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Phosphorylation of Cellulose with Phosphorous Acid and Thermal Degradation of the Product

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Synopsis

The reaction of cellulose with phosphorous acid in molten urea afforded a white, water-soluble product. The product was a monoester of phosphorous acid, and all the phosphorus residues were in phosphonic form, i.e., cellulose phosphonate. Quantitative addition of acrylonitrile to the P—H bonds in cellulose phosphonate occurred in the presence of sodium ethoxide. By alkali hydrolysis of the adduct, a polyelectrolyte having two different ionization groups, P—OH and COOH, could be prepared. Thermal degradation of three cellulose phosphonates, ammonium cellulose phosphonate (I), ammonium cellulose 2-cyanoethylphosphonate (II), and ammonium cellulose 2-carboxyethylphosphonate (III), was examined. All three samples decomposed at a temperature around 270°C, but their thermal behaviors were different. Replacement of hydrogen in the phosphonic residue by 2-cyanoethyl and 2-carboxyethyl groups retarded dehydration of cellulose. Sample I had a satisfactory flame retardance; samples II and III were not flame resistant. Reduction of flame retardance may be due to the electron-withdrawing effect of the cyano and carboxyl groups.

INTRODUCTION

This paper describes the reaction of cellulose with phosphorous acid and the thermal degradation of the products.

The flame retardance of phosphorus-containing cellulose depends on the structure of the phosphorus compounds,[1] but the most suitable composition has never been elucidated. Extensive investigations on the effect of phosphorus components on flame retardance need to be continued.

Nifantiv[2] and Laszkiewicz[3] have reported that modification of poly(vinyl alcohol) with phosphorous acid gave a phosphonate having reactive P—H bonds. The phosphonate can be added to unsaturated compounds, ketones, etc. If the reaction product of cellulose with phosphorous acid has P—H bonds, the product can be used as the precursor for the preparation of a wide variety of phosphorus-containing cellulose.

EXPERIMENTAL

Reaction of Cellulose with Phosphorous Acid

1. Ground filter paper (80 mesh, Toyo Roshi Ltd., Code No. 2) was used. The cellulose sample was swollen at room temperature in 70% aqueous solu-

tion of zinc chloride for 1 hr and washed with dry ethanol until chloride ion was absent from the filtrate. Urea (43.7 g) was added to a 500-ml, four-necked flask equipped with a nitrogen inlet, a condenser, a thermometer, and a stirrer. The urea was heated to 140°C, flushed with nitrogen, and the swollen cellulose (7 g) and phosphorous acid (36 g) were added portionwise to the molten urea. The reaction was allowed to proceed for an adequate time at 150°C. The reaction mixture was dissolved in 1*N* aqueous sodium hydroxide and precipitated with ethanol. The precipitate was collected by centrifugation. This process was repeated three times. The modified cellulose was dried over phosphorus pentoxide under reduced pressure.

2. A bleached and mercerized cotton broadcloth (120 g/m^2) was used. Twenty fabric samples (12 × 20 cm) were added to a solution of urea (120 g) in dimethylformamide (1.5 liter) contained in a 3-liter, four-necked flask equipped with a nitrogen inlet, a thermometer, a condenser, and a stirrer. The solution was heated to 130°C, and phosphorous acid (80 g) was added. The reaction was allowed to proceed for an adequate time at 150°C. The fabrics were washed with water until phosphorous acid was absent from the filtrate and dried under reduced pressure.

Reaction of Phosphorylated Cellulose with Acrylonitrile

1. A dry sample (1.26 g) of phosphorylated cellulose (16.2$_4$ wt-% phosphorus) was added to a solution of sodium ethoxide (0.02 g) in dry ethanol (30 ml) contained in a 100-ml, four-necked flask equipped with a nitrogen inlet, a thermometer, a condenser, a dropping funnel, and a magnetic stirrer. Freshly distilled acrylonitrile (0.86 g) was added dropwise to the ethanol solution, and the reaction was allowed to proceed for 1 hr at room temperature under nitrogen atmosphere. The product was filtrated, washed with dry ethanol, and dried over phosphorus pentoxide under reduced pressure.

2. In a similar way, 20 phosphorylated fabric samples were allowed to react with acrylonitrile (62 ml) in the presence of sodium ethoxide (0.92 g) dissolved in 1.5 liter ethanol. The reaction was allowed to proceed for 2 hr at room temperature.

Infrared Spectrum

The infrared spectra of products were examined as KBr discs using a Nihon-Bunko Spectrophotometer IRA-1.

pH Titration Curve

A pH titration curve was obtained using a Metron Herisan Potentiograph E336A. A sample was dissolved in water and ion exchanged with Amberlite IR-120B ion exchange resin. The solution was titrated with carbonate-free potassium hydroxide under nitrogen atmosphere.

Thermogravimetry

Samples (50 mg) were placed in the quartz pans provided with a Shinku-Riko thermogravimetric analyzer. All analyses were carried out under vacuum (10^{-3} mm Hg) at a programmed rate of 4.0°C/min.

Flammability Test

The oxygen index method (ASTM D2863-70) was used to compare the flammability of modified fabrics.

RESULTS AND DISCUSSION

Reaction of Cellulose with Phosphorous Acid

Laszkiewicz[3] has reported that the reaction of poly(vinyl alcohol) with phosphorous acid in benzene afforded a mixture of mono- and diester; most of the acid residues were in the phosphonic form.

The reaction of cellulose with phosphorous acid at 150°C for 2 hr afforded a white, water-soluble product (4 g, 16.2_4 wt-% phosphorus). The typical infrared spectrum of the product is shown in Figure 1. Strong absorptions at 2370, 1210, and 970 cm^{-1} were observed. These bands were attributed to P—H, P=O, and P—O—C groups, respectively.[4,5] The pH titration curve (Fig. 2) shows that the product is characteristic of monobasic acid. The ratio of free hydroxyl groups to phosphorus element in the product was determined to be 0.93_3 from the results of pH titration and phosphorus analysis. An additional experiment was used for the identification of the product: the phosphorylated cellulose was treated with acrylonitrile in the presence of sodium ethoxide.[6] The infrared spectrum of the treated sample is shown in Figure 1. The strong absorption band attributed to P—H bonds disappeared; a new absorption appeared at 2290 cm^{-1} (C≡N). The amount of nitrile groups in the product was 13.4 wt-%. This value is comparable to the

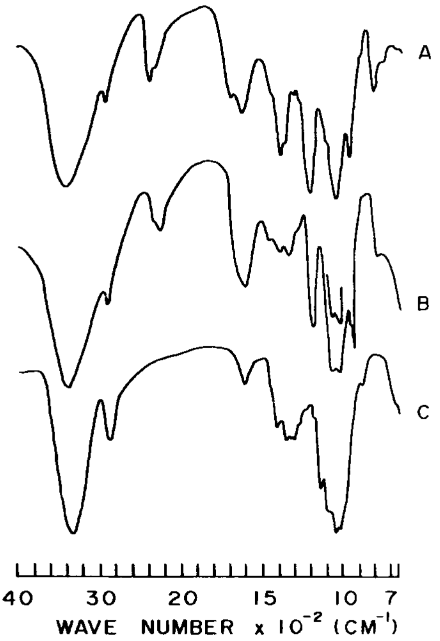

Fig. 1. Infrared spectra of modified cellulose: (A) treated with phosphorous acid; (B) treated with acrylonitrile; (C) cellulose.

TABLE I
Reaction of Cellulose with Phosphorous Acid and Phosphoric Acid

Reaction time, hr	Reaction temperature, °C	Degree of esterification	
		Phosphorous acid	Phosphoric acid
0.5	150	0.59_5	0.11_9
1.0	150	0.97_9	0.18_0
2.0	150	1.5_5	0.23_0
4.0	150	1.7_9	0.30_1
8.0	150	2.0_5	0.33_2

calculated value on the basis that all phosphorus residues are in phosphonic form and that quantitative addition of acrylonitrile to P—H bonds is accomplished.

These results substantiate that the product of cellulose with phosphorous acid is a monoester and all the phosphorus residues are in the phosphonic form. An explanation for yielding the only monoester on the reaction of cellulose with phosphorous acid cannot be offered at the present time. It has been reported that the reaction of cellulose with phosphoric acid in a molten urea medium afforded only a monoester,[7] so urea may be playing a role in the formation monoester.

Table I compares the reactivities of phosphorous acid and phosphoric acid. The relative reactivity of phosphorous acid with cellulose was higher than that of phosphoric acid. Phosphorous acid favors the preparation of phosphorus-containing cellulose. Furthermore, the P—H bonds in cellulose phosphonate are as reactive as in simple analogs, e.g., the quantitative addition which acrylonitrile undergoes. By alkali hydrolysis of the adduct of acrylonitrile, a polyelectrolyte having two different ionization groups, P—OH and COOH, could be prepared. Figure 2 shows the pH titration curve of a dibasic product obtained by alkali hydrolysis of the adduct.

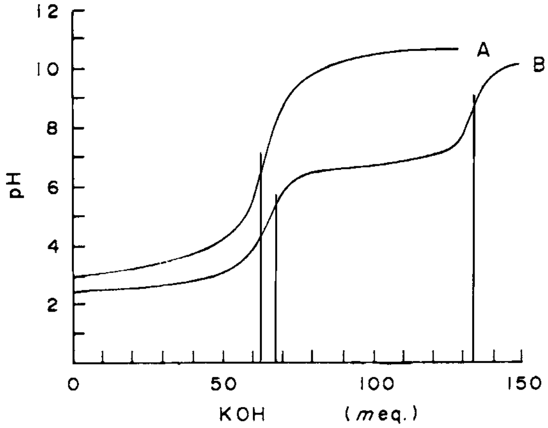

Fig. 2. pH Titration curves of modified cellulose: (A) treated with phosphorous acid; (B) alkali-hydrolyzed.

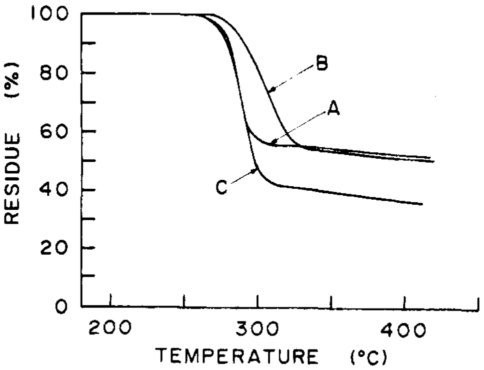

Fig. 3. TG curves of cellulose phosphonates: (A) ammonium cellulose phosphonate (3.54 wt-% phosphorus); (B) ammonium cellulose 2-cyanoethylphosphonate (3.54 wt-%); (C) ammonium cellulose 2-carboxyethylphosphonate (3.54 wt-%).

Thermal Degradation of Cellulose Phosphonates

Typical TG curves of three cellulose phosphonates, ammonium cellulose phosphonate (I), ammonium cellulose 2-cyanoethylphosphonate (II), and ammonium cellulose 2-carboxyethylphosphonate (III), are shown in Figure 3. All three samples decomposed at temperature around 270°C, but their thermal behaviors were different. For sample I, a rapid weight loss occurred and a large amount of residue was yielded. The rate of weight loss of sample II

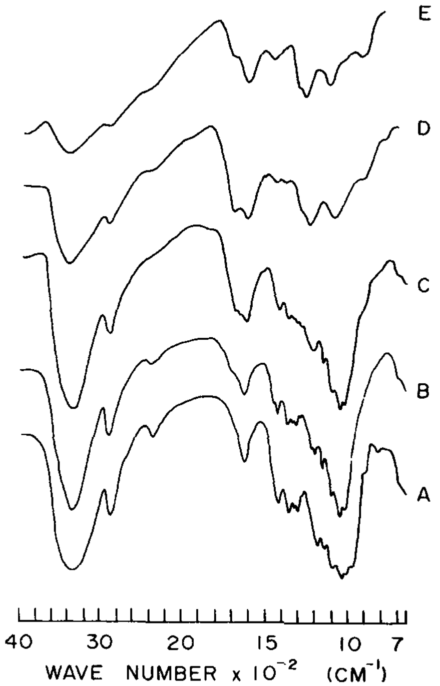

Fig. 4. Infrared spectra of ammonium cellulose phosphonate (3.54 wt-% phosphorus): (A) original; (B) degraded at 250°C; (C) degraded at 270°C; (D) degraded at 290°C; (E) degraded at 400°C.

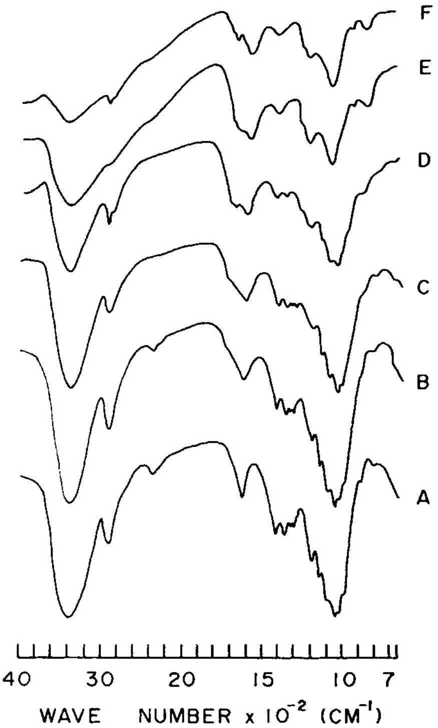

Fig. 5. Infrared spectra of ammonium cellulose 2-cyanoethylphosphonate (3.54 wt-%): (A) original; (B) degraded at 290°C; (C) degraded at 310°C; (D) degraded at 330°C; (E) degraded at 350°C; (F) degraded at 400°C.

was slow; a large amount of residue was yielded. Sample III gave a high rate of weight loss and left little residue.

The changes in infrared spectra of the three samples on heating are shown in Figures 4, 5, and 6, respectively. From Figure 4, the changes in the infrared spectrum of sample I were as follows: at a temperature of 250°C, where an initial weight loss was detected, the P—H bonds at 2370 cm^{-1} became weak in absorbance, and a shoulder at 1250 cm^{-1} (P=O) appeared. The absorption at 2370 cm^{-1} disappeared at 270°C; the absorption at 1630 cm^{-1} (C=C) appeared. The absorption at 1630 cm^{-1} shifted to 1600 cm^{-1} (conjugated double bond) at 290°C; each band due to cellulose disappeared. The intense absorptions at 1250 and near 1000 cm^{-1} (conjugated double bond) remained. Further changes in the infrared spectrum could not be observed on heating at temperatures above 290°C. These changes were similar to those reported previously for cellulose phosphates.[8]

It is assumed that sample I on heating yields predominately polyene structure in cellulose chains. As shown in Figure 5, the thermal degradation of sample II was different from that of sample I. No significant change in the infrared spectrum could be detected even when weight loss occurred to the extent of 30%. Significant changes appeared at 330°C, where the final decomposition was in progress. The spectrum of its residue was similar to that of sample I degraded at 290°C. There were the intense absorptions due to conjugated double bonds.

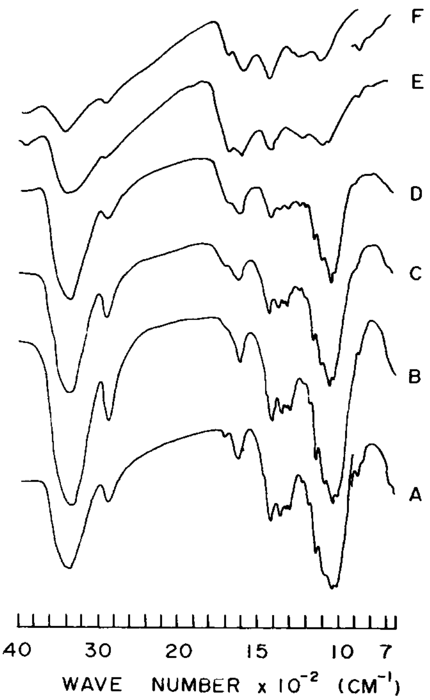

Fig. 6. Infrared spectra of ammonium cellulose 2-carboxyethylphosphonate (3.54 wt-%): (A) original; (B) degraded at 270°C; (C) degraded at 290°C; (D) degraded at 310°C; (E) degraded at 330°C; (F) degraded at 400°C.

For sample III, a weight loss of more than 50% occurred before significant changes in the infrared spectrum were observed. It has been reported that the introduction of phosphoryl groups into cellulose accelerates dehydration and leads to a large amount of residue containing conjugated double bonds.[8] The above results confirm that the transformation of hydrogen to 2-cyanoethyl and 2-carboxyethyl groups retards dehydration.

Flammability

Results of the oxygen index value for the three modified fabrics are listed in Table II. Sample I had satisfactory flame retardance; samples II and III

TABLE II
Oxygen Index Value for Cellulose Phosphonates

Sample	P, %	Oxygen index, %
I	0.162	18.9
	1.04	22.4
	3.54	29.2
II	0.162	18.9
	1.04	24.1
	3.54	24.6
III	0.162	18.0
	1.04	19.7
	3.54	20.2
Control		17.8

failed to be flame retardant. Since cellulose alkylphosphonates, such as cellulose methylphosphonate[9] and cellulose ethylphosphonate,[10] were known to have effective flame retardance, it is assumed that the presence of cyano and carboxyl groups inhibits the flame retardant properties.

Tesoro and co-workers[11] have reported a synergistic effect between phosphorus and nitrogen for flame retardance. Systems including nitrogen compounds, such as amides, melamines, and amines, were suitable. While Barker and co-workers[12] have reported on the synergistic effect of nitrogen-containing phosphonates, the introduction of cyano groups in phosphonates was unfavorable. The mode of their synergistic action is unknown.

Finally, the inhibition of cyano and carboxyl groups in flame retardance is considered. It has been reported that the formation of polyene structure in cellulose chains depresses flammable, volatile products and leads to flame retardance. The infrared spectra of the three modified celluloses show that the presence of cyano and carboxyl groups retards the formation of polyene structure in cellulose chains. This retardation may be due to the electron-withdrawing effect of cyano and carboxyl groups since the polyene structure is formed by *cis*-β-elimination of phosphorus ester groups.[9]

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