

Flame-Retardant Properties of Cellulose Phenylthiophosphonate

K. KATSUURA and N. INAGAKI, *Polymer Chemistry Section, Faculty of Engineering, Shizuoka University, 432 Japan*

Synopsis

The effects of sulfur atoms on the thermal degradation and flammability of cellulose phenylthiophosphonate were investigated using thermogravimetry, IR spectrometry, and limiting oxygen index flammability tester. Introduction of sulfur atoms instead of oxygen atoms in the phosphonyl groups had little influence on the thermal degradation of cellulose. The thermal reactions were altered by ion exchange with sodium ions, and degradation of the cellulose chains was retarded. Cellulose phenylthiophosphonate was self-extinguishing above 4.64% phosphorus content. The flame-retardant properties remained when the cellulose phosphorus ester was ion exchanged with sodium ions. It was concluded that introduction of sulfur atoms into phosphorus esters of cellulose was effective in preventing the decrease in flame-retardant properties by ion exchange in laundering.

INTRODUCTION

This paper elucidates the effects of sulfur atoms on the thermal degradation and flammability of cellulose phenylthiophosphonate. In our previous papers¹⁻³ it was shown that phosphorus esters of cellulose had good flame-retardant properties and that phosphorous acid was an excellent phosphorylating agent causing no strength loss or discoloration of cellulose. However, the esters have an undesirable characteristic, i.e., the flame retardancy decreases upon ion exchange with sodium and calcium ions in laundering.¹ This disadvantage hinders the acceptance of esterification as a durable flame-retarding treatment.

Lewin et al.⁴ have reported that a combination of phosphorylation and sulfation procedures is a feasible approach to minimizing the decrease in flame retardancy by ion exchange. A sulfur content of 1.7-1.8 wt-% and a P/S weight ratio of 1.3-2.0 gave optimum results. These results are suggestive of an interaction between phosphorus and sulfur atoms. Thermal degradation and flame retardancy of sulfur-containing phosphorus esters are therefore of interest. Cellulose phenylthiophosphonate was chosen for study.

EXPERIMENTAL

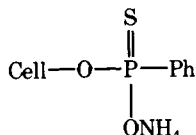
Materials

Phenylphosphonothioic dichloride, PhP(S)Cl_2 (I), phenylphosphonic dichloride, PhP(O)Cl_2 (II), phenylphosphonous dichloride, PhPCl_2 (III), and phenyl phosphorodichloridate, PhOP(O)Cl_2 (IV) were prepared according to the literature.⁵⁻⁸ The products were identified by IR and NMR spectroscopy. Other chemicals were analytical-grade materials and were used without further purification.

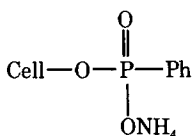
Preparation of Modified Celluloses

Ground filter paper (20 mesh, Toyo Roshi Kaisha Ltd., Code No. 2) and bleached and mercerized cotton broadcloth (120 g/m²) were used as cellulose materials.

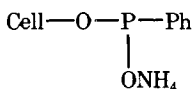
Four phosphorylated cellulose samples were prepared, namely, cellulose phenylthiophosphonate (PS),



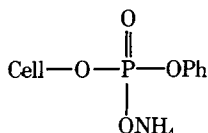
cellulose phenylphosphonate (PO),



cellulose phenylphosphonite (P)



and cellulose phenyl phosphate (PO₂)



A dry cellulose sample (4.86 g, 0.03 mole) was treated with a mixture of one of the phosphorylating agents I, II, III, and IV (0.045 mole) and urea (7.2 g, 0.12 mole) in dry pyridine (300 ml) at 110°C for an adequate time under nitrogen atmosphere. The products were washed with water and ethanol until no phosphorus compound could be detected in the filtrate, then dried over phosphorus pentoxide under reduced pressure.

Products were identified by IR spectroscopy. The modified cellulose samples used for this study are shown in Table I together with phosphorus and sulfur contents.

Thermogravimetry

A Shinku Riko thermogravimetric analyzer DGC 3 was used. Ground samples (80 mesh) of about 100 mg were weighed into quartz pans (8 mm I.D. × 8 mm) and the pans placed on the top of a Chromel-Alumel thermocouple and heated under vacuum (10⁻³ torr) or in air at a programmed rate of 2°C/min.

TABLE I
Sample Phosphorus and Sulfur Contents and Thermogravimetric Values (Under Vacuum)

Sample	P, %	S, %	Threshold temperature for weight loss, °C	Residue at 350°C, %
PS-1 ^a	1.34	1.29		
PS-2 ^a	1.58	1.49		
PS-3 ^a	4.64	4.17		
PS-4	6.81	5.89	190	37
PS-5	8.63	7.55	190	40
PO-1 ^a	2.16			
PO-2 ^a	2.22			
PO-3 ^a	3.69			
PO-4	4.32		183	40
P-1 ^a	0.72 ₃			
P-2	1.13		211	33
P-3 ^a	1.37			
P-4 ^a	1.59			
P-5	2.13		197	41
P-6	3.24		187	50
PO ₂ -1 ^a	1.10			
PO ₂ -2 ^a	5.71			

^a Cotton broadcloth was used as cellulose material.

Nuclear Magnetic Resonance and Infrared Spectroscopy

NMR spectra were obtained using tetrachloromethane and tetramethylsilane as internal standard on a Hitachi spectrometer R-24. Infrared spectra were recorded on a Nihon Bunko spectrometer IRA-1 and IRA-2 using KBr discs.

Flame Retardancy Test

The oxygen index test (ASTM D-2863-70) was used to evaluate the flammability of the treated fabrics.

RESULTS AND DISCUSSION

Thermogravimetry

Typical thermogravimetric curves for three of the modified celluloses are shown in Figure 1. Curves for the sample PO₂ have already been given in a previous paper,⁹ so they are not dealt with here. Similar weight loss curves for PS and PO samples were obtained. The PS sample began to decompose at 190°C, and at 350°C there was a residual weight of about 40%. Sample P had a smaller weight loss at 350°C than samples PS and PO. The figure shows that introduction of a sulfur atom instead of an oxygen atom in phosphonyl groups has little influence on the thermal degradation. Degradation reactions of cellulose are accelerated and result in large amounts of residual products.

It is well known that cellulose phosphorus esters have ion-exchangeable groups and that flame-retardant properties are removed by ion exchange with sodium and calcium ions in laundering. Our report¹⁰ has shown that the ion exchange influences the thermogravimetric curves. The threshold temperature for weight

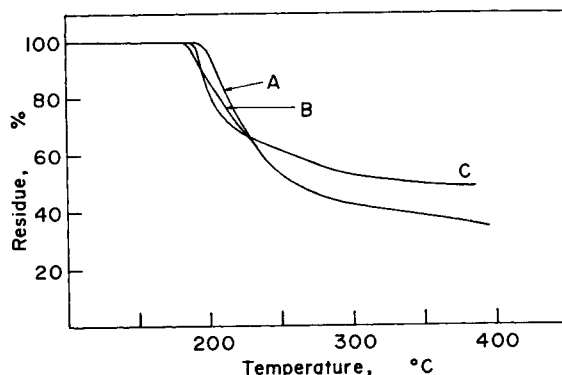


Fig. 1. Thermogravimetric curves for modified celluloses (under vacuum): (a) Cellulose phenylthiophosphonate (PS-4); (b) cellulose phenylphosphonate (PO-4); (c) cellulose phenylphosphonite (P-6).

loss is shifted to higher temperatures and the amount of residual products is reduced, i.e., the degradation reaction of the cellulose is retarded by the ion exchange and carbonization is inhibited.

Thermogravimetric curves for sodium salts of the samples PS and PO, which were impregnated with 1*N* sodium hydroxide solution for five days, are shown in Figure 2. The threshold temperatures for weight loss and amounts of residual products at 400° and 500°C are listed in Table II. The threshold temperatures for both the ion-exchanged samples PS-3-Na and PO-3-Na shifted to higher

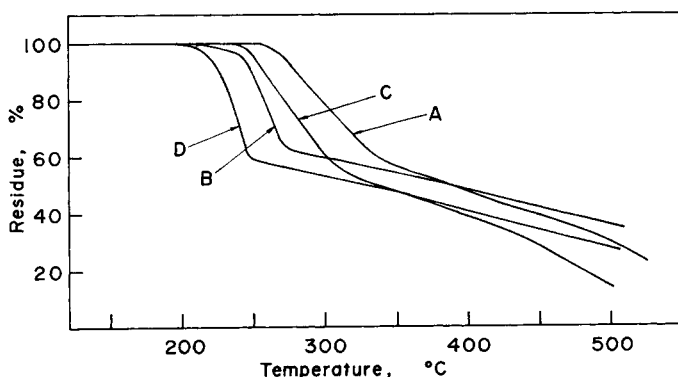


Fig. 2. Effect of sodium ion on thermogravimetric curves (in air): (a) Sodium salt of cellulose phenylthiophosphonate (PS-3-Na); (b) cellulose phenylthiophosphonate (PS-3); (c) sodium salt of cellulose phenylphosphonate (PO-3-Na); (d) cellulose phenylphosphonate (PO-3).

TABLE II
Effect of Ion Exchange with Sodium Ions on Thermal Degradation (In Air)

Sample	Threshold temperature for weight loss, °C	Residue at 400°C, %	Residue at 500°C, %
PS-3	200	50	36
PS-3-Na	240	48	29
PO-3	180	41	28
PO-3-Na	230	38	15

values compared with the untreated samples; the amount of residual products at 500°C decreased.

The mode of action of phosphorus compounds as flame retardants had been proposed to be acceleration of dehydroxylation of cellulose and formation of conjugated double bonds in cellulose chains.^{1,2} Since the carbonized cellulose chains are thermally stable, the evolution of flammable gases is retarded and the cellulose becomes self-extinguishing. Therefore two factors, that is, yielding of carbonized products before the pyrolysis temperature of cellulose is reached and thermostable products remaining above that the temperature, are requirements for the enhancement of flame-retardant properties. Considering the thermogravimetric results within the framework of our concept, it is inferred that introduction of sulfur atoms would be unfavorable to prevent the decrease of flame-retardant properties of cellulose phosphorus esters by ion exchange with sodium ions.

Infrared Spectra of Residual Products

The infrared spectra of the residual products from heating of the PS and P samples at the prescribed temperatures are shown in Figures 3 and 4. Our previous report,⁹ in which changes in infrared spectra for the PO sample were

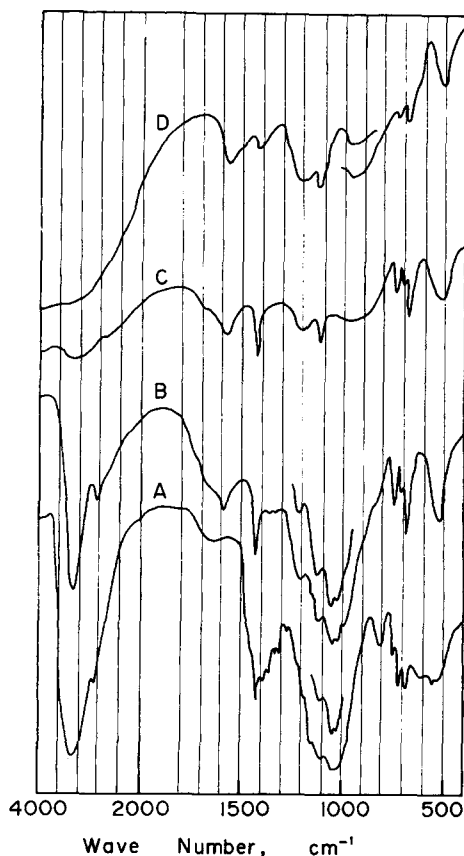


Fig. 3. Infrared spectra of cellulose phenylthiophosphonate (PS-5): (a) Untreated; (b) degraded at 205°C; (c) degraded at 245°C; (d) degraded at 400°C.

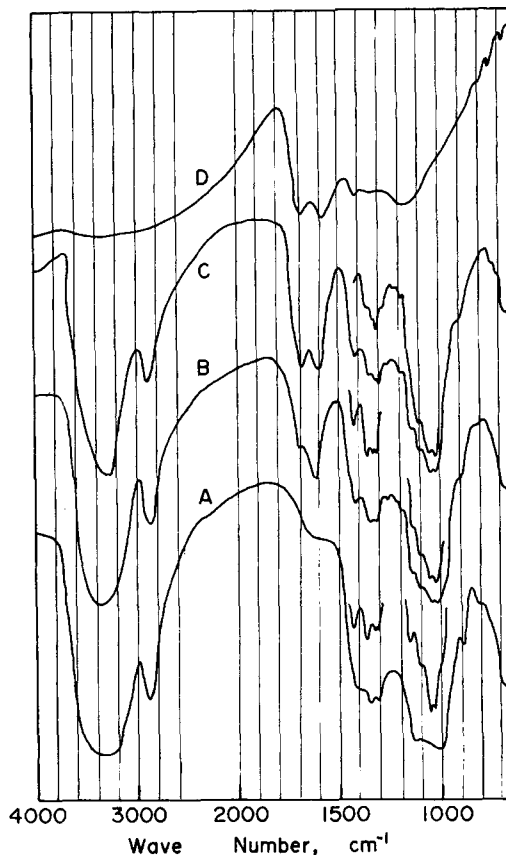

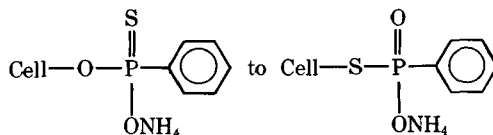


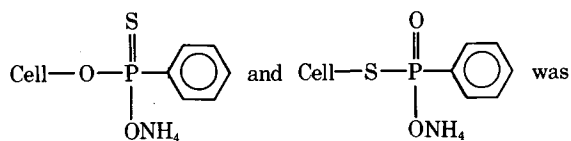
Fig. 4. Infrared spectra of cellulose phenylphosphonite (P-6): (a) Untreated; (b) degraded at 235°C; (c) degraded at 270°C; (d) degraded at 370°C.

discussed, had shown the following. In an initial weight loss region, peaks at 1630 (C=C) and 1000 cm^{-1} (C=C) appeared. In the final weight loss region each characteristic band of cellulose disappeared and the absorption band at 1630 cm^{-1} shifted to 1600 cm^{-1} (conjugated double bonds).

For the PS sample, remarkable changes were observed. At 205°C, where a weight loss of about 10 wt-% had occurred, absorption at 710 cm^{-1} due to P=S groups became less intense; new peaks at 1590 (C=C), 1230 (P=O), and 510 cm^{-1} (P—S) appeared. At 245°C each characteristic band of cellulose disappeared, but bands attributed to P— groups (1135 cm^{-1}), P=S (710 cm^{-1}), and P—S (510 cm^{-1}) remained. The absorption at 1600 cm^{-1} due to conjugated double bonds was of lower intensity than for the PO sample. At 400°C a similar spectrum was obtained except that the band at 1590 cm^{-1} became highly intense. These spectra indicate that the transformation of



occurs in an initial weight loss region and then the mixture of



degraded in a rapid weight loss region. The introduction of sulfur atoms retards the formation of conjugated double bonds by β -elimination of phosphorus ester groups.¹

For the P sample new peaks at 1700 (C=O) and 1270 cm^{-1} (P=O) appeared at 230°C. At 270°C the absorption of C=O groups became intense. Each characteristic band of cellulose remained up to 270°C. At 370°C only two peaks due to C=O and C=C groups were observed. These spectral changes show that the P sample is oxidized more easily than the PS sample and that carbonization of the P sample is retarded.

Sodium salts of the PS and PO samples gave peculiar infrared spectra (Figs. 5 and 6). At 250° and 270°C, where a rapid weight loss took place, each band of cellulose, especially C—O groups at 1160, 1110, 1050, and 1020 cm^{-1} , became of lower intensity. At 300° and 330°C, absorptions of CH₂ groups at 2880 and 1317 cm^{-1} , of CH groups at 1370 and 1280 cm^{-1} , and OH groups at 1336 cm^{-1} were missing. Absorptions at 1090, 1055, 1025, and 995 cm^{-1} , which correspond to C—O groups in pyranose rings, remained; but intensities of these bands were low. New bands at 1700 (C=O), 1600 (conjugated double bonds), 1220 (P=O),

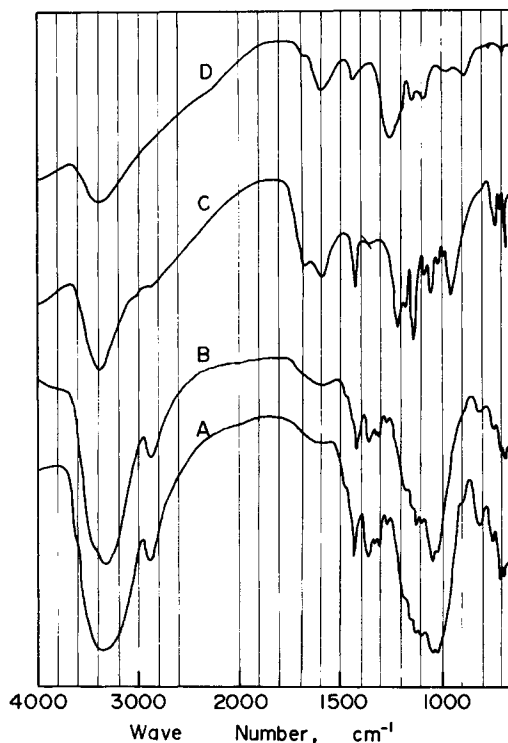


Fig. 5. Infrared spectra of sodium salt of cellulose phenylthiophosphonate (PS-3-Na): (a) Un-treated; (b) degraded at 270°C; (c) degraded at 330°C; (d) degraded at 420°C.

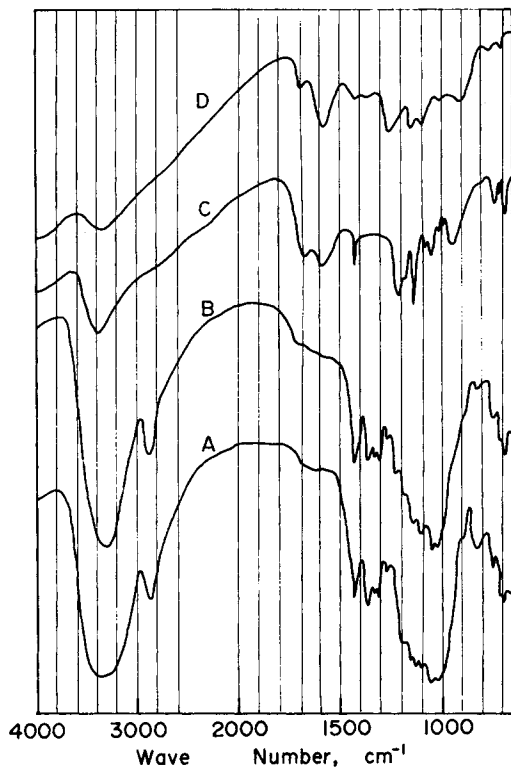




Fig. 6. Infrared spectra of sodium salt of cellulose phenylphosphonate (PO-3-Na): (a) Untreated; (b) degraded at 250°C; (c) degraded at 300°C; (d) degraded at 420°C.

1140 [P—O—(C)] and 960 cm^{-1} [(P)—O—C] appeared. Bands at 1430, 750, and 690 cm^{-1} due to P— groups became of high intensity. At 420°C absorptions due to C—O groups were missing, and bands at 1430, 750, and 690 cm^{-1} due to P— groups became of lower intensity. The band at 1220 cm^{-1} shifted to 1260 cm^{-1} , and its intensity was high. Intense absorptions only at 1600 and 1260 cm^{-1} were observed. From these spectra the following becomes apparent: (1) By ion exchange with sodium ions, degradation of cellulose chains is retarded. (2) A considerable amount of conjugated double bonds is formed on degradation of sodium salts of the PS and PO samples. These degradation reactions are in contrast with that of the sodium salt of cellulose phosphate, which degraded to monocarbonyl cellulose.¹⁰ It is inferred that the PS and PO samples would have flame-retardant properties even if ion exchanged with sodium ions.

Flammability

Results of *LOI* values for the four modified fabrics and their sodium salts are shown in Table III. The PS sample as well as the PO sample had flame-retardant properties. The PS sample with a phosphorus content of 4.64 wt-% was self-extinguishing. The efficiency of flame retardancy was lower than that of the PO sample. The PO₂ sample had the greatest efficiency of the four modified fabrics.

TABLE III
LOI Values of Modified Fabrics

Sample	P, %	S, %	LOI, %
PS-1	1.34	1.29	21.8
PS-2	1.58	1.49	21.9
PS-2-Na			21.0
PS-3	4.64	4.17	28.3
PS-3-Na			26.4
PO-1	2.16		23.5
PO-2	2.22		23.7
PO-2-Na			21.3
PO-3	3.69		28.1
PO-3-Na			23.7
P-1	0.72 ₃		20.2
P-3	1.37		20.8
P-4	1.59		21.7
PO ₂ -1	1.10		27.9
PO ₂ -2	5.71		31.6
Control			17.8

When ammonium ions in the PS and po samples were ion exchanged with sodium ions, the flame-retardant properties of the PO sample were impaired, but the decrease for the PS sample was lower. This decrease for the PS sample permits its use as a flame-retardant material. From the results it is concluded that introduction of sulfur atoms into phosphorus esters of cellulose is an effective approach to the prevention of decrease of flame-retardant properties during laundering.

The authors thank Messrs. T. Ohshima and T. Mori, students of Shizuoka University, Japan, for experimental assistance.

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Received February 3, 1977

Revised March 31, 1977