone through hydrolytically stable P–C bonds¹⁵. The phosphorylation of VOH units, on the other hand, gives rise to hydrolytically unstable P–O–C bonds.

The method used was adapted from that described by Weiss *et al.*¹². First, 30 g of LDPE were placed in a 1 litre round-bottomed flask with 640 cm³ of PCl_3 , previously purified by distillation under dry N_2 . Dry N_2 was passed through the mixture, which was maintained at 70°C, during which time the LDPE dissolved. After dissolution, the temperature was lowered to 60°C and the reaction was started by passing dry O_2 (instead of the N_2) through the solution. After 4 h, the solution was allowed to cool and the unreacted PCl_3 and the POCl_3 were removed by distillation at 76°C (740 mmHg), with occasional addition of dry chlorobenzene to keep the LDPE in solution. The mixture was then cooled further and the solid LDPE was collected and slowly added to deionized water to hydrolyse the first formed phosphonyl dichloride groups to phosphonic acid groups. The final product was collected by filtration, washed several times

with deionized water and then dried by pumping at room temperature in a vacuum oven.

Phosphorus analysis

Phosphorus analyses were carried out by the molybdovanadophosphoric acid method¹⁶. Approximately 7–12 mg of sample were weighed into a 100 cm³ glass beaker and to this were added 5 cm³ of conc. HNO₃ (for phosphorylated PVOH) or 5 cm³ of Analar conc. perchloric acid (for the other polymer samples). The beaker was then placed on a hot plate, covered with a watch glass and the contents boiled rapidly for at least 30 min or until the solution became clear (small amounts of deionized water were added from time to time to prevent the solution from boiling dry).

The digested polymer sample was then transferred, with rinsing with deionized water, from the beaker to a 50 cm³ volumetric flask. To this solution were then added 5 cm³ each of 50% v/v aqueous HNO₃, ammonium metavanadate solution (1.25 g in 500 cm³ deionized water) and ammonium molybdate solution (25 g in 500 cm³ deionized water). The volume was then made up to 50 cm³ with deionized water. After 30 min, the absorbance at 400 nm of an aliquot of this solution relative to that of a reagent blank solution at the same wavelength was measured using a Pye Unicam SP8-400 u.v./visible spectrometer. From this absorbance, the percentage by weight of phosphorus in the sample was calculated. Each polymer sample was analysed for phosphorus in triplicate to reduce experimental errors. The procedure was calibrated using standard solutions of KH₂PO₄ of known concentration.

Instrumental analyses

Infra-red spectra of polymers were recorded on Perkin-Elmer 1720-X and Nicolet MS-X Fourier-transform spectrometers. Samples for i.r. analysis were either cast as films from solutions in CHCl₃ or water, or prepared as dispersions in spectroscopic-grade KBr. Thermal characterization was carried out using a Perkin-Elmer TAC-7 system consisting of a TGA-7 thermogravimetric analyser and a DSC-7 differential scanning calorimeter. A Cambridge Stereoscan 600 was used for scanning electron microscopic (SEM) analysis of polymer chars.

Measurement of flammability by limiting oxygen index (LOI)

The LOI is the minimum concentration of O₂ in a mixture of O₂ and N₂ (expressed as per cent by volume) that will just support flaming combustion. The LOI thus provides a simple measure of flammability; the higher the LOI, the lower the flammability. LOI values were measured either on thin film samples (14 cm × 6 cm × ca. 0.1 mm) or on plaques (10 cm × 6 mm × 3 mm) using a Stanton Redcroft FTA Flammability Unit. Metal frames were used to support the polymer samples upright inside the glass chimney of the apparatus. The O₂ and N₂ flow rates were adjusted so that the total flow rate was always 18 litre min⁻¹, but the O₂ to N₂ ratio was varied. The O₂ concentration was set initially to 25% and the gas allowed left to purge the apparatus for 30 s. A butane burner was then used to ignite the top of the sample (held for 1 s). If the sample did not burn then the oxygen concentration was increased. If combustion of the sample

did occur, then the oxygen concentration was reduced. The LOI was located in this way, in each case replacing a partly burned sample with a fresh sample of the same size.

Films of PVOH and phosphorylated PVOH were prepared by solvent casting from 10% w/v solutions in deionized water on levelled glass plates. The films were dried at room temperature, peeled from the glass and cut to size. Plaques of LDPE, EVOH and of phosphorylated EVOH and phosphonylated LDPE were prepared by compression moulding 3 g samples between either Teflon sheets or metal plates covered with mould release paper, at ca. 200°C, and then cutting to size.

Measurement of heat of combustion by bomb calorimetry

Heats of combustion were measured using a bomb calorimeter calibrated with benzoic acid. The benzoic acid was compressed into a pellet with a Ni-Cr wire passing through it, and connected across two terminals of the steel bomb. The bomb was filled to a pressure of 25 atm with O₂ and tightly sealed. The bomb was then placed inside a copper calorimeter filled with 1100 cm³ of water and insulated by air and water outer jackets. After thermal equilibrium was reached, a current was applied so that the sample in the bomb ignited. The rise in temperature was measured using a thermometer calibrated in 0.01 K increments. The temperature rise, together with the known heat of combustion of benzoic acid, was then used to calculate the heat capacity of the calorimeter. The combustion procedure was repeated for each of the polymer samples of interest using samples in the form of films, tightly wrapped around Ni-Cr wires. From the temperature rise accompanying the combustion of each sample, together with the heat capacity of the calorimeter, the heat of combustion of each polymer was calculated.

RESULTS

Table 1 gives the results of phosphorus analyses, t.g.a., LOI measurements, burning tests and measurements of heats of combustion for all the phosphorylated PVOH samples and also relevant results for the sample of PVOH with which H₃PO₄ was merely mixed. Table 2 contains similar data for the phosphorylated samples of EVOH and the phosphonylated sample of LDPE. I.r. spectra for unmodified PVOH and a sample of phosphorylated PVOH are shown in Figure 1.

DISCUSSION

Phosphorylation of PVOH with H₃PO₄ in aqueous solution

Table 1 shows that for phosphorylations of PVOH with aqueous H₃PO₄ at concentrations ranging from 0.25 to 5.7 M, there is reasonable agreement in all but one case (sample 6) between the weights of polymer recovered and the theoretical final weights based on measured phosphorus contents. It can also be seen that, as the concentration of H₃PO₄ used is increased, so the degree of phosphorylation of PVOH increases. However, when H₃PO₄ concentrations above 5.7 M were used, the phosphorus content of the product did not increase any further but rather the polymer became increasingly brown

Table 1 Analytical data for phosphorylated PVOH samples

Sample number	Concn. of H ₃ PO ₄ (mol l ⁻¹)	Initial mass of polymer (g)	Recovered mass of phosphorylated polymer (g)	P in polymer (wt%)	Fraction of repeat units phosphorylated	Predicted mass of phosphorylated polymer (g)	Residue from t.g.a. in N ₂ ^a (wt%)	Residue from t.g.a. in air ^a (wt%)	P in residue after burning in air (wt%)	LOI (%O ₂ by volume)	Specific heat of combustion, ΔH (kJ g ⁻¹)
Reactions of PVOH with H ₃ PO ₄ in aqueous solution											
1	—	—	—	0	0	—	5.4	0.5	0	19.8	21.5
2	0.25	30.67	30.01	0.6	0.009	31.16	7.9	2.5	1.6	22.4	21.2
3	0.50	30.74	30.09	1.2	0.018	31.72	11.0	4.4	2.6	27.6	19.8
4	1.00	30.05	30.85	1.9	0.028	31.60	13.1	5.0	6.3	36.4	18.1
5	1.50	30.59	34.29	4.5	0.072	34.61	27.5	18.1	10.1	44.1	12.3
6	2.00	30.04	31.29	4.8	0.078	34.29	28.8	19.2	14.1	48.0	13.6
7	3.80	30.07	34.53	5.3	0.087	34.83	28.8	18.0	15.7	48.1	14.4
8	5.70	30.03	34.66	5.5	0.091	35.00	30.0	19.0	16.3	48.9	16.2
Reactions of PVOH with H ₃ PO ₄ and H ₃ PO ₃ in suspension											
9	H ₃ PO ₃	24.24	29.66	9.4	0.166	30.08	22.0	8.6	20.1	39.7	15.7
10	H ₃ PO ₄	24.72	29.50	8.1	0.145	31.26	29.9	18.0	18.5	70.6	11.0
Dried physical mixture of PVOH with H ₃ PO ₄											
11	—	—	—	6.5	—	—	—	18.0	15.0	46.0	13.5

^a Determined by weighing sample at beginning and end of t.g.a. run and not from the plotted thermogram

Table 2 Analytical data for phosphorylated EVOH samples and for phosphorylated LDPE

Sample number	VOH content (mol%)	Initial mass of polymer (g)	Recovered mass of phosphorylated polymer (g)	P in polymer (wt%)	Fraction of repeat units phosphorylated	Predicted mass of phosphorylated polymer (g)	Residue from t.g.a. in N ₂ (wt%) ^a	Residue from t.g.a. in air (wt%) ^a	P in residue after burning in air (wt%)	LOI of original polymer (%O ₂ by volume)	LOI of phosphorylated polymer (%O ₂ by volume)	Specific heat of combustion before phosphorylation, ΔH ₀ (kJ g ⁻¹)	Specific heat of combustion after phosphorylation, ΔH (kJ g ⁻¹)
Reactions of EVOH with H ₃ PO ₄ in suspension													
12	12	30.34	33.37	3.5	0.037	33.34	5.4	1.0	4.2	18.0	21.1	40.8	41.3
13	43	30.36	34.72	5.6	0.072	35.54	9.1	4.0	10.2	19.2	26.9	34.6	19.0
14	56	29.95	37.26	8.3	0.126	38.12	14.5	8.0	15.6	19.0	32.7	33.6	26.5
15	61	30.45	35.29	6.2	0.088	36.13	12.0	4.7	12.5	19.4	27.5	27.3	18.5
16	74	30.26	34.64	5.6	0.084	34.08	14.0	5.0	9.2	19.6	28.8	27.9	24.4
Phosphorylation of LDPE													
17	0	30.33	38.34	9.2	0.109	39.77	8.0	4.0	11.3	18.7	25.7	45.6	24.4

^a Determined by weighing sample at beginning and end of t.g.a. run and not from the plotted thermogram

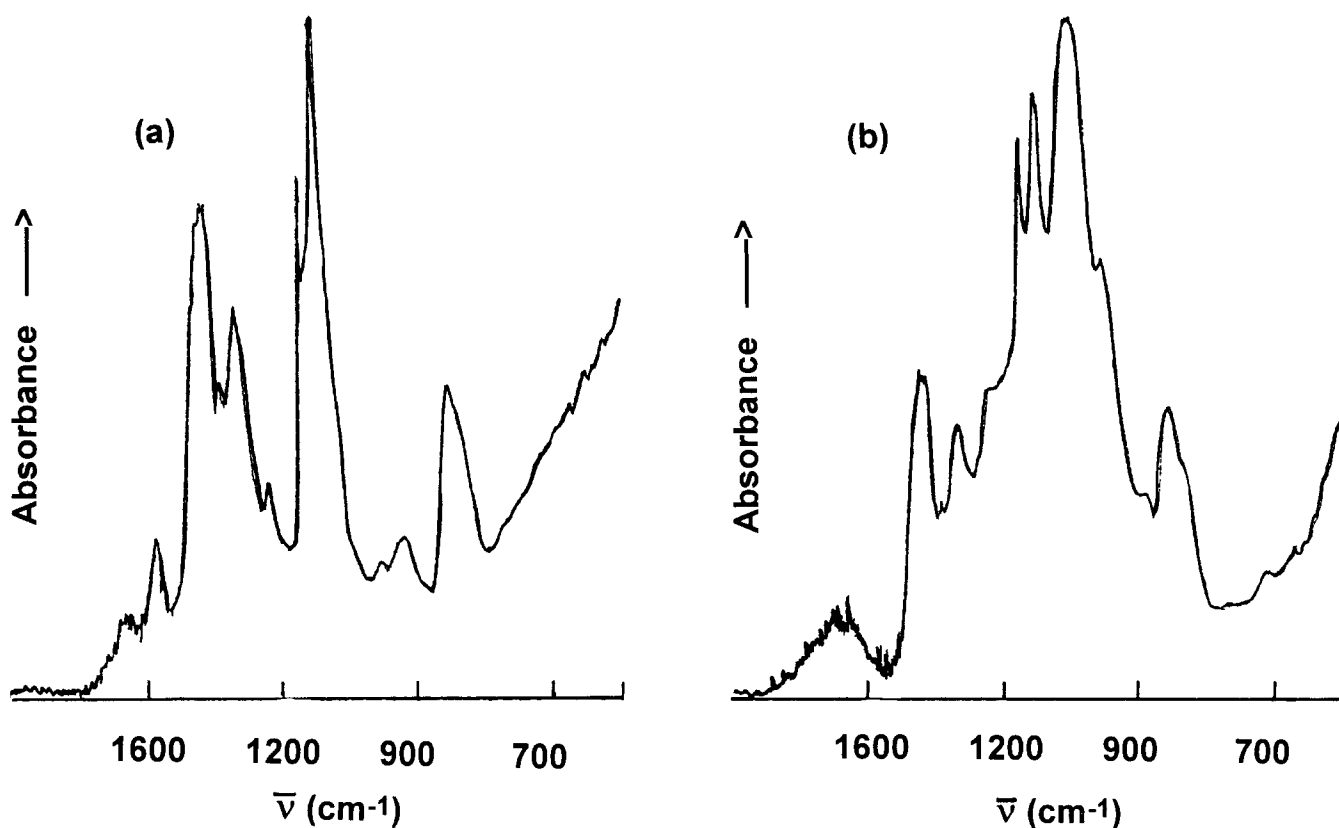
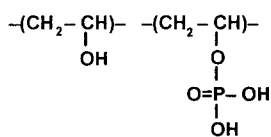


Figure 1 I.r. spectra ($700\text{--}2000\text{ cm}^{-1}$) of (a) PVOH and (b) phosphorylated PVOH containing 4.8% by weight of phosphorus (sample 6)

in colour. The phosphorylated PVOH samples were found to dissolve in both water and dimethylsulfoxide (DMSO) (showing that they had not become crosslinked) and they could be reprecipitated with no reduction in phosphorus content. We take these observations as evidence that at the lower H_3PO_4 concentrations the phosphorus was bonded chemically to the PVOH, and was not present merely in an occluded form, but that as the concentration of H_3PO_4 was increased above 5.7 M there was a tendency for the polymer to be dehydrated (leading to conjugation and hence colour) rather than to be phosphorylated.

I.r. spectra of phosphorylated PVOH samples contain an absorbance at $1050\text{--}950\text{ cm}^{-1}$ characteristic¹⁷ of the P–O stretch in alkyl phosphates and phosphites and which does not appear in the spectrum of PVOH itself (see *Figure 1*). Also, the strong absorbance at 1096 cm^{-1} in the spectrum of PVOH, arising from the C–O stretch and O–H bend, is decreased in intensity in the spectra of the phosphorylated samples, indicating the replacement of some of the C–O–H bonds by C–O–P bonds. We conclude, therefore, that treatment of PVOH in aqueous solution with H_3PO_4 (at 5.7 M and below) leads to what are essentially copolymers consisting of phosphorylated and unphosphorylated VOH units and having the structure shown in I.



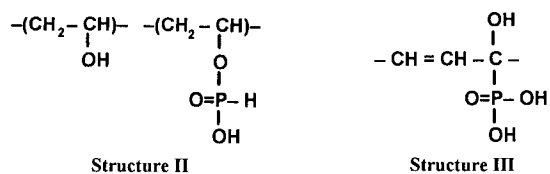
Structure I

The mole fractions of phosphorylated units given in *Table 1* have been calculated assuming structure I for the phosphorylated polymers. Although these fractions increase as the concentration of H_3PO_4 is increased, they do not do so in a linear fashion, but begin to level off at acid concentrations above 1.5 M. This provides further evidence for a dual effect of H_3PO_4 on PVOH, i.e. phosphorylation at lower concentrations competing with dehydration at higher concentrations.

Phosphorylation of PVOH with H_3PO_4 and H_3PO_3 in suspension

In the reactions of PVOH with H_3PO_4 and H_3PO_3 in suspension, the polymer did not dissolve at any point. Even so, it can be seen from *Table 1* that high levels of phosphorus incorporation were obtained. The reason for this could be that the azeotropic removal of water with the benzene encourages phosphate ester formation. The products from these reactions were pale brown, indicating that some dehydration of the PVOH had occurred in addition to phosphorylation.

The i.r. spectra of the phosphorylated samples were similar to those of the samples phosphorylated in solution, i.e. they both contained a broad, strong absorption band at ca. 1000 cm^{-1} characteristic of an alkyl phosphate or phosphite. The structure of the sample phosphorylated with H_3PO_4 in suspension is expected to be the same as those of the samples phosphorylated in solution (structure I). We assume, however, that the sample phosphorylated with H_3PO_3 has the structure shown in II (i.e. contains phosphite groups), although it has been suggested that treatment of PVOH with H_3PO_3 can lead also to some dehydration followed by reaction to give phosphonate groups (structure III)¹⁸.

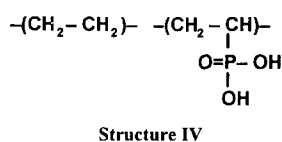


Phosphorylation of EVOH with H₃PO₄ in THF solution

It can be seen from Table 2 that the mole fractions of phosphorylated units in the phosphorylated EVOH copolymers are comparable with those in the phosphorylated PVOH samples. However, given that the EVOH copolymers contain lower mole fractions of VOH units than PVOH, the fractions of such units phosphorylated in the copolymers are clearly significantly greater than the levels achieved for PVOH. This may be due to the use of THF as solvent rather than water; in water an equilibrium will be established between phosphorylated and non-phosphorylated VOH units, since water can hydrolyse phosphorylated units fairly readily. I.r. spectra of the phosphorylated EVOH samples, like those of the phosphorylated PVOH samples, display a strong absorption at ca. 1000 cm⁻¹ associated with the presence of phosphate groups.

Oxidative chlorophosphonylation of LDPE

The i.r. spectrum of the phosphonylated LDPE contains broad absorptions at 1050–950 cm⁻¹, not present in the spectrum of LDPE itself, and is similar to that previously published¹². We assume, therefore, that the phosphonylated polymer has the previously reported structure, IV.



D.s.c. traces (Figure 2) reveal that phosphonylation of LDPE leads to a loss of crystallinity, shown by the smaller melting endotherm for phosphonylated LDPE compared with that of untreated LDPE. This provides further evidence for chemical modification of the polymer backbone.

T.g.a. of PVOH and of phosphorylated PVOH

T.g.a. traces for PVOH and for two solution-phosphorylated PVOH samples (samples 4 and 5)

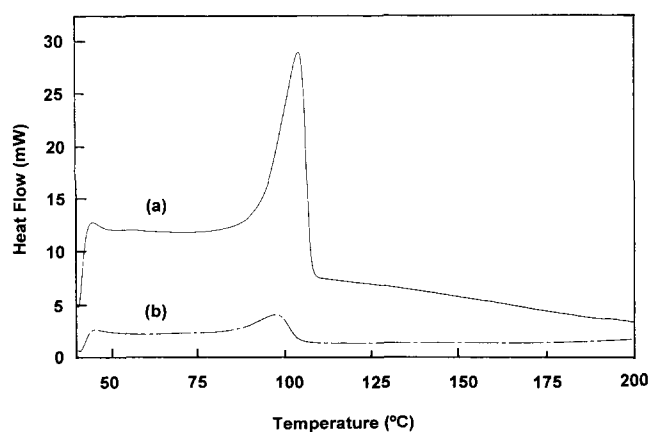


Figure 2 D.s.c. traces recorded with heating under nitrogen at 10°C min⁻¹ for (a) LDPE and (b) phosphonylated LDPE (sample 17)

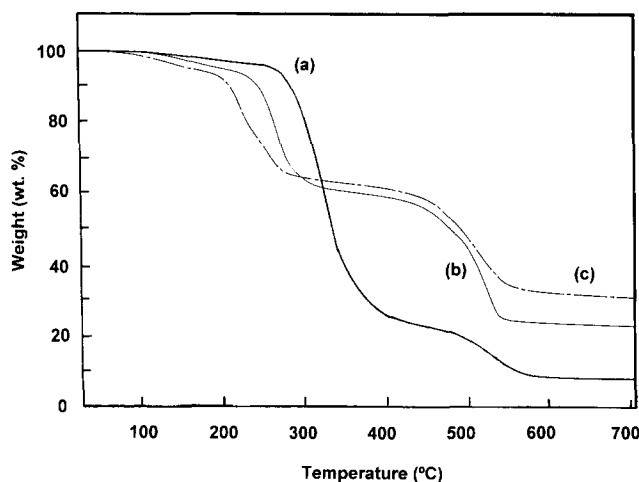
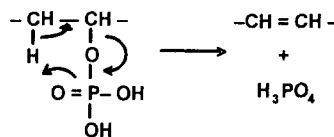
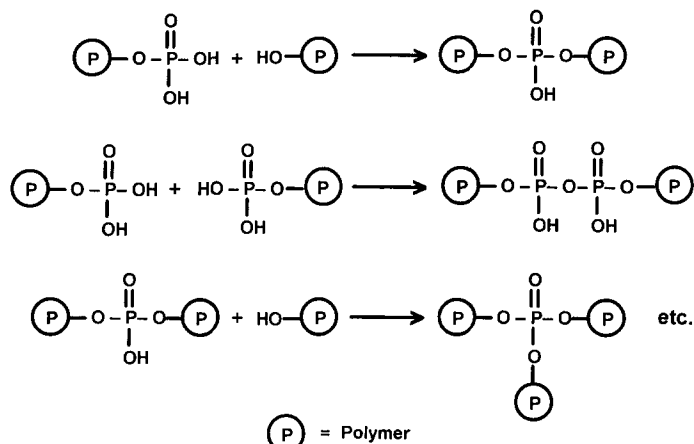


Figure 3 T.g.a. traces recorded with heating under nitrogen at 20°C min⁻¹ for (a) PVOH, (b) phosphorylated PVOH containing 1.9% by weight of phosphorus (sample 4) and (c) phosphorylated PVOH containing 4.5% by weight of phosphorus (sample 5)



Scheme 1



Scheme 2

containing different levels of phosphorus are shown in Figure 3. The traces were recorded with heating under nitrogen at a rate of 20°C min⁻¹. All of the traces show that weight loss occurs in two stages and that, at the end of the runs, considerable amounts of residue (char) remain. From these traces it may be noted also that, with increasing phosphorus content, (i) the first stage of decomposition is more pronounced, and occurs at a lower temperature and over a narrower range of temperature, and (ii) the weight of residue remaining at the end of decomposition increases. These features have been seen before and have been explained in terms of increased dehydration in the first stage of decomposition through intramolecular elimination of H₃PO₄ (Scheme 1) followed by decreased chain scission in stage two owing to the formation of di- and triphosphate crosslinks (Scheme 2)^{11,19}. Accelerated water loss is seen also in cellulosic polymers and is

believed to contribute to a flame-retardant action by quenching the flame²⁰.

The thermal decomposition of PVOH also produces organic volatiles, which contribute fuel to any flame²¹. However, less volatile organic material is likely to be produced from the phosphorylated samples because of increased crosslinking via the phosphate groups, leading to the retention of more organic material in the form of a char. Thus such samples would be expected to be more flame retardant than the parent polymer.

PVOH samples reacted in suspension with H_3PO_4 and with H_3PO_3 also undergo a two-stage decomposition process under N_2 similar to that of the PVOH samples phosphorylated in aqueous solution. However, the weight of residue at the end of decomposition is lower when H_3PO_3 is used as the phosphorylating agent, probably because phosphite groups have less potential for crosslinking (they can only form diphosphite crosslinks) than phosphate groups.

Comparison of the t.g.a. traces of phosphorylated PVOH in air and nitrogen atmospheres

Figure 4 shows t.g.a. traces of a sample of the same phosphorylated PVOH (sample 6) in air and nitrogen atmospheres. It can be seen that, in air, the residue begins to decompose at 650°C and that the decomposition continues to beyond 900°C. However, the weight of residue produced in a N_2 atmosphere remains almost unchanged after about 700°C. Taken together, these results indicate that only oxidative degradation occurs above 700°C. The weights of residue from t.g.a. experiments for PVOH samples containing various phosphorus contents in both air and N_2 atmospheres are given in Table 1. In each case, it can be seen that the weight of residue in air is lower than that in N_2 , indicating that the residue is oxidizable to some degree. In general, at higher phosphorus contents a larger proportion of the residue remains unoxidized.

T.g.a. traces of poly(ethylene-co-vinyl alcohol)s (EVOH) before and after phosphorylation

T.g.a. traces recorded in air for an EVOH copolymer containing 5.6% by weight of phosphorus (sample 13) and for the unmodified precursor EVOH are shown in Figure 5. Similar traces were obtained for the other modified and unmodified EVOH samples. For EVOH

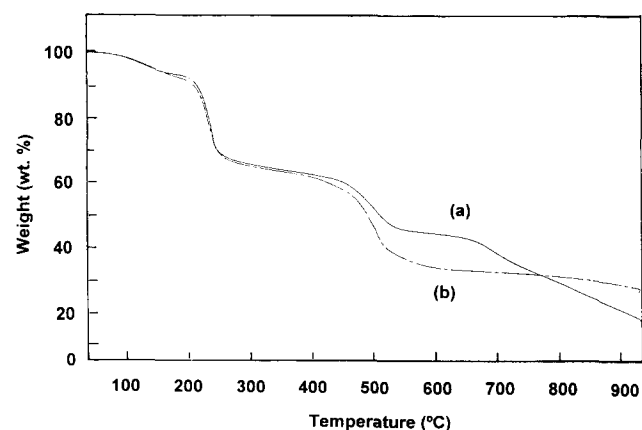


Figure 4 T.g.a. traces for phosphorylated PVOH containing 4.8% by weight of phosphorus (sample 6) recorded with heating at $30^\circ\text{C min}^{-1}$ (a) in air and (b) under nitrogen

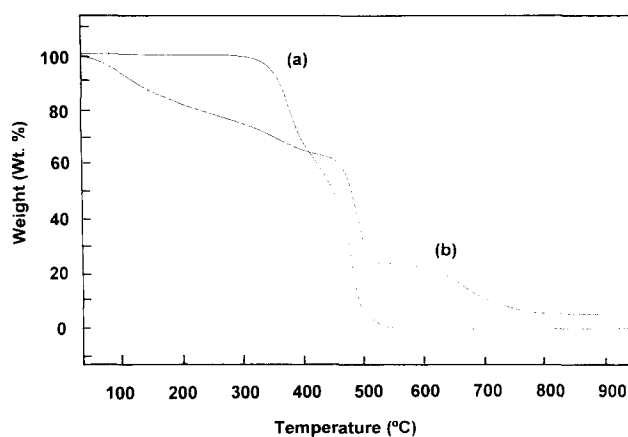


Figure 5 T.g.a. traces recorded with heating at $30^\circ\text{C min}^{-1}$ in air for (a) EVOH containing 74 mol% VOH and (b) for the same copolymer after phosphorylation to give 5.6% by weight of phosphorus (sample 16)

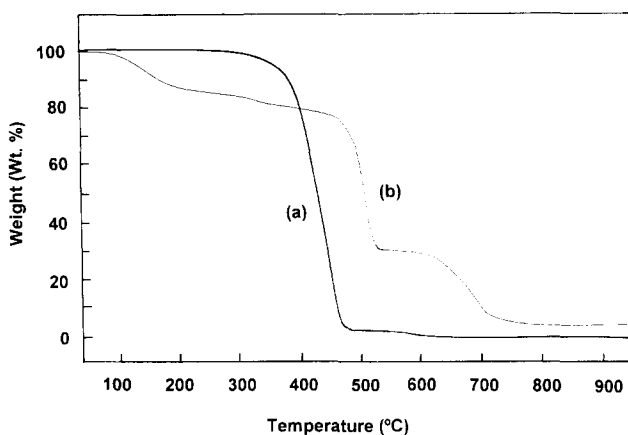


Figure 6 T.g.a. traces recorded with heating in air at $30^\circ\text{C min}^{-1}$ for (a) LDPE and (b) phosphonylated LDPE containing 9.2% by weight of phosphorus (sample 17)

also there is evidence for a two-stage decomposition leading ultimately to the formation of a char. Once again, the volatile degradation products are expected to be water and various small organic fragments, with water predominating in the early stages of decomposition. As in PVOH, phosphorylation leads to evolution of water earlier in the degradation cycle but ultimately to increased yields of char, presumably through crosslinking of phosphate groups, and has implications for the flame retardance of these copolymers (see later).

T.g.a. traces of low-density polyethylene (LDPE) before and after phosphorylation

T.g.a. traces of LDPE before and after reaction with PCl_3 followed by hydrolysis (sample 17) are shown in Figure 6. Whereas LDPE degrades in a single stage, phosphonylated LDPE shows a two-stage decomposition. The decrease in mass between 100 and 450°C is probably primarily due to water given off during a crosslinking reaction similar to that which occurs with phosphorylated PVOH and EVOH, and the later decrease is probably due to loss of volatile material associated with the well known chain depolymerization of ethylene sequences. This later decrease in weight occurs at a higher temperature (500°C) in the phosphonylated sample than in untreated LDPE (450°C) and is also less pronounced, probably owing to the stabilizing effect of

the crosslinks. The small weight loss in a third stage may be associated with the breakdown of these crosslinks. The less pronounced decomposition of the phosphonylated LDPE, together with the reduction in the amount of volatile material produced and consequent formation of some residue, may be a reason for the increased flame retardance brought about by phosphorylation (see later).

Variation of LOI with phosphorus content of the phosphorylated PVOH

The LOI data presented in Table 1 show that there is a steady increase in LOI value with increasing phosphorus content in the phosphorylated PVOH samples. The best correlation is between the increase in LOI (compared with the value for unmodified PVOH) and the fraction of VOH units phosphorylated (x); these data conform to the equation:

$$\text{Increase in LOI} = 329x$$

with a correlation coefficient of 0.986 (a significant correlation at the 95% confidence level).

It will be noted that when PVOH contains 9.4% by weight of phosphorus in the form of phosphite groups (introduced by reaction with H_3PO_3 in suspension), the LOI value is approximately half the value expected for a PVOH containing the same percentage by weight of phosphorus in the form of phosphate. This finding, together with the observation made above that the PVOH containing the phosphite groups also gives a lower char yield than that containing phosphate groups, points towards the importance of a condensed-phase mechanism of flame retardation, i.e. a mechanism in which the formation of an essentially incombustible char protects the underlying layers of organic polymer from combustion.

The flame retardance of PVOH containing non-bonded phosphorus in the form of occluded H_3PO_4 is also good ($\text{LOI}=46$, phosphorus content=6.5% by weight), although it can be seen from the data in Table 1 that it is less flame retardant than would be expected if the PVOH were to contain the same concentration of phosphorus in the form of attached phosphate groups. Probably this is because much of the non-attached H_3PO_4 volatilizes before it can exercise a flame-retardant effect.

LOI values of phosphorylated EVOH and phosphonylated LDPE

Table 2 shows the variation in LOI with mole percentage of VOH for phosphorylated EVOH copolymers and for phosphonylated LDPE. There is, of course, some variation in the phosphorus content of these materials, and this must be taken into account when interpreting the significance of the LOI values. Nevertheless, it can be seen that, when the VOH content is decreased, the effect of bound phosphorus on the LOI, and hence its flame-retarding efficiency, also decreases. The effect is also seen when one compares the LOI values of phosphorylated PVOH and phosphonylated LDPE; phosphorylated PVOH with a phosphorus content of 5.5% by weight has an LOI of 48.9, whereas phosphonylated LDPE with a phosphorus content of 9.2% by weight has an LOI of 25.7. Interestingly, for the phosphorylated EVOH copolymers, the most significant correlation is between the increase in LOI and the fraction

of total repeat units phosphorylated (y) rather than between the increase in LOI and the fraction of VOH units phosphorylated (x). For the former the equation is:

$$\text{Increase in LOI} = 109y$$

with a correlation coefficient of 0.991 (a significant correlation at the 95% confidence level).

The reasons for the variations in LOI are probably twofold. First, polymers containing high concentrations of VOH units are more able to crosslink with phosphate groups, a necessary prerequisite for the formation of a protective char; and secondly, long sequences of ethylene units will be susceptible to random chain scission. This second reaction will be responsible for increased production of volatiles, possibly including fragments containing phosphate groups. Premature loss of phosphorus from the burning polymer will reduce flame retardance.

Correlation of LOI with the weights and compositions of char residues

The literature suggests that, in general, the LOI of a polymer is proportional to the amount of residue formed on combustion²² (although such a correlation was not found for halogen-containing polymers). It is thus of interest here to look for a correlation between LOI and weights of residue remaining from the t.g.a. experiments on the phosphorylated samples carried out in both air and N_2 . It can be seen from Table 1 that, for the phosphorylated PVOH samples, as the LOI increases, the weights of residue increase to a maximum of approximately 19% by weight in O_2 and 30% by weight in N_2 . This shows that, in these samples, the phosphorus-containing groups are functioning as a flame retardant by a char-forming, i.e. a condensed-phase, mechanism. However, there must also be a significant contribution from a vapour-phase mechanism, especially at higher LOI values (>50); the LOI of carbon-black rod is 56–63²³, and therefore flame retardants giving LOIs above this value must act not only by forming a carbonaceous char but also in some vapour-phase process as well, such as that observed for phosphorus-containing additives in some non-hydroxylated polymers¹⁰. For the phosphorylated EVOH samples also there is a correlation between char yields recorded in the t.g.a. experiments and LOI values (see Table 2), again indicating the importance of a condensed-phase component to flame retardation.

The degree to which phosphorus remains in the residue after burning relates to its efficiency as a flame retardant and also provides evidence for the importance or otherwise of the condensed-phase mechanism of flame retardance. Table 1 also shows that for the PVOH samples phosphorylated in solution, the degree to which phosphorus is retained in the residue after burning is approximately constant. Statistical analysis of these data show that they conform to the equation:

$$\%P \text{ in residue} = 2.52 \times \%P \text{ in polymer}$$

with a correlation coefficient of 0.974 (a significant correlation at the 95% confidence level).

As mentioned above, in the t.g.a. experiments carried out in air, the quantity of residue at the end of decomposition peaked at around 19% by weight. If similar behaviour were to be followed in the burning experiments, the concentration of phosphorus after

burning should be about five times the value before burning, i.e. the gradient of the line described by the equation above should be approximately 5 and not 2.52. This shows that in the burning experiments, as with the t.g.a. experiments, not all the phosphorus remains unvolatilized. This also provides evidence for a vapour-phase component to flame retardation.

For the phosphorylated EVOH samples as well, there is a strong linear correlation between the phosphorus content of the char residue formed on burning in air and the phosphorus content of the copolymer. The equation in this case is:

$$\%P \text{ in residue} = 1.96 \times \%P \text{ in copolymer}$$

with a correlation coefficient of 0.980 (a significant correlation at the 95% confidence level). In these samples also, therefore, there is evidence for a condensed-phase mechanism of flame retardation but with a significant vapour-phase component as well. In the EVOH copolymers, less dehydration to form a char can take place owing to the lower VOH contents.

Heats of combustion

The heats of combustion, ΔH , for the phosphorylated PVOH samples (Table 1) show a strong correlation with the fraction of repeat units phosphorylated (x). The

relevant equation is:

$$\Delta H = 20.8 - 7.44x$$

with a correlation coefficient of -0.915 (a significant correlation at the 95% confidence level). This correlation is to be expected given that the amount of material combusted decreases as the amount of phosphorus in the polymer increases. For the EVOH samples, phosphorylation also tends to decrease ΔH (see Table 2) in accordance with expectations, although for these samples there is no obvious correlation between the decrease in ΔH and the fraction of repeat units phosphorylated, presumably because the compositions of the EVOH samples also vary.

Examination of char residues from phosphorylated PVOH by scanning electron microscopy (SEM)

The structures of the char residues from PVOH with phosphorus contents of 0, 0.6, 1.5 and 5.5% by weight respectively were examined by SEM to look for any obvious differences. The resulting SEM micrographs are shown in Figure 7; all are recorded at a magnification of $\times 100$. It can be seen that the char from the untreated PVOH shows little evidence of intumescence (bubbling), but that the chars from the phosphorylated materials show signs of having been blown to a certain extent by

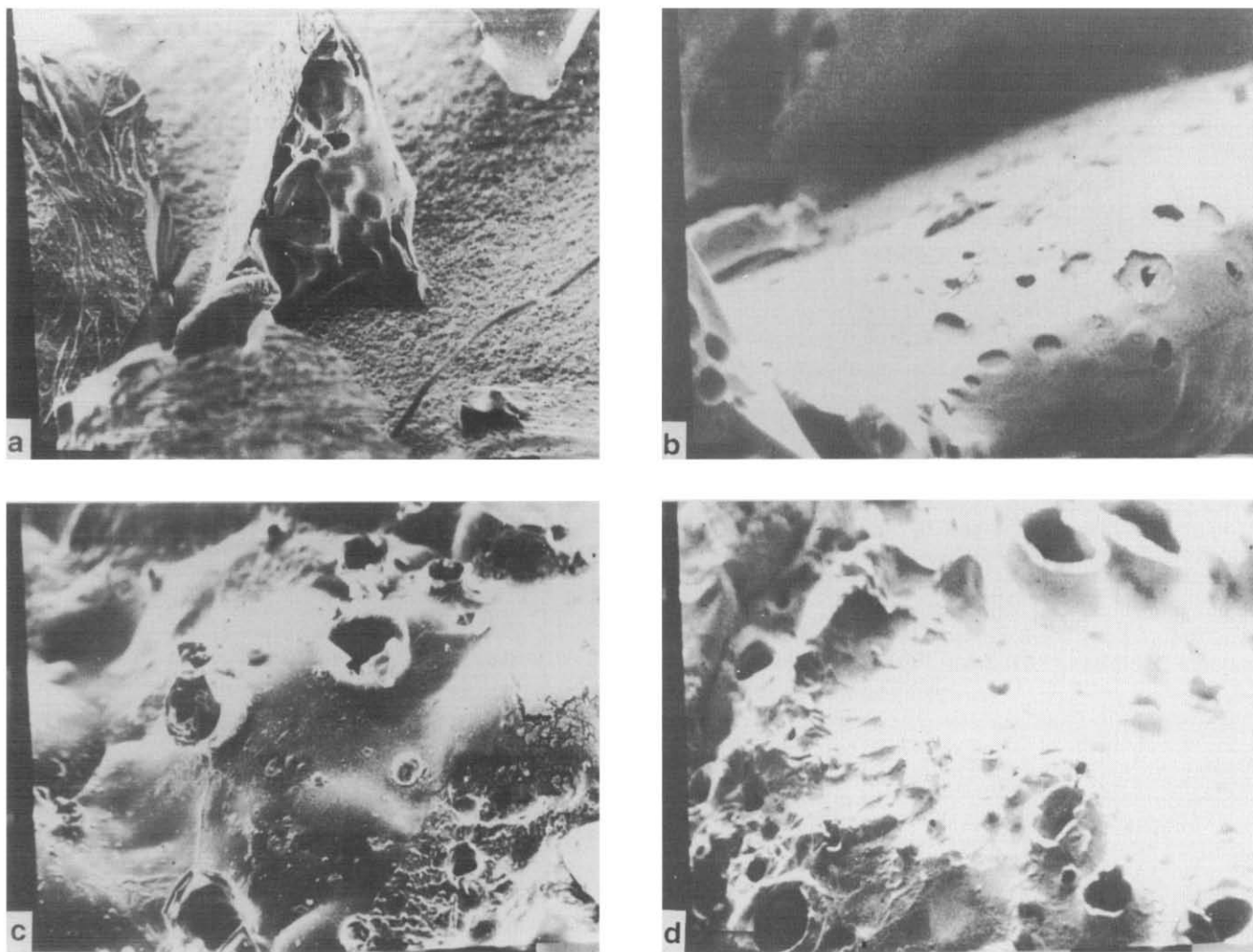
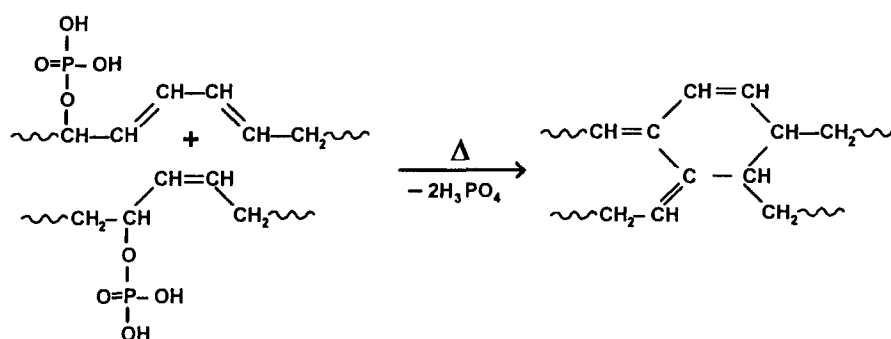


Figure 7 SEM micrographs of char residues from the burning of PVOH samples 1, 2, 3 and 8, containing (a) 0, (b) 0.6% by weight, (c) 1.5% by weight and (d) 5.5% by weight of phosphorus, respectively (all recorded at a magnification of $\times 100$)



Scheme 3

evolved gases. This intumescence is desirable in flame retardancy as it helps to protect the underlying polymer from heat. Intumescence in this case arises probably mainly from the evolution of water vapour. Also from Figure 7 it can be seen that the bubbling is most evident for the polymer containing 5.5% by weight of phosphorus, commensurate with this polymer displaying the best flame retardance of the four.

Mechanism of char formation

Undoubtedly, the first stages of char formation during combustion involve elimination of water, in part catalysed by phosphate or phosphonate groups (e.g. Schemes 1 and 2). However, we can only speculate about the later stages in which an involatile carbon- and phosphorus-rich residue is formed. It is possible that these later stages involve a series of intra- and/or intermolecular Diels-Alder reactions between adjacent unsaturated sequences accompanied by some elimination of phosphate groups (e.g. Scheme 3). However, much of the phosphorus probably becomes bound in ultimately as involatile polyphosphate since only about half escapes from the residue. We note that a mechanism involving consecutive Diels-Alder reactions and phosphate elimination steps has been proposed by Camino *et al.* to account for the formation of incombustible chars in polymers containing pentaerythritol diphosphate as a flame retardant²⁴.

CONCLUSIONS

Phosphorylation of PVOH and EVOH can be achieved using H_3PO_4 and H_3PO_3 , both in suspension and in aqueous solution. LDPE can be phosphonylated via a chlorophosphonylation reaction.

Covalently bound phosphorus is most effective as a flame retardant, as expected, with the most highly hydroxylated polymers, i.e. with PVOH and with EVOH samples containing the most VOH. However, even in the absence of VOH groups (i.e. with LDPE), an improvement in flame retardancy can be achieved.

The mechanism of flame retardancy in these systems appears to involve both vapour-phase and condensed-phase components; increasing the level of phosphorus incorporated increases both the char yield on combustion and the LOI.

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