Phosphate-Containing Flame-Retardant Polymers with Good Compatibility to Polypropylene. I. The Effect of Phosphate Structure on Its Thermal Behavior

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ABSTRACT: Phosphate-containing flame-retardant polymers were synthesized via a partial-substitution reaction of poly(vinyl acetate) with stearylphosphonic chloride (SPPC) and diethylchlorophosphate in various substitution ratios. SPPC had been previously synthesized from phosphonic dichloride and stearyl alcohol. The synthesized SPPC and the flame-retardant polymer products were characterized by Fourier transform infrared (FTIR) spectra analysis. The quantitative analysis of phosphorus in the polymer products was carried out by EDS (Energy Dispersion Spectrummeter) analysis. The real substitution ratios of the polymer products were estimated by the atomic number ratio of carbon and phosphate in products from EDS data. Variations in the glass-transition temperature and thermal-decomposition temperature of the products were investigated. The char of polymer products produced after thermogravimetric analysis (TGA) was also analyzed by FTIR, and the results show that different phosphate substitution leads to different char developments during the heating of TGA. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1125–1135, 2001

**Key words:** flame-retardant polymer; intumescence; phosphate substitution

INTRODUCTION

The intumescent flame-retardant system is a special class among all the flame-retardant additives.[1–4] Intumescent polymeric compositions undergo an expansion to form a protective foamed char layer when exposed to flaming temperatures. The function of this char layer is to interrupt the fuel and heat transfer between the flaming zone and the material surface.[5–9] Various intumescent flame-retardant additives have been developed, and ammonium polyphosphate is the most famous for its high flame retardancy, especially when it is employed in combination with pentaerythritol and melamine.[10–12] However, the ammonium polyphosphate/pentaerythritol/melamine system is not the best solution for the intumescent flame retardation of polymers because of its poor compatibility with the matrix, moisture sensitivity, and migration problems.

A good way to improve on the previously mentioned disadvantages is to introduce phosphorus into the polymer chain.[13–16] Phosphorus-containing molecules can be introduced into the backbone
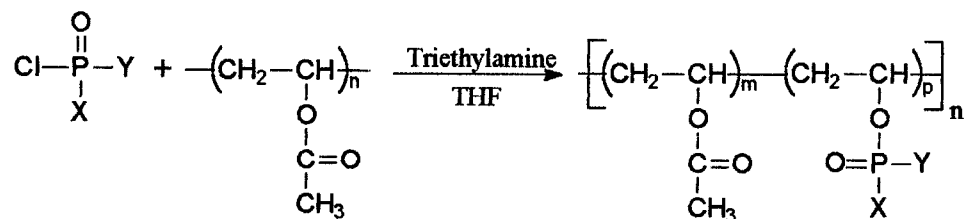
Product D, X = Y = OC₂H₅

Product S, X = OC₁₈H₃₇ ; Y = Ph

For Product S:
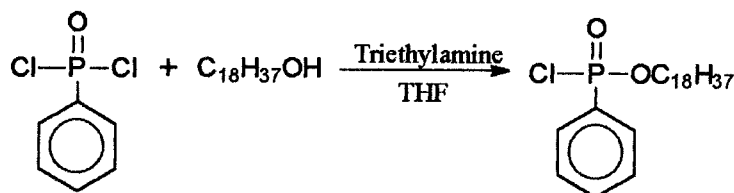
Scheme 1

or side group of a polymer. For the former case, a phosphorus-containing monomer was employed to join a polymerization reaction with other monomers. The most popular method for preparing polyphosphates and polyphosphonates is based on the esterification of diols with an equimolar amount of dichlorophosphates and phosphonyl dichloride, respectively.[17–19] For the latter case, it is a substitution reaction on a polymer with reactive sites, in which phosphate, phosphonate, or phosphoric acid is used to react with the functional group of the polymer.[20–22] The problems of

migration and moisture sensitivity are successfully conquered; however, the compatibility of the phosphorus-containing polymer and polymers with low polarity, such as polyolefins, is still not acceptable. In this study, phosphate-containing polymers were prepared by the latter method with the substitutive molecules stearylphosphonic chloride (SPPC) and diethylchlorophosphate (DECPa) with different polarity adjustments. The effects of these two molecules on the thermal properties and char formation of the polymer products are compared and discussed.

Table I   Feed Compositions and Product Yields of Phosphate-Containing Polymers

Sample Code	PVAc (g)	Desired Substitution Ratio[a]	Phosphate (mol)	Phosphate (g)	Stearyl Alcohol (g)	Weight of Product (g)	Yield[b] (%)
D Product (DEPCa)							
D05	30	0.5	0.1744	30.09	—	43.78	84.1
D06	30	0.6	0.2093	36.11	—	46.78	85.3
D07	30	0.7	0.2442	42.14	—	48.98	82.7
S Product (PPDC)							
S04	30	0.4	0.1395	27.20	37.74	70.92	83.8
S05	30	0.5	0.1744	34.00	47.18	81.45	84.3
S06	30	0.6	0.2093	40.81	56.61	89.47	81.2
S07	30	0.7	0.2442	47.61	66.05	97.17	78.6

[a] The molar ratio of the acetate in PVAc that was desired to be substituted by phosphate.
[b] This was estimated by dividing the weight increase of the polymer products after substitution with the weight sum of phosphate and stearyl alcohol in feed.
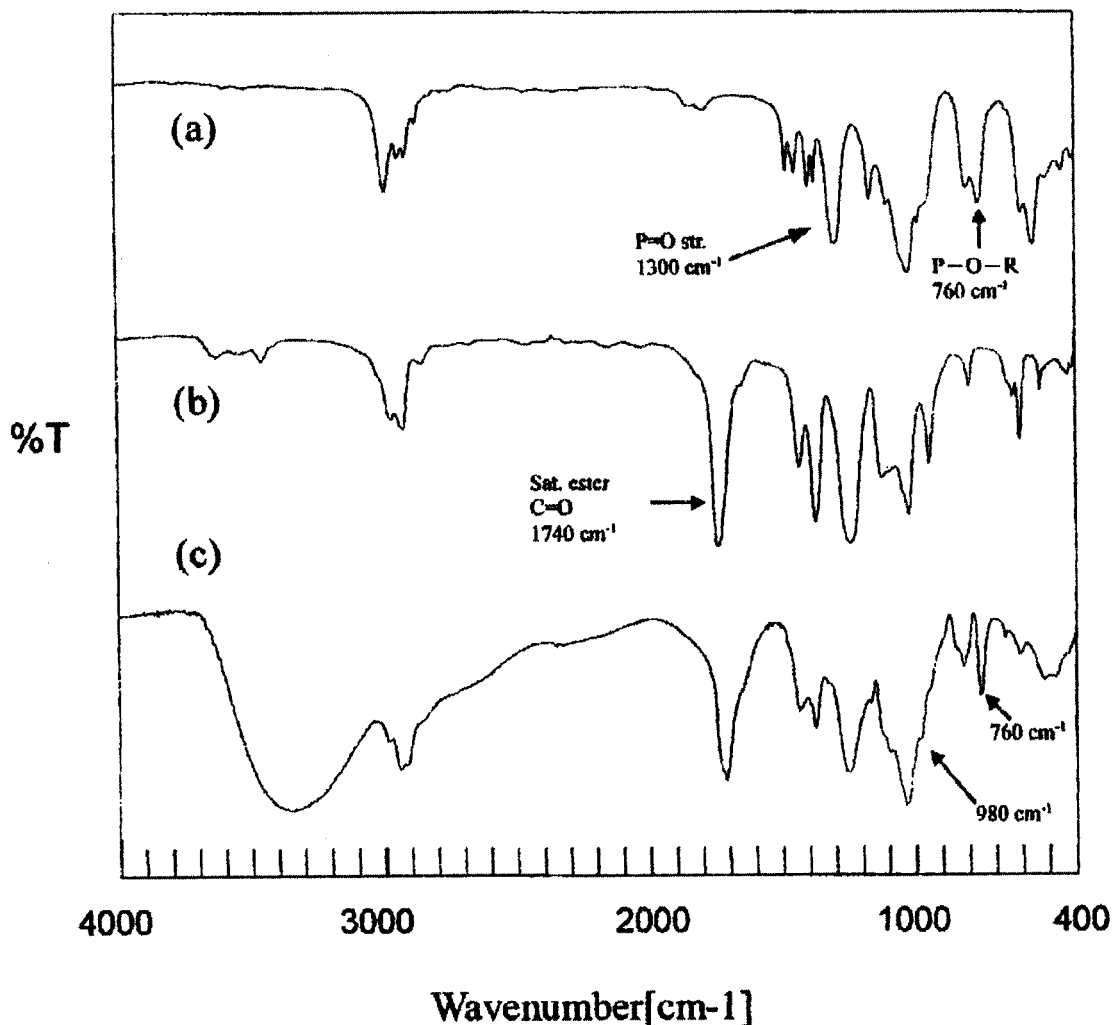
Figure 1   FTIR spectra of (a) DECPa, (b) PVAc, and (c) DECPa-substituted PVAc.

EXPERIMENTAL

The average molecular weight of poly(vinyl acetate) (PVAc) was about 101,600 in this study. Phenylphosphonic dichloride (PPDC) and DECPa were both reagent-grade products of Acros Organics Co. (Geel, Belgium). The stearyl alcohol (SA; 1-octadecanol) used was a first-grade reagent of Wako Pure Chemical Industries, Ltd. (Japan). Reagent-grade tetrahydrofuran (THF) was dehydrated before use by CaH_2 and was recovered by distillation under reduced pressure.

The synthesis process of the study is shown in Scheme 1, in which the phosphate used for D products was DECPa and that for S products was SPPC. The synthesis was carried out in a flask equipped with a magnetic stirrer, an addition funnel, and a reflux condenser. The feed composi-

tions of all products are listed in Table I. For the preparation of D products, 30 g of PVAc and 17.6–24.7 g of triethylamine were dissolved in 300 mL of THF in a flask, and then 30.09–42.14 g of DECPa was added drop by drop into the solution with an addition funnel for different substitution ratios. The reaction was carried out at 60°C for 3 h with nitrogen purging.

The synthesis of S products began with the monosubstitution of PPDC with SA. For the preparation of S products, 37.74–66.05 g of SA and 14.1–24.7 g of triethylamine were dissolved in 40–70 mL of THF. Then, the solution was added drop by drop to a PPDC/THF solution (50% v/v), in which the amount of PPDC ranged from 27.20 to 47.61 g, respectively. This reaction proceeded at 30°C for 1 h. The final solution was then added to a solution of PVAc (30 g) and THF (300 mL).
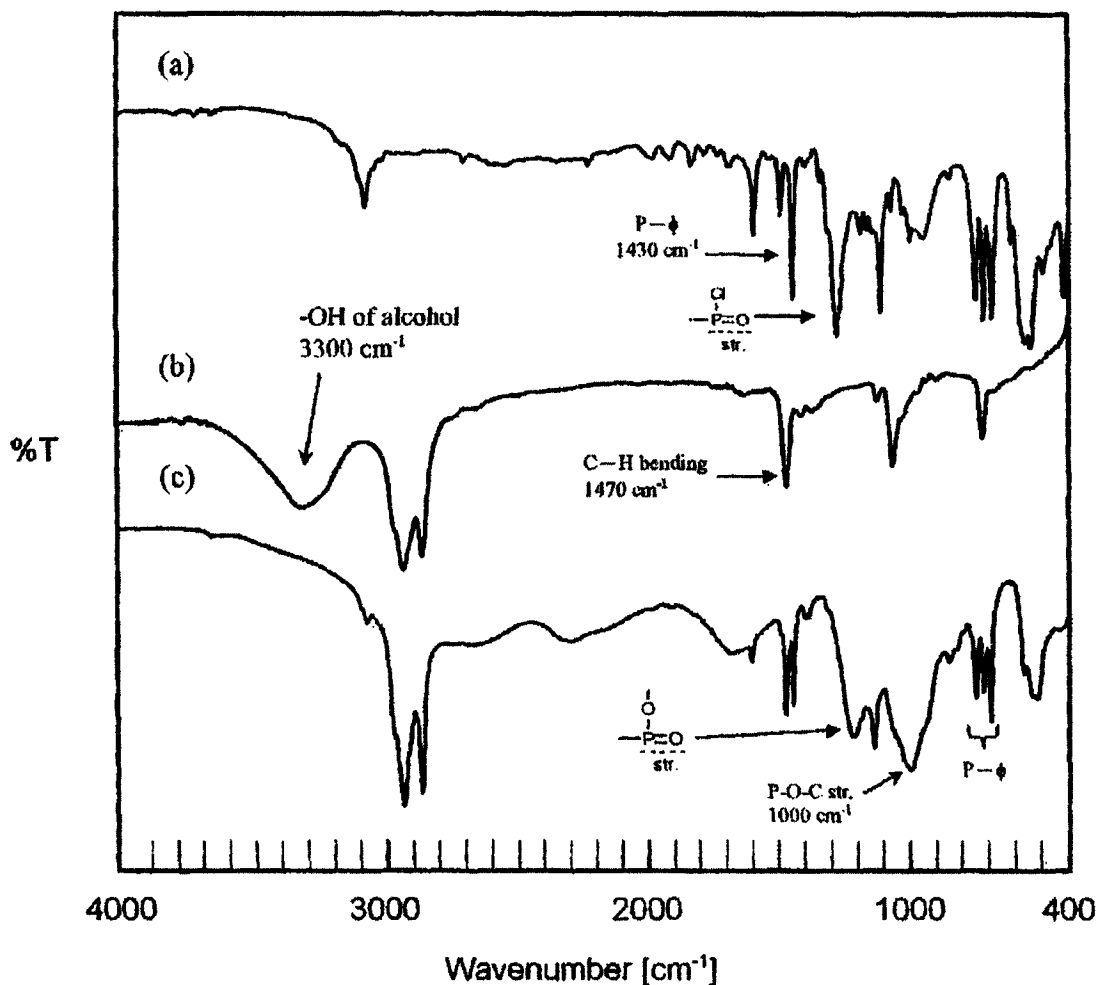
Figure 2 FTIR spectra of (a) PPDC, (b) SA, and (c) SA-monosubstituted PPDC.

This reaction proceeded at 60°C for 3 h, and nitrogen purging was used in both reactions.

After the reaction was completed, the resulting solution was concentrated with a rotary evaporator at 40°C and reduced pressure and then left to cool at room temperature. The product was precipitated in distilled water and dried and dissolved in THF to precipitate again. The precipitation process was repeated three times to obtain a high-purity product. For the purification of S products, unreacted SA and SA-monosubstituted PPDC were extracted by hexane. The final polymer product was dried in a vacuum oven at 30°C under a reduced pressure to a constant weight.

Infrared spectra of the products were determined with a Jasco Fourier (Japan) transform infrared (FTIR) E-300 spectrometer. EDS analysis was carried out to investigate the phosphorus concentration and phosphate substitution ratio of the products. The analysis was carried out with a Hitachi

S2460N scanning electronic microscope machine with an EDS analysis module. Thermal degradations of the samples were investigated via thermogravimetric analysis (TGA) with a DuPont U.S.A. 2000 thermal analyzer and a TGA model 951. TGA was performed at a heating rate of 15°C/min and a nitrogen flow rate of 40 mL/min. Differential scanning calorimetry (DSC) analysis was performed with the same thermal analyzer system with a DSC 910. The heating rate was 10°C/min, and the nitrogen flow rate was 30 mL/min.

RESULTS AND DISCUSSION

It is usually not very easy to identify the phosphate structure of samples with only an FTIR spectrum because the bands of phosphate ester are similar to those of carboxylic ester. For in-
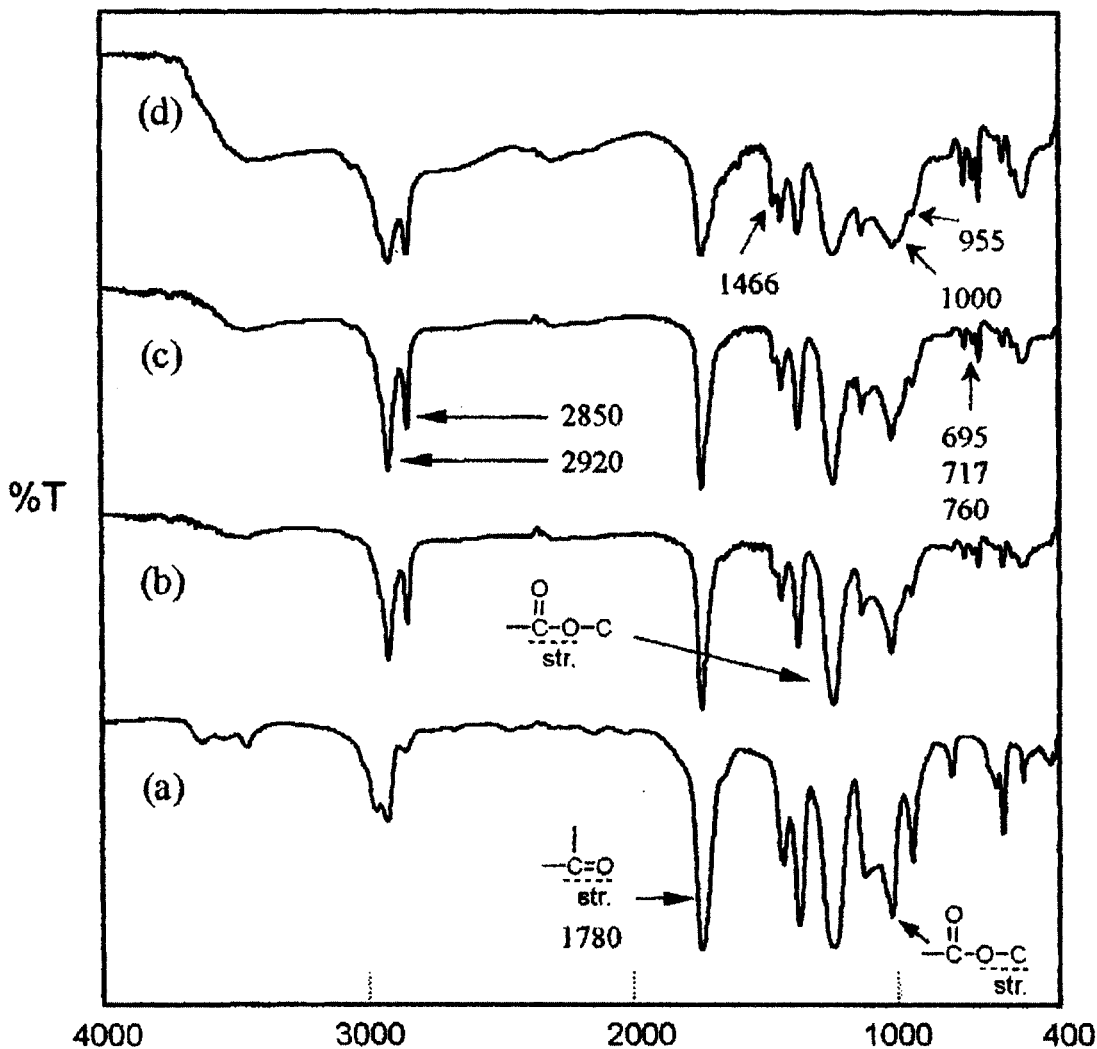
Figure 3 FTIR spectra of products (a) S04, (b) S05, (c) S06, and (d) S07.

stance, a strong band of 1300 cm^{-1} in the spectrum in Figure 1(a) is the absorption of P=O stretching in DECPa, in which the phosphorus attaches to chlorine. This band shifts to 1250 cm^{-1} after the reaction of DECPa with PVAc; however, the band of C—O stretching in the carbonyl group of PVAc appears at the same position. As a result, this cannot be considered a strong evidence for the combination between DECPa and PVAc. Similarly, the band of P—O—C stretching (980 cm^{-1}) is also near that of C—O—C stretching (1050 cm^{-1}) in the FTIR spectrum. The P—O—C stretching in the spectrum in Figure 1(c) shows an obscure shoulder beside a much stronger peak of the C—O—C stretching; however, a medium-intensity band at 760 cm^{-1} in the spectra in Figures 1(a) and 1(c) is considered to be the absorption of the P—O—R structure. This

band offers circuitous evidence for the existence of a substitution reaction between PVAc and DECPa.

The reaction between PPDC and SA is easily confirmed because the P=O (1250 cm^{-1}) and P—O—C (1000 cm^{-1}) bands can easily be found without the confusion of PVAc (Fig. 2). Three-teeth-fork-shaped bands found around 720 cm^{-1}, which belong to phosphorus attaching to a phenyl group, can be considered a characteristic of PPDC or SPPC. Figure 3 shows the spectra of polymer product S with different phosphate-substitution ratios. The situations for identifying phosphate group in products are similar to the previously mentioned case of DECPa-substituted PVAc. However, not only does the shoulder at 1000 cm^{-1} get stronger as the substitution ratio rises but so do the three-teeth-fork-shaped bands. Because
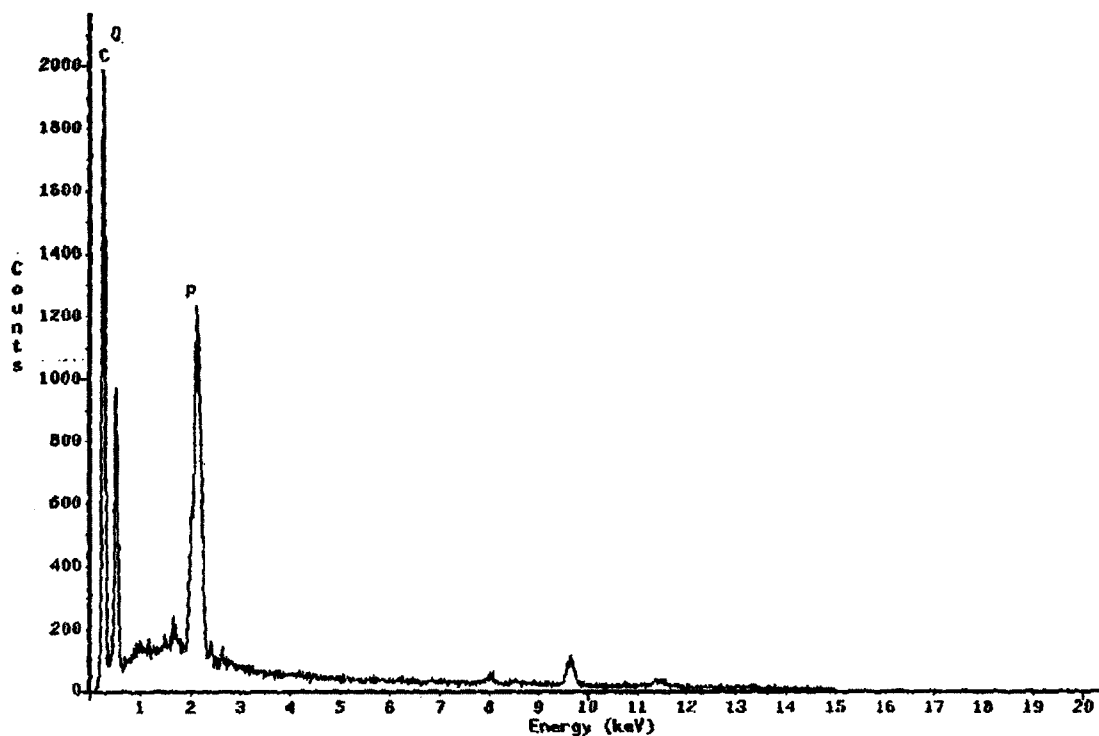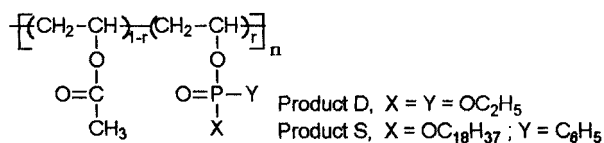
Sample: Product S05

Element	Relative k-ratio	Relative k-ratio (calc.)	ZAF	Atom %	Element Wt%		Wt% Error (1-Sigma)	Stoichiometry
C-K	0.83050	0.44938	1.428	72.33	64.48	+/-	0.60	73.078
O-K	0.08936	0.04835	5.806	25.30	30.07	+/-	0.95	24.000
Cl-K	0.00167	0.00090	1.222	0.05	0.11	+/-	0.02	0.043
P-K	0.07847	0.04246	1.259	2.32	5.34	+/-	0.09	1.850
Total				100.00	100.00			

Stoichiometry results are based upon 24 Oxygen atoms

Figure 4 EDS spectrum and data of product S05.

finding direct evidence for the phosphorylation of PVAc is difficult, it cannot be proven with just this circuitous evidence. Consequently, an EDS elemental analysis was also needed.

With EDS analysis, not only can the existence of phosphorus be detected, but a quantitative analysis of phosphorus can also be done. Figure 4 shows an example of an EDS analysis spectrum and data for product S05. The atomic percentage of carbon and phosphorus of each sample was measured, and then the C/P atomic ratio of each sample was given. The C/P atomic ratio was used to estimate the practical substitution ratio of the polymer products. The calculations were based on the following deductions. First, the practical substitution ratio was assumed to be r as shown in the following formula:

Product D, X = Y = OC_2H_5
Product S, X = $OC_{18}H_{37}$; Y = C_6H_5

Therefore, the relationship between C/P and r for product D can be described with the following equations:

$$\frac{C}{P} = \frac{4(1-r) + 6r}{r} = 2 + \frac{4}{r} \qquad (1)$$

$$r = \frac{4}{\left(\dfrac{C}{P}\right) - 2} \qquad (2)$$

Table II   Estimated Phosphate-Substitution Ratio of Products with the Data of EDS Analysis

| Sample Code	C/P by Atom	Acetate-Substituted Ratio of Product **r**	Substitution Efficiency[a] (%)
D Product			
D05	10.791	0.455	91.0
D06	9.648	0.523	87.2
D07	8.483	0.617	88.1
S Product			
S04	—	—	—
S05	31.176	0.435	87.0
S06	29.828	0.511	85.2
S07	28.826	0.586	83.7

[a] This was obtained by dividing the actual acetate-substituted ratio of product **r** by the desired substitution ratio.

Based on the same calculation, the relationship between C/P and r for product S can be described by the following equation:

$$r = \frac{4}{\left(\dfrac{C}{P}\right) - 22} \tag{3}$$

The C/P ratio of each product obtained from EDS analysis and the practical substitution ratio r are listed in Table II. The practical substitution ratio of each product was found to be over 80% of the desired substitution ratio.

The phosphate group in the flame-retardant polymer product acted as a dehydrating agent, which promoted the generation of char. Unfortunately, the strong dehydration tendency of materials usually brought weak thermal stability, and the TGA diagrams in Figures 5 and 6 are good examples. All the products showed an obvious decrease in thermal stability. The thermal-degradation-onset temperature of the flame-retardant polymer products decreased to about 250°C with the substitution of SPPC. However, the temperature decreased to about 130°C with DECPa. The higher thermal stability of S products might have been caused by the existence of a phenyl group in the side group. It is clear that the D products, which used DECPa, were not suitable for the application of a flame retardant for blending because of their poor thermal stability. The intermediate char yield of all the products was increased by both phosphate substituents and made all the samples not ignited by a constant flame under atmosphere. All samples generated glassy
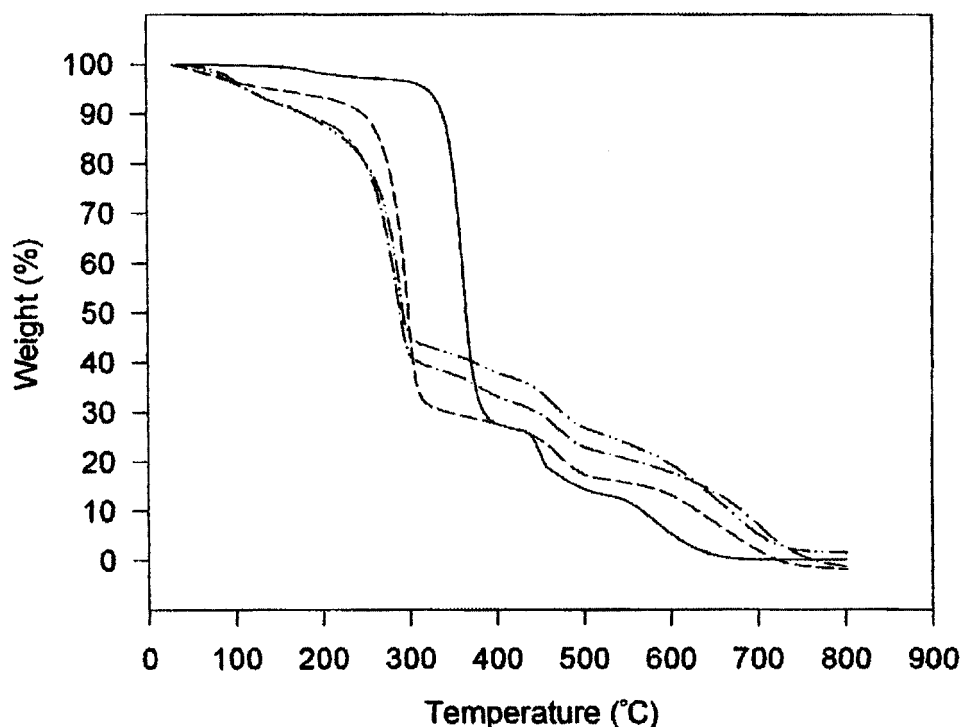
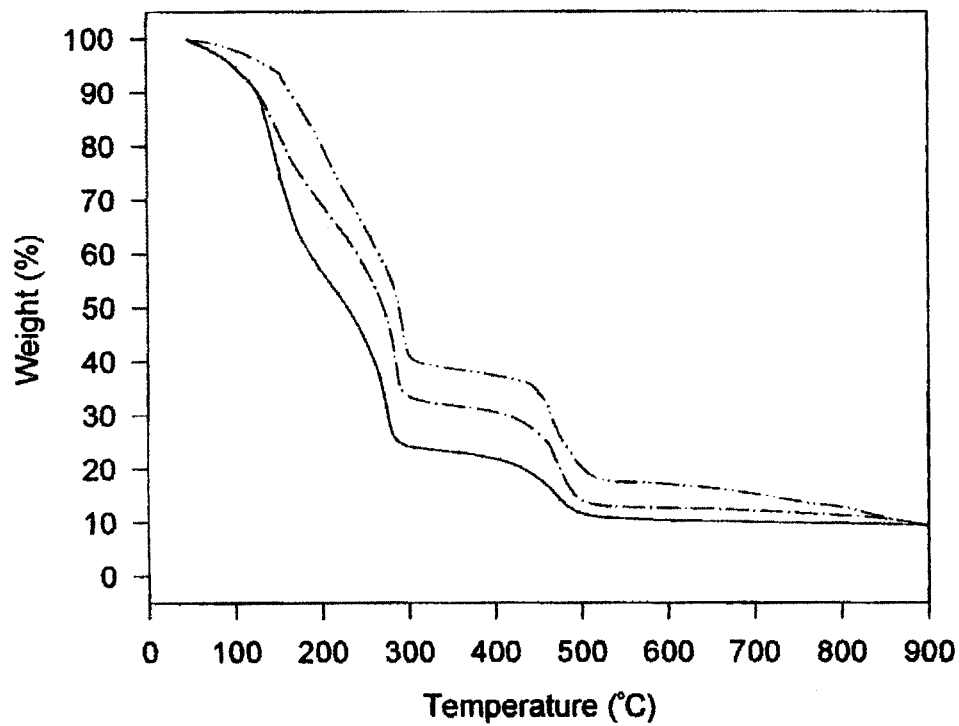**Figure 5**   TGA diagrams of PVAc (——) and products S05 (– – –), S06 (– · –), and S07 (– · · –).

Figure 6   TGA diagrams of products D05 (——), D06 (– · –), and D07 (– · · –).
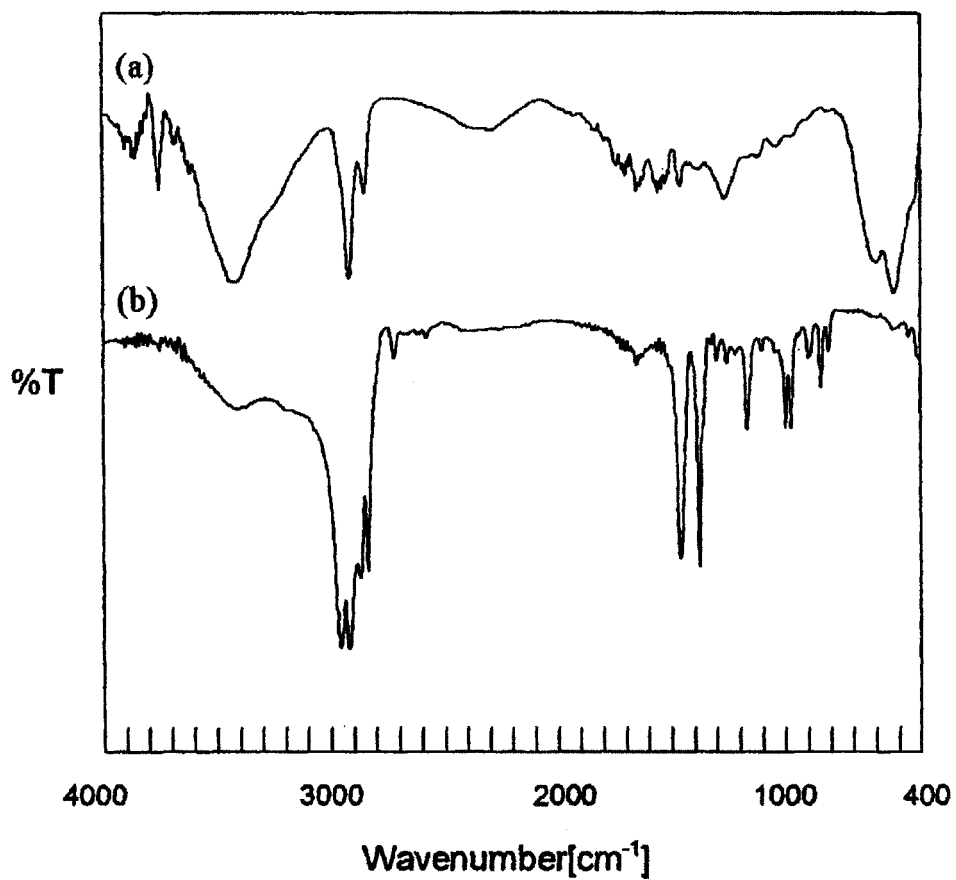

Figure 7   FTIR spectra of chars from products (a) D05 and (b) S05 under 800°C after TGA.
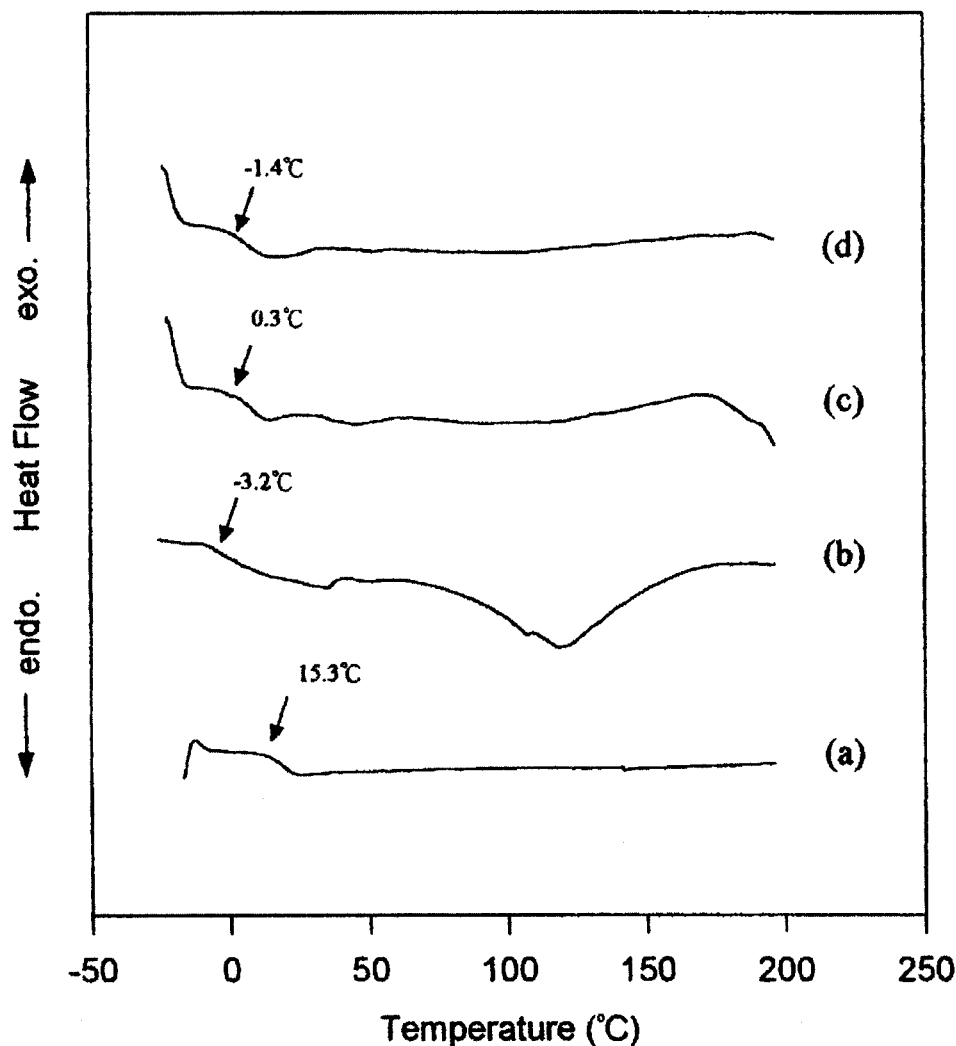
Figure 8   DSC diagrams of products (a) D05, (b) D06, and (c) D07.

char after TGA to 800°C. After the FTIR analysis of the char, it was concluded that the different phosphate substituents in the products led to a different chemical structure of the char. The FTIR spectra in Figure 7 reveals that the final char of product S contained P—O—C ($1000 \ \text{cm}^{-1}$), P—O—P ($978 \ \text{cm}^{-1}$), —CH_3 (2920, 2850, and $1376 \ \text{cm}^{-1}$), and C—H and —CH_2— ($1460 \ \text{cm}^{-1}$) structures; however, none of these bands was found in the final char of product D.

The typical glass transition of samples in DSC analysis showed a baseline shift in the DSC heat-flow curve. The glass-transition temperature (T_g) of the samples shifted to a lower temperature with a higher substitution ratio (Figs. 8 and 9). The decrease in the T_g of the samples was chiefly caused by the introduced

P—O—C structure, which is a soft and flexible structure. More P—O—C in products is believed to cause a greater decrease in T_g, so this explains why the T_g of D products was lower than that of S products.

CONCLUSION

Although direct evidence of a reaction between phosphate and PVAc in this study was not easy to find with FTIR analysis alone, the reaction could be proven in retrospect with the results of EDS analysis. The polymer products with both phosphate substituents showed good flame resistance under atmosphere; however, a loss in thermal stability was the price. The thermal stability loss
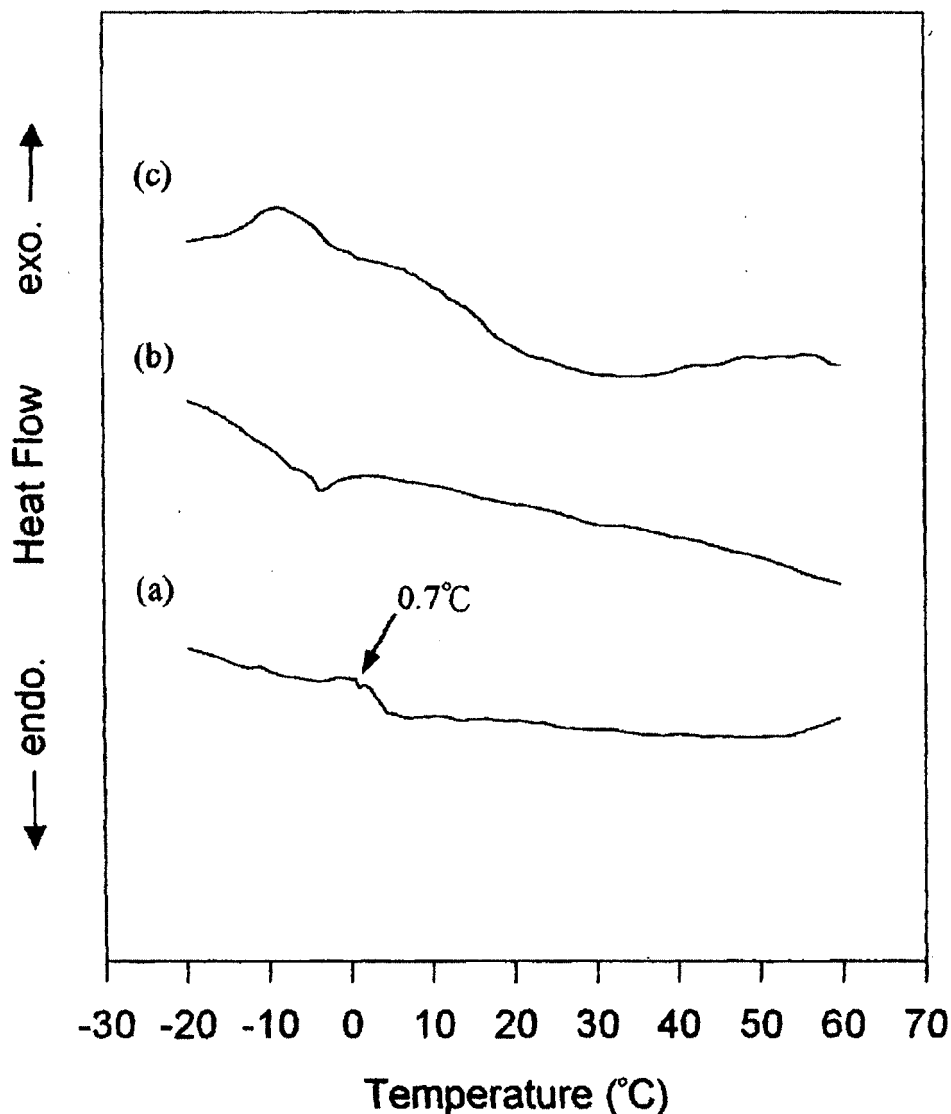
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Figure 9 DSC diagrams of (a) PVAc and products (b) S05, (c) S06, and (d) S07.

of the D products was not able to pass the processing temperature of melt blending; hence, the D products did not fit the original target of this study, which was to design and obtain a flame retardant for a polyolefin resin. Conversely, the thermal stability of the S products was higher than 250°C, and the stearyl group was compatible with polyolefin. The S products were obviously superior to the D products according to the requirements of this study.

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