

Reactions of Some Phosphorus Compounds with Cellulose Dissolved in Aqueous Alkaline Solution

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ABSTRACT: Dissolution of cellulose in aqueous hydroxide offers a procedure for regeneration of cotton or wood celluloses. The aqueous NaOH system for dissolving cellulose seems to have considerable potential for fiber production and also as a medium for preparing cellulose derivatives. Reactions with phosphoric and phosphorous acids, phenyl- and phenoxy phosphonic dichlorides, and an amido phosphite oligomer on aqueous dissolved cellulose are described. The resulting products are characterized by analyt-

ical and spectral methods (infrared and X-ray diffraction) to determine phosphorus and nitrogen content, substitution degree, and polymerization degree. Particular attention was given to the effects produced by chemical modification on the crystalline pattern of microcrystalline cellulose. Some remarks are also made about the thermooxidative behavior of phosphorylated cellulose. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 327–333, 2003

INTRODUCTION

Chemical modification of cellulose materials continues to provide new derivatives with specific end uses. The discovery of novel solvent and solution complexes for cellulose created opportunities for more diverse synthesis pathways and derivative types. Although functionalization opportunities with cellulose are limited to hydroxyl groups, some differences do exist between the reactivity of primary and secondary OH groups, which depend on the solvent employed. Four solvent systems are known as supporting chemical modification reactions¹; they are, dissolution with nonderivatizing solvents, dissolution with partial functionalization with reactive solvents, dissolution by derivatization with introduction of solubilizing substituents that protect the OH groups during subsequent reaction, and dissolution by chemical modification with substituents that provide access to subsequent substitution reactions.

The first class includes a variety of nonaqueous solvents or solvent complexes with single or multiple components [i.e., single solvent: *N*-alkylpyridinium halogenide or oxide of tertiary amine; nonaqueous solvents complexes: dimethyl sulfoxide (DMSO)–methylamine, DMAc–LiCl, SO₃–triethylamine]. A few solvent systems, which realize a complete disruption of the hydrogen bonds, belong to the second class [i.e., formic acid trifluoroacetic acid, *N,N*-dimethylform-

amide (DMF)–N₂O₄, paraformaldehyde–DMSO, trimethylchlorosilane–DMF, and urea in melt]. Cellulose dissolution represents an acceptable method for cellulose regeneration, but the use of these solvent systems for chemical modification is limited.

Recently, Yamashiki et al.² and Kamide et al.³ proposed an aqueous solvent system for dissolving steam-exploded chemical wood pulp, yet complete dissolution of all kinds of celluloses was not attained. Isogai and Atalla⁴ proposed another method to dissolve cellulose in aqueous NaOH, by freezing the cellulose suspension at –20°C. We used this technique to prepare cellulose derivatives with phosphorus compounds. The reaction parameters were established, and all products were characterized by analytical and spectral methods. Some data about the thermal stability of these products were also discussed.

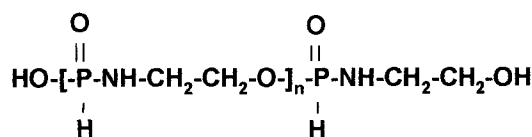
EXPERIMENTAL

Materials

Avicel 101 (AVI; microcrystalline cellulose for tabletting application) was obtained from Trademark FMC Corporation. Phosphoric acid (85% solution in water) and phosphorus acid (99%) were obtained from Aldrich. Sodium hydroxide (>98%), as in pellets, was obtained from Fluka-Chemie G (CH-9470 Buchs).

Phenylphosphonic dichloride [C₆H₅P(O)Cl₂] and phenyloxyphosphonic dichloride [C₆H₅OP(O)Cl₂] were synthesized according to published methods^{5,6} and purified by distillation under reduced pressure: [C₆H₅P(O)Cl₂]: bp, 137–138°C at 15 mmHg; *d* = 1.197; MW = 194.9; ¹H-NMR: H₁, H₅ 7.97–8.07 ppm; H₂, H₄

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Structure 1

Elementary analyses

P%		N%		C%		H%	
Theoretical	Experim.	Theoretical	Experim.	Theoretical	Experim.	Theoretical	Experim.
27.58	27.97	12.06	11.57	20.68	19.96	6.03	6.86

7.63–7.74 ppm; $[\text{C}_6\text{H}_5\text{PO}(\text{O})\text{Cl}_2]$: bp, 241–243°C; $d = 1.41$; MW = 210.9; $^1\text{H-NMR}$: H_1 , H_5 7.16–7.32 ppm; H_2 , H_4 7.21–7.27 ppm.

Poly(amido ethyl)phosphite (PAEF) was synthesized according to the literature method (see Structure 1).⁷ PAEF melts at 60–80°C, decomposes in air up to 280°C, and is soluble in water, ethyl alcohol, and a water/ethyl alcohol/acetone mixture. Infrared spectra absorption bands indicate a $\text{P}=\text{O}$ group at 1250–1300 cm^{-1} , a $\text{P}-\text{O}-\text{CH}_2$ group at 1030–1050 cm^{-1} , and an $\text{NH}-\text{P}(\text{O})$ group at 789–1040 and 645–875 cm^{-1} .

ANAL. Calcd for PAEF: C, 20.68%; H, 6.03%; N, 12.06%; P, 27.58%. Found: C, 19.96%; H, 6.86%; N, 11.57%; P, 27.97%.

Methods

The phosphorus content was determined by the molybdenum-blue method. The degree of transformation was calculated with Scondac's equation,⁸ and the substitution degree (DS) was determined according to Rozmarin's equation.⁹ The degree of polymerization (DP) was determined in Cuen solution.¹⁰

Infrared spectra were recorded on a Unicam SP 100 spectrophotometer with KBr pellets. The H bond energy¹¹ and relative values of optic density (RVOD)¹² were calculated from the infrared spectra asymmetry indexes.¹³ X-ray diffraction (XRD) patterns of both cellulose and modified celluloses were collected on a Dron-2 apparatus equipped with a Co anticathode, using $\text{CoK}\alpha_1$ radiation at $\lambda = 1.78892 \text{ \AA}$. The crystallinity indices were calculated from the XRD patterns.¹⁴ The D-spacing of lattice planes was calculated with Bragg's equation ($\Lambda = 2d \sin \theta$).

Dissolution of microcrystalline cellulose in aqueous NaOH

Two grams of AVI were suspended in 54 mL of water. Then, 5 g of NaOH in pellet form were added, and the mixture was shaken at room temperature to dissolve the NaOH. The suspension, containing 8.5% cellulose

in NaOH solution, was shaken again on glass until the temperature of the mixture became 2–3°C. Then the suspension was cooled at –20°C for 24 h. Next, 41 mL of water was added to the resultant frozen mass, and the mixture was gently shaken at room temperature. (In this procedure, if gel-like material appears after 2 days, 2 g of NaOH should be added and the freezing step should be repeated.) The resultant solution contains 2% cellulose in 7% aqueous NaOH. A fraction of the dissolved cellulose sample was poured into aqueous acetic acid, and the regenerated cellulose was isolated by filtration, washing with water and acetone, and drying under vacuum conditions. The DP for AVI (DP^{AVI}) is 130, and that for regenerated AVI after dissolution in aqueous NaOH was 100.

Reaction of aqueous cellulose solutions with phosphorus compounds

Reaction with phosphoric acid (R_1)

A solution of 1 g of AVI in aqueous NaOH solution was treated at room temperature with 4.5 mL of 85% H_3PO_4 in 31 mL of water. The gel-like material that formed was stirred for 0.5 h at room temperature. An aliquot (1/3 by weight) was separated and precipitated in 200 mL of methyl alcohol. The remaining gel-like material was heated at 100°C with stirring for 60 min and precipitated in methyl alcohol. The solid material was suspended in fresh water for 24 h and then dried on P_2O_5 under vacuum.

The resultant products are white powders that are insoluble in water, aqueous NaOH conc. solution, acetone, and DMF. The phosphorylated product at room temperature (R_1^{rt}) had a yield of 94.4%, DS = 0.56, and P% = 8.42. At 100°C (R_1^{100}), the phosphorylated product had a yield of 75%, DS = 1.19, and P% = 14.39. The IR spectra for this product showed absorption bands at 1000–1400 cm^{-1} for $\text{P}-\text{OH}$, 520–600 cm^{-1} for $\text{P}(\text{O})\text{H}$, 3460 cm^{-1} for OH, 2940 cm^{-1} for CH, CH_2 , 1650 cm^{-1} for H–OH in water, 1430 cm^{-1} for CH, CH_2 , 1075 for C–OH, and 905–910 cm^{-1} for the pyranose ring.

TABLE I
Experimental Conditions and Analytical Characterisation of Treated Cellulose

Parameter	AVI	AVI ^R	R _I ^{RT}	R _I ¹⁰⁰	R _{II} ^{RT}	R _{II} ¹⁰⁰	R _{III}	R _{IV}	R _V
Temp (°C)	—	-18	25	100	25	100	100	100	100
Time (min)	—	24	30	60	30	60	60	60	60
Mole reagent added/ 0.006 mole AVI	—	0.075 NaOH	0.33 H ₃ PO ₄	0.33 H ₃ PO ₄	0.5 H ₃ PO ₃	0.5	0.043	0.07	0.06
DP	130	100	—	120	—	112	96	94	108
P%	0	—	8.42	14.39	7.94	10.65	8.76	0.78	0.23
DS [9]	0	0	0.56	1.21	0.49	0.72	0.65	0.04	0.01
Transf. degree (%) [8]	—	—	—	Negative value	—	95.06	59.93	3.89	1.21
Crystallinity index (%)	82	79	0	0	0	0	0	88	79

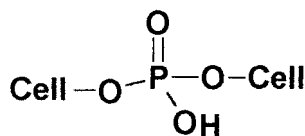
Reaction with phosphorous acid (R_{II})

A solution of 1 g of AVI in aqueous NaOH solution was treated at room temperature with 4 g of H₃PO₃ dissolved in 19 mL of water. The gel-like material that formed was stirred for 0.5 h at room temperature. An aliquot (42% by weight) was separated and precipitated in 200 mL of methyl alcohol. The remaining gel-like material was diluted with 20 mL of water and heated at 100°C with stirring for 60 min and then precipitated in methyl alcohol. The fibrous material was suspended in water for 24 h and then dried on P₂O₅ under vacuum.

The resultant products are white powders that are insoluble in water, aqueous NaOH conc. solution, acetone, and DMF. The phosphonous product at room temperature (R_{II}^{RT}) had a yield of 78.75%, DS = 0.49, and P% = 7.94. At 100°C (R_{II}¹⁰⁰), the phosphonous product had a yield of 92%, DS = 0.72, and P% = 10.79. The IR spectra for this product showed absorption bands at 2320 cm⁻¹ for P—H, 1250 cm⁻¹ for P=O, 1000–1060 cm⁻¹ for P—O—Alkyl, 3460 cm⁻¹ for OH, 2940 cm⁻¹ for CH, CH₂, 1650 cm⁻¹ for H—OH in water, 1430 cm⁻¹ for CH, CH₂, 1075 for C—OH, and 905–910 cm⁻¹ for the pyranose ring.

Reaction with an amido ethyl phosphite oligomer (R_{III})

A solution of 1 g of AVI in aqueous NaOH solution was treated, with stirring at room temperature, with 10 g of PAEF dissolved in 10 mL of water. A moderate exothermic reaction took place. The viscous solution was stirred for 60 min at 100°C. After cooling, the viscous material was precipitated twice in methyl alcohol, redissolved in water, and precipitated in ethyl



Structure 2

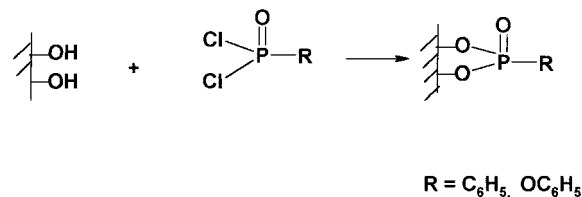
alcohol. The product (R_{III}) had a yield of 75%, DS = 0.65, and P% = 8.76. The IR spectra for this product showed absorption bands at 2350 cm⁻¹ for P—H, 1250 cm⁻¹ for P=O, 1000–1060 cm⁻¹ for P—O—Alkyl, 715–750 cm⁻¹ for P—NH; 3460 cm⁻¹ for OH, 2940 cm⁻¹ for CH, CH₂, 1650 cm⁻¹ for H—OH in water, 1430 cm⁻¹ for CH, CH₂, 1075 for C—OH, and 905–910 cm⁻¹ for the pyranose ring.

Reactions with aryl phosphonic dichloride (R_{IV} and R_V)

In a solution containing 2% AVI in 7% aqueous NaOH solution, 16 mL of pyridine and 21 mL of aryl phosphonic dichloride were added with stirring. The reaction was exothermic. The mixture was heated under reflux for 60 min. After cooling, the pyridine hydrochloride was filtered out, and the solution was dialyzed in water to remove any trace of unreacted reagents or Py · HCl. The solution was concentrated under reduced pressure, and the phenoxyphosphonic dichloride-treated cellulose product was precipitated in acetone and dried under vacuum in a yield of 65%. The R_{IV} product had a DS = 0.042, and P% = 0.78. The R_V product had a DS = 0.012, and P% = 0.23. The IR spectra for this product showed absorption bands at 1370 cm⁻¹ for P=O, 1040–1190 cm⁻¹ for P(O)aryl, 3460 cm⁻¹ for OH, 2940 cm⁻¹ for CH, CH₂, 1650 cm⁻¹ for H—OH in water, 1430 cm⁻¹ for CH, CH₂, 1075 for C—OH, and 905–910 cm⁻¹ for the pyranose ring.

RESULTS AND DISCUSSION

The data concerning the experimental conditions and analytical characterization of frozen cellulose and cel-



Scheme 1 Formation of cyclic diesters.

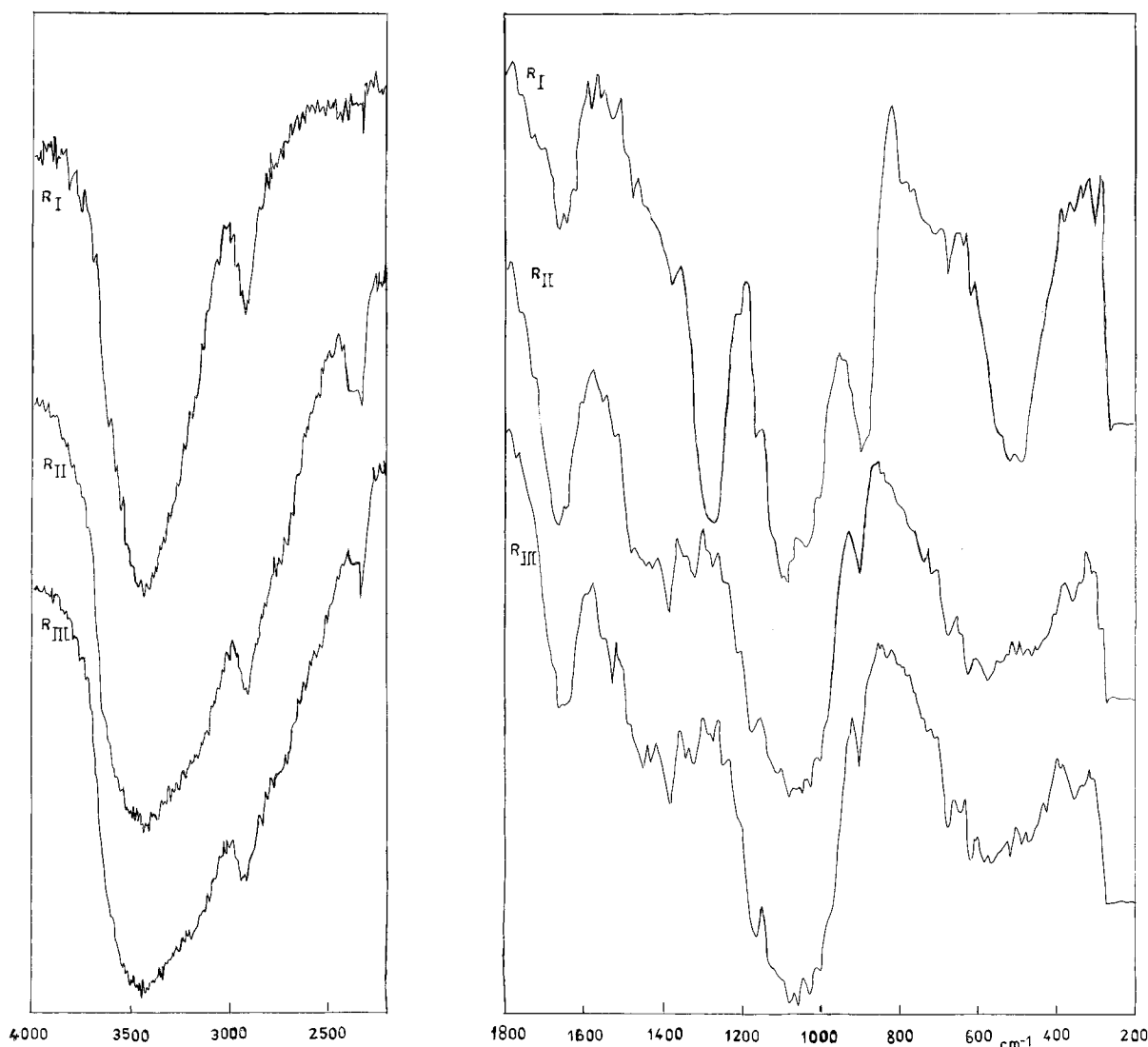


Figure 1 Infrared spectra for cellulose treated with H_3PO_4 (R^I), H_3PO_3 (R^{II}), and poly(amido ethyl)phosphite (R^{III}).

lulose that was chemically modified with phosphorus compounds are shown in Table I. Detailed studies on derivatization of cellulose with phosphorus-containing compounds, especially work concerning syntheses and reaction mechanisms, seem to be lacking. Phosphorylation of cellulose with phosphoric or phosphorous acid in the presence of urea,¹⁵ at temperatures in the range 140–150°C, leads to products with DS values

in the range 0.5–0.9. Reid and Mazzeno¹⁶ suppose that mainly a phosphorylation of primary hydroxyl groups takes place. Taking into account the insolubility of phosphorylated products in water and in organic solvents, we suppose that such products are crosslinked as a result of the interaction between the OH groups from different chains and phosphoric acid. For a DS value of <0.5 , the phosphorylated product could have

TABLE II
RVOD, Asymmetry Index, and H-Bond Energies Calculated from IR Data

Parameter	Absorption Band (cm^{-1})	Group	AVI	AVI ^R	R_I^{100}	R_{II}^{100}	R_{III}	R_{IV}	R_V
RVOD	3395–3460	OH	2.32	2.3	3.62	1.91	1.81	—	—
	1650	C=O	0.52	0.94	0.44	0.77	0.66	—	—
	1050	C–OH	2.87	2.37	4.46	2.49	2.34	—	—
	900	Pyranose ring	0.45	0.46	2.48	0.42	0.46	—	—
Asym. Index			1.09	0.81	0.66	0.67	0.47	0.53	0.61
E_H (Kcal)			0.44	0.43	0.36	0.40	0.32	0.316	0.325

the structure shown in Structure 2 or one P(O)OH group per two anhydroglucose units belonging to different macromolecular chains. For a higher DS value, we suppose that a second hydroxyl group is substituted, so two P(O)OH groups are linked per two anhydroglucose units.

When phosphorylation reagents are H_3PO_4 , H_3PO_3 , or PAEF, the reactions take place in the crystalline zone. All products are amorphous materials. When phosphonic acid dichlorides are used as reagents, cyclic diesters may be formed (see Scheme 1). The cyclic structures are probably responsible for the modified atomic structure illustrated by the XRD pattern.

The IR spectra of the products that resulted from the reaction of frozen cellulose with aromatic phosphoric dichloride are difficult to interpret because of the low transformation degree and overlapping of the absorption bands. Despite this difficulty, some differences between the IR spectra of both unmodified and modified materials may be observed. A sharp peak is observed at 1350 cm^{-1} that can be attributed to the P=O absorption. The absorption bands for P—O—Ar appear at 1191 and $860\text{--}990\text{ cm}^{-1}$. On the other hand, the IR spectra of the products that resulted from the reaction of cellulose with phosphoric and phosphorous acids were highly modified (Fig.1). Characteristic absorptions for P(O)OH groups at 550 cm^{-1} and for P—H groups at 2350 cm^{-1} were noticed. The latter vibration is also observed for cellulose treated with poly(amido ethyl)phosphate. This last spectrum also presents a characteristic absorption band for the P—NH group at $715\text{--}750\text{ cm}^{-1}$ and for the P—Alkyl group at 1380 cm^{-1} .

Some interesting remarks may be made by comparing the RVOD values, asymmetry indexes, and H-bond energies (Table II). The relative values for O—H vibration increase after treatment with phosphorous compounds, especially in the case of phosphoric acid. Also, the relative values for C—OH vibration at 1050 cm^{-1} are higher for all phosphorous derivatives. This result is due to the superposition of the vibrations of P=O, P—OAlk, and P—OAr on the C—OH vibration. The characteristic vibration for the pyranose ring is high, and an increase in the amorphous structure is evident. The high value of the C=O vibration for compounds that resulted from treatments of cellulose with phosphoric acid, phosphorous acid, or PAEF may indicate a slight oxidizing action of such reagents.

Modifications of the atomic structure of cellulose that was treated with phosphorous compounds and respectively frozen at -20°C are compared with the initial microcrystalline structure of cellulose in Figure 2. Microcrystalline cellulose displays a classic diffraction pattern, with a diffraction maximum (002) occurring with the highest intensity at a $2\theta = 25.6^\circ$ angle. The diffraction maximum (020) is very poorly represented on the diffractogram. The second diffraction

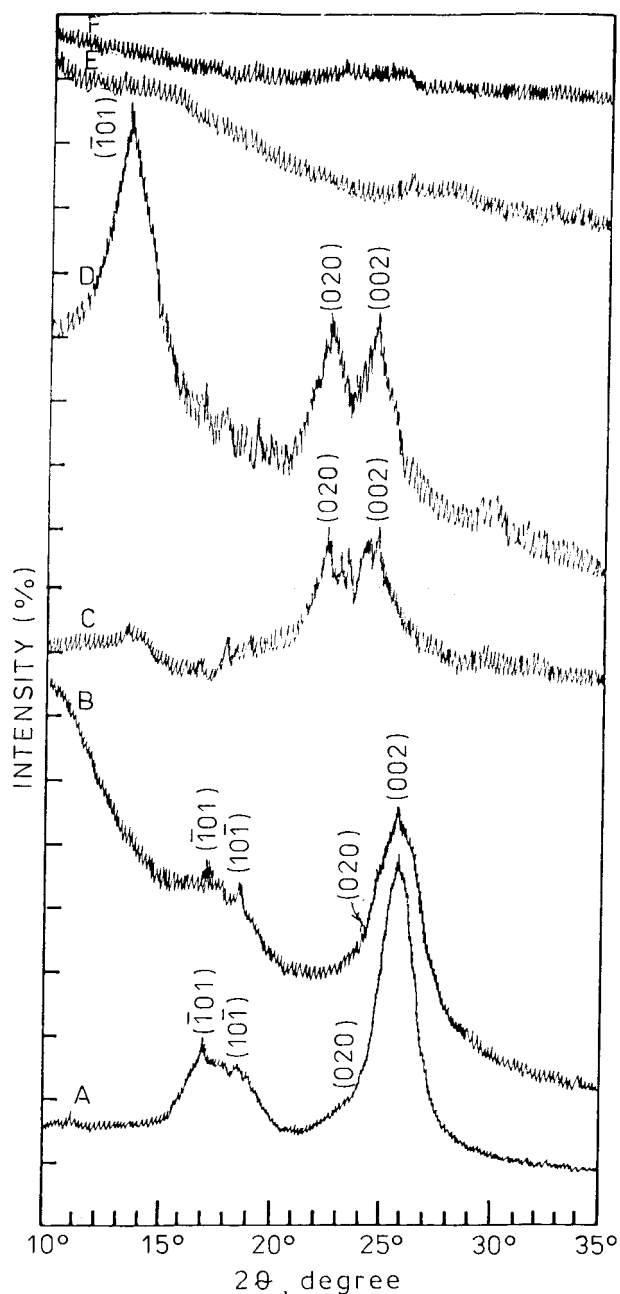


Figure 2 The modification of the atomic structure of cellulose treated with phosphorus compounds and frozen at -20°C in aqueous NaOH compared with the starting microcrystalline cellulose: (A) starting cellulose; (B) cellulose regenerated from frozen solution; (C) cellulose treated with phenyl phosphonic dichloride; (D) cellulose treated with phenoxy phosphonic dichloride; (E) cellulose treated with poly(amido ethyl)phosphite; (F) cellulose treated with H_3PO_3 .

maximum, appearing at $2\theta = 16.46^\circ$, corresponds to the lattice planes family $(\bar{1}01)$. Another diffraction maximum appears nearby at $2\theta = 17^\circ$, which corresponds to the lattice plane family (101). The results of diffraction analysis on the initial microcrystalline cellulose are shown in Table III.

TABLE III
XRD Analysis of Initial Microcrystalline Cellulose

Peak	2θ	d_{hkl} (Å)	hkl	Intensity (%)
1	16.46	6.24	$\bar{1}01$	28
2	17.00	6.05	$10\bar{1}$	27
3	23.30	4.42	020	22
4	25.60	4.03	002	59

The diffraction pattern of regenerated cellulose after freezing presents the following special features:

- The first diffraction maximum(002) remains unaffected.
- Some modifications appear at ($\bar{1}01$) and ($10\bar{1}$). These peaks appear at the same angles of 2θ as in the case of initial cellulose, but are poorly represented.

Treatment of cellulose with phenyl phosphonic dichloride modified the entire atomic structure as follows:

- The diffraction maximum (020) is strongly marked and has an intensity equal to that of the diffraction maximum (002)
- The main diffraction maximum (002) is substituted with the doublet (020) and (002)
- The diffraction maxima are moved to angles lower than $2\theta = 25^\circ$
- The diffraction maximum (002) now appears at an $2\theta = 24.5^\circ$. Diffraction maxima (020) are also shifted to the left at $2\theta = 22^\circ$. Shifting towards the left of these two peaks of treated cellulose exceeds a 2θ value of 1° .
- The entire atomic structure of treated cellulose is dominated by two lattice planes, which is in contrast with the initial cellulose, whose structure is dominated by a single lattice plane (002)

Cellulose treated with phenoxy phosphonic dichloride is similar to that of the preceding sample, with the following differences:

- A new and very strong diffraction maximum appears at $2\theta = 13^\circ$, corresponding to the lattice plane (101) and dominating the entire structure; it corresponds to a d -spacing of $d_{101} = 7.90$ Å.
- An important growth of d -spacing can be observed; that is, from 6 Å (for initial cellulose) to 7.90 Å (for the treated cellulose).
- The doublet (020)(002), with two distinct peaks, is very well represented on the diffraction pattern.
- The diffraction maxima (020) and (002) are shifted towards the left; that is, to lower degrees than in the initial cellulose positions.

TABLE IV
XRD Analysis of Treated Cellulose with Phenoxy Phosphonic Dichloride

Peak	2θ	d_{hkl} (Å)	hkl	Intensity (%)
1	13.00	7.90	$\bar{1}01$	95
2	22.25	4.63	020	64
3	24.42	4.23	002	63

The results for the diffraction analysis for phenoxy phosphonic dichloride-treated cellulose are shown in Table IV. The crystallinity index of microcrystalline cellulose is compared with those of thermally and chemically treated celluloses in Table V. The diffraction pattern of celluloses treated with H_3PO_4 or H_3PO_3 acids, as well as with poly(amide ethyl)phosphite are typical for amorphous materials.

It is known that the thermooxidative behavior of cellulose is a complex process because it is carried out by depolymerization and oxidation reactions leading to some gaseous products, a solid residue with coal-like aspects, and a levoglucosan-containing tar that gives flammable gases after decomposition. The first step of pyrolysis for untreated cellulose involves the cleavage of glycosidic linkages, especially in the less ordered regions. The second step of the degradation involves the production of levoglucosan in the areas of high packing density. The initial stages of pyrolysis showed a low production of levoglucosan and a large amount of volatile materials. Later, the yield of levoglucosan increased and remained constant. The fragmentation of levoglucosan that followed is a free-radical mechanism that produces gases, aldehydes, ketones, and unsaturated products.

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for both microcrystalline and chemically modified celluloses can be used to evaluate the thermooxidative destruction steps and the kinetic parameters using the method of Coats and Redfern.¹⁷

The values of activation energy, weight losses, and reaction orders for the main steps of the thermooxidative destruction of cellulose are compared with those for cellulose treated with some phosphorus com-

TABLE V
Crystallinity Index of Initial Cellulose and of Thermally or Chemically Modified Celluloses

Sample number	Sample	Crystallinity index (%)
1	Cellulose	82
2	Thermally treated (frozen) cellulose	79
3	Cellulose treated with phenyl phosphonic dichloride	79
4	Cellulose treated with phenoxy phosphonic dichloride	88

TABLE VI
Thermooxidative Behavior of Initial and Chemically Treated Celluloses

Sample*	Step I					Step II					Residue at 500° C (%)	Step III				
	T_i	T_m	ΔW (%)	E_A (kJ/mol)	n	T_i	T_m	ΔW (%)	E_A (kJ/mol)	n		T_i	T_m	ΔW (%)	E_A (kJ/mol)	n
AVI	37	74	4.5	59.24	1.4	220	320	75	135.34	1.4	8	419	498	16.5	134.3	1
R ^I	23	82	14	58.8	1.7	130	192	30.25	42.95	1.4	58	—	—	—	—	—
R ^{II}	—	—	—	—	—	80	200	25.5	41.89	1.4	62	—	—	—	—	—
R ^{III}	49	150	14.5	34.77	1.5	218	270	6	113.65	0.2	68	270	290	14.5	59.78	0
R ^{IV}	—	—	—	—	—	171	208	3.5	93.53	0.1	40	213	262	34	147.2	1.3
R ^V	35	92	9.25	20	1.1	230	310	52	135.9	1.6	29	—	—	—	—	—

pounds in Table VI. Water desorption occurred at 100°C and continued up to 100°C, especially for samples treated with phosphoric or phosphorous acid. Weight losses are higher for these samples and for samples treated with poly(amido ethyl)phosphite. However, a decrease in the activation energies is observed. A connection may be established between the lack of crystallinity of the three treated samples and the cleavage of glycosidic linkages at lower temperature. It seems that in the samples treated with phenyl phosphonic dichloride, in which the phosphorus content is the lowest, depolymerization is minimized and a new ordered structure is formed.

Depolymerization of dehydrated species took place in the 220–400°C range, completing with levoglucosan production. Maximum temperature of decomposition (T_m), weight losses (ΔW), and energy of activation (E_A) values for treated cellulose indicates a decrease of the activation energies and weight losses, along with a significant increase in the decomposition residue. These phenomena are higher for cellulose samples treated with a phosphorus- and nitrogen-containing compounds, which indicates the formation of nonvolatile, cross-linked species containing numerous P—N or P=N bonds.¹⁶

CONCLUSIONS

The possibility of preparing phosphorus-containing celluloses by treatment of microcrystalline cellulose dissolved in aqueous solutions with phosphorus compounds is discussed. Various phosphorus compounds were used; such as, acids, dichlorides, and a phosphorus- and nitrogen-containing polymer. Moderate temperatures and short periods of time were used and some differences were observed in connection with the degree of transformation. Also, the effects produced by the chemical modification on the crystalline

pattern of cellulose are discussed. Treatment with phosphorus acids and phosphorous- and nitrogen-containing polymer gave amorphous materials, and treatment with phosphonic dichloride modified the diffraction pattern of cellulose. The dependence of the thermal behavior of phosphorylated celluloses on the type of phosphorus compound used in the reaction was also investigated.

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