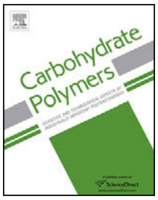
Carbohydrate Polymers 106 (2014) 121–127

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Phosphorylation of Kraft fibers with phosphate esters

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ARTICLE INFO

Article history:
Received 18 November 2013
Received in revised form 13 January 2014
Accepted 21 January 2014
Available online 31 January 2014

Keywords:
Phosphate esters
Kraft fibers
Urea
Phosphorylation
Phosphorus content

ABSTRACT

Phosphate esters, derived from two different long-chain aliphatic alcohols, were used as phosphorylating reagents for Kraft pulp fibers. High phosphorus contents and almost non-degraded fibers were obtained by following this pathway. The phosphorylation efficiency was influenced by the alkyl chain length of PEs since the phosphorus content in modified fibers was higher for the shorter chain reagent. Due to the heterogeneous reaction environment, the amount of grafted phosphorus was found to be almost three times higher at the surface than in the bulk of the fibers. Analyses also indicated that the phosphorus was bonded to fibers as a phosphate-like structure. Furthermore, the situation seemed to be different for the fiber surface where significant amounts of phosphorus were present in more complex structures like pyrophosphate or even oligo-phosphate.

1. Introduction

The chemical modification of cellulose, which is the most abundant natural polymer on earth, was and continues to be of great interest. It is an essential step in order to impart desirable properties which normally do not characterize the original polysaccharide. Phosphorylation is one of these modifications. It is well known that phosphorus-containing cellulose derivatives exhibit specific properties such as: flame retardancy (Blanchard & Graves, 2003; Inagaki, Nakamura, Asai, Katsuura, 1976), soil and dye resistance in fabrics (Blanchard, Bruno, & Graves, 1980), corrosion and scale inhibition (Kowalik et al., 2000), ion exchange capacity for some transition metals and radioactive elements (Suflet, Chitanu, & Popa, 2006), osteogenic activity (Leone et al., 2008), high adsorption of serum proteins (Kim, Jeong, Shin, Oh, Kim, & Rhee, 1998) etc. The grafting reaction of phosphorus compounds to cellulose can be conducted in many ways: with pentavalent (V) or tervalent (III) phosphorus reagents, by direct or indirect bonding of phosphorus functions to cellulose, using cellulose or cellulose derivatives as substrates, with or without catalysts, in heterogeneous or homogeneous reaction environment, etc. (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 2004a; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 2004b; Nifant'ev, 1965). Phosphorus derivatives such as H_3PO_4, P_2O_5, and $POCl_3$ are the most frequently employed phosphorylating agents for pentavalent phosphorus. These reagents, usually leading to anionic cellulose phosphates, show a lower esterification reactivity than the similar derivatives of trivalent phosphorus and cause a higher degradation of the cellulose substrate (Klemm et al., 2004b; Nifant'ev, 1965). This drawback is partially overcome if urea is introduced in the phosphorylation system as a catalyst. The reaction efficiency significantly increases and the polysaccharide chains are less degraded (Nifant'ev, 1965).

In this study, phosphate esters (PEs), derived from two different long-chain aliphatic alcohols, were used as new phosphorylating reagents for chemical pulp fibers obtained by the Kraft process. The main objectives of this work were to (1) evaluate the effectiveness of the procedure and (2) to elucidate the nature of the chemical bonds developed between reagents. The proposed reaction follows a pathway similar to classic cellulose phosphorylation in the presence of molten urea. The net benefit of this new method is to obtain almost non-degraded fibers with high phosphorus contents

2. Experimental

2.1. Reagent preparation

2.1.1. Reactants

The cellulose substrate used in this study was bleached softwood Kraft fibers (KF) provided by Kruger Wayagamack (Trois-Rivières, Canada). All reactants used were reagent grade or better. They were purchased from different suppliers: fatty alcohols, 1-octanol (C8) and 1-octadecanol (C18), and phosphorus pentoxide (Sigma–Aldrich), urea (Alfa Aesar) and hydrochloric acid, methanol and ethanol (Fisher Scientific). Hydrochloric acid and sodium hydroxide standard solutions were purchased from Fluka.

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http://dx.doi.org/10.1016/j.carbpol.2014.01.070

2.1.2. Phosphate esters synthesis (phosphorylating reagents)

Phosphate esters were synthesized from the reaction of phosphorous pentoxide (P_2O_5) and two long-chain aliphatic alcohols: 1-octanol or 1-octadecanol (Tsuyutani, Shibata, Aizawa, Sakata, & Morishita, 2004). The molar ratio of the three reactants (fatty alcohol, P_2O_5 and H_2O) was set to 2:1:1 to ensure high yield and good selectivity. The reaction medium was heated at 60–80 °C for several hours until solid residues of P_2O_5 in the reaction system were at a minimum. The purification process of the obtained products was described previously (Belosinschi, Chabot, & Brouillette, 2012). It consisted of three successive water/solvent extractions. Purified PEs were found to be composed predominately of the mono-alkyl structure (~100% for C18 and 90% for C8) as determined by acid–base titration.

2.1.3. Phosphorylation of Kraft fibers

Phosphorylation of KF with phosphoric acid and PEs was conducted in molten urea with the method described by Inagaki et al. for phosphorylating cellulose with phosphorus acid (Inagaki et al., 1976). A similar procedure was proposed by Pieschel et al. to obtain highly substituted starch phosphates (Pieschel et al., 2004). The cellulose, phosphorylating reagents and urea molar ratio was 1:3:17. The phosphorylating reagent and urea were placed in a crystallizing dish and put in a vacuum oven. Ground KF (10 g) was added to the mixture when it was totally melted, and kept at 150 °C for 3 h under vacuum (~500 mm Hg). After the reaction, the products were placed in 2 L of deionized water and allowed to cool at room temperature. Then, the modified fibers were repulped in a laboratory pulp disintegrator for 10 min and washed sequentially with deionized water and an alcohol blend (15% methanol/85% ethanol vol%) until the filtrate was clear. The fibers treated with PEs were further Soxhlet extracted with the alcohol blend and dried at room temperature. A portion of each modified fiber sample was treated twice with 0.1 N HCl for 30 min to protonate acidic groups. The residual acid was subsequently eliminated by washing the fibers with deionized water until the absence of chloride ions in the filtrate. The characterization procedure described below was performed on both types of phosphorylated fibers: before and after acid treatment.

2.2. Characterization of modified fibers

2.2.1. pKa measurements

The degree of degradation of the fiber substrate is related to the acidic strength of the phosphorylating reagent. Stronger acids will cause more degradation. However, measuring the dissociation constant (pKa) of products with low water solubility, like PEs, can be difficult. In order to estimate with accuracy the pKa for these compounds, several water–organic solvent binary systems were tested. The methanol–water pair worked well for the phosphate ester with a shorter chain PEC8, but it was impossible to find a suitable pair for the longer chain PEC18. Therefore, the pKa values were measured at four different molar fractions of methanol in water. Aqueous pKas for the PEC8 were then calculated by the molar fraction method with a linear extrapolation to 0% methanol (Demiralay & Yilmaz, 2012), as seen in Fig. 1.

Around 100 mg of PEC8 were dissolved in specific water–methanol mixtures (100 ml) and titrated with a carbonate-free 0.04 N sodium hydroxide solution prepared with the same binary solvent system. All mixtures had the same ionic strength (0.1 M KCl) and were freshly prepared shortly before being used. All pH values were recorded with a Mettler–Toledo SevenMulti pH conductivity meter equipped with an Inlab Expert Pro pH electrode. The titration cell was thermostated externally at 25 ± 0.1 °C with a Kruss Neslab RTE-111 heater/cooler system. The reaction environment was kept carbon dioxide free by continuously purging with nitrogen gas. One blank and duplicate sample titrations were carried out for each methanol–water mixture.

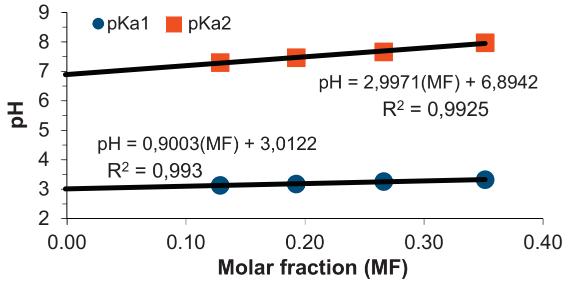


Fig. 1. Determination of pKa values for PEC8.

2.2.2. Elemental analysis

The determination of the amount of phosphorus in modified fiber samples was performed by UV–visible spectrometry. Fiber samples were digested in a strong oxidizing system consisting of concentrated sulfuric acid and hydrogen peroxide. This treatment transformed all the phosphorus into phosphate. Under acidic and reducing conditions, the phosphate can participate quantitatively in the color reaction with ammonium molybdate to form molybdenum blue (Mahadevaiah et al., 2007). The optical density of the resulting solution was measured at a wavelength of 715 nm with a Hach model FN1280x spectrophotometer. Phosphorus concentration was calculated with a calibration curve in the 0.3–60 ppm range using a dibasic phosphate standard solution.

Nitrogen determination was performed on a Shimadzu TOC-VCPH total carbon analyzer using digested samples prepared in the same manner as described in the case of phosphorus determination.

2.2.3. Degree of polymerization of fibers

The average degree of polymerization (DP) of fiber samples was calculated from intrinsic viscosities (Genung, 1964). Pulp viscosity was measured according to TAPPI method T230 (TAPPI, 2004), in which fibers are dissolved in a copper ethylenediamine solution.

2.2.4. Fiber length distribution

Variations in the fiber length distribution after phosphorylation were determined by fiber length analysis. A decrease in DP will cause a reduction of the mean fiber length (Sawoszczuk et al., 2004). The mean fiber length was measured with a fiber quality analyzer (Optest Equipment). The mean arithmetic length was reported.

2.2.5. Infrared spectroscopy

Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer equipped with a Smart iTR over a wavenumbers range from 400 to 4000 cm^{-1}. A total of 16 scans was averaged at a resolution of 1 cm^{-1}.

2.2.6. Nuclear magnetic resonance (NMR)

^{13}C NMR measurements were performed on a Varian 300 INOVA spectrometer using cross-polarized magic angle spinning (CPMAS) techniques for samples in the solid state. Spectra were recorded at a frequency of 100 MHz. Solid-state ^{31}P (CPMAS) NMR were performed on a Bruker DPX spectrometer at a frequency of 161 MHz. The chemical shifts were expressed in parts per million (ppm) relative to the reference standard (orthophosphoric acid) which is assigned the 0 ppm value. All spectra were acquired at a spin rate of 10 kHz.

2.2.7. X-ray photoelectron spectroscopy (XPS)

XPS analysis were recorded on a Kratos Ultra electron spectrometer (Kratos Analytical), using a monochromatic aluminum anode X-ray source (Al Kα, $E = 1486.6$ eV, fwhm = 0.85 eV, 15 kV, 5 mA, 2250 W) with a detection angle of 90° relative to the surface. The disc-formed samples, compressed at 20,000 kPa for 5 min, were investigated under ultrahigh vacuum condition (10^{-9} Torr). The binding energy survey spectrum for each sample was acquired in the 0 to 1300 eV range. The low-resolution survey scans were taken with a 1 eV step and 160 eV analyzer pass energy. The high-resolution elemental scans were taken with a 0.1 eV step and 40 eV analyzer pass energy. The Casa XPS software was used for analyzing collected data: background subtraction (Shirley-type), peak integration, fitting and quantitative chemical analysis.

2.2.8. Scanning electron microscopy (SEM)

The morphology of fiber samples was studied using scanning electron microscopy (SEM) with a JEOL JSM T300 microscope. The operation was conducted in secondary electron mode at a beam current of 100 μA with an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Phosphorylation reaction

The phosphorylation reaction between PEs and KFs follows the principle of polysaccharides phosphorylation proposed by Inagaki et al. (Inagaki et al., 1976). The heat treatment (in our case 3 h at 150 °C) and the presence of urea are essential to introduce the phosphate moiety in the polysaccharide substrate. Temperature and vacuum conditions ensure the continuous elimination of water. With removing one product from the reaction system, the reaction equilibrium will move to the right, therefore phosphorylation efficiency increases. Nevertheless, the key role in this phosphorylation reaction is played by urea. According to the available reports (Gotlieb & Capelle, 2005; Kim et al., 2002; Yurkshtovich, Yurkshtovich, Kaputskii, Golub, & Kosterova, 2007), urea displays multiple functions in such reactions: catalyst/solvent, buffer and ureide and carbamate formation. By maintaining the temperature over the melting point of urea, its decomposition is promoted along with the liberation of active ammonia which is proposed to react with phosphate and generate an ammonium phosphate intermediate (Gotlieb & Capelle, 2005; Yurkshtovich et al., 2007). This intermediate accumulates in the polysaccharide and is believed to work as the main phosphorylating reagent. In this study, the combination of the presence of free ammonia with high temperatures caused the saponification (esterolysis) of PEs to occur prior to the phosphorylation reaction. The following analyses will confirm that only the phosphate moiety of the PE molecule was grafted to the fibers. Despite this, the modified KF obtained here can be regarded as typical phosphorylated cellulose. The specific properties of these phosphorylated fibers make this derivation pathway interesting.

During the reaction, the acidity of the system was partially neutralized by setting free ammonia. The acidity of PEs ($pKa_1 = 3.01$) was found to be lower than that of phosphoric acid ($pKa_1 = 2.15$), but high enough to degrade the cellulose substrate at high temperatures. Many unsuccessful trials showed that phosphorylation cannot be conducted without urea as catalyst and its buffer effect. For example, the reaction with PEs at 150 °C completely degraded the fibers while at 100 °C, the fiber length was not affected, but only insignificant amounts of phosphorus were detected in the final product.

3.2. Fiber degradation

The degradation of cellulosic substrates during phosphate functionalization is perhaps the largest drawback of most phosphorylation procedures, especially when high phosphorus contents are targeted. Aggressive acidic environments, high temperatures and long reaction times lead inevitably to the deterioration of the fiber structure. Several complementary techniques were employed in this study to monitor fiber degradation like the average degree of polymerization, fiber quality analysis and scanning electron microscopy. The degree of polymerization (DP) of cellulose chains is an important indicator of the intrinsic resistance of fibers. The DP of unmodified KF was measured to be about 1200, which is in good agreement with common values for this type of material. However, measurements were impossible to conduct on phosphorylated fibers since they do not dissolve in cupriethylenediamine, the cellulose solvent used for viscosity measurements.

Table 1
Effect of phosphorylating reagent on fiber characteristics.

Fiber type	Phosphorus content (wt%)	Mean fiber length (mm)
KF	0.00	1.39 ± 0.03
KF-PE C8	7.23	1.34 ± 0.02
KF-PE C18	5.17	1.35 ± 0.04
KF-H3PO4	10.68	0.334 ± 0.007

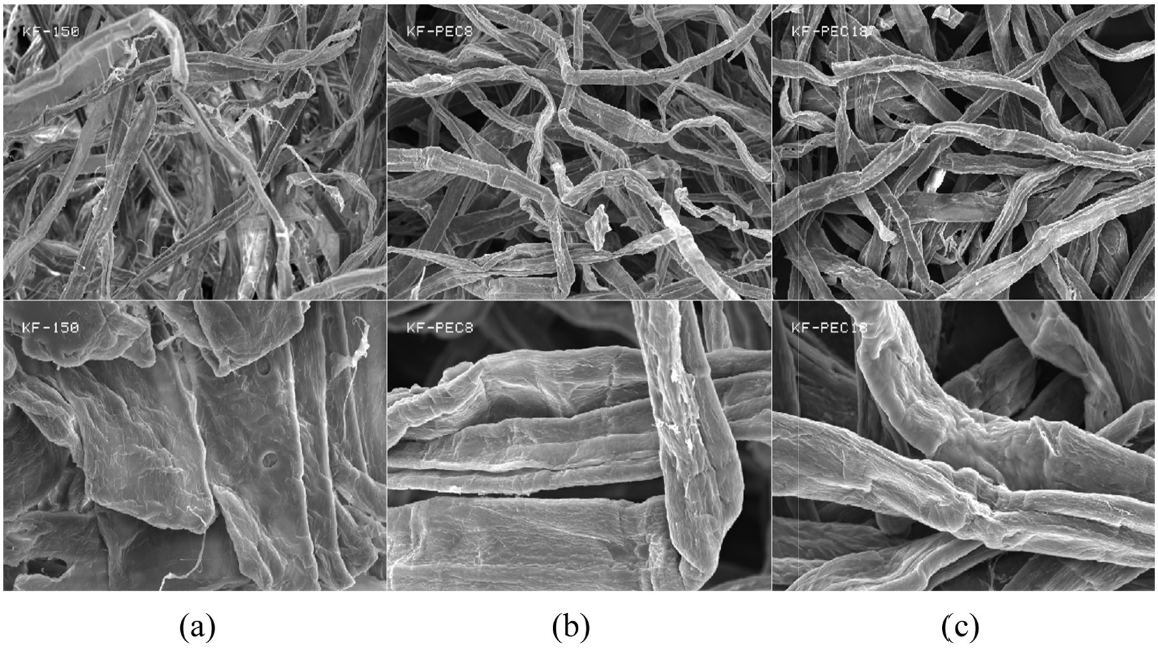
Table 1 shows the mean length of fibers measured before and after phosphorylation with PEs. Data from a supplementary test conducted with phosphoric acid are also included. Under the same phosphorylating conditions, phosphoric acid showed the highest reactivity (highest phosphorus content) compared to its organic derivatives, but caused a severe degradation of the fibers. They lost on average around 1 cm in length and their color turned to dark brown. In contrast, fibers treated with PEs contained less phosphorus but kept their white appearance and length dimension compared to untreated KF.

Scanning electron microscopy images, shown in Fig. 2, illustrate limited differences in KF morphology before and after treatment with PEs. However, the small amount of microfibrils located at the surface of unbeaten KF disappeared after phosphorylation. This phenomenon can be explained by the acidolysis occurring in the reaction environment, affecting firstly exposed microfibrils. Both FQA and SEM techniques confirmed milder conditions for PEs-urea phosphorylating reagents which resulted in modified fibers with good appearance and quality.

3.3. FTIR characterization

Infrared spectra of the phosphorylating reagents and products (after acid treatment) are shown in Fig. 3A. PE reagents can be characterized by two categories of absorption bands related to carbon and phosphorus functionalities. The alkyl chain is identified by the absorption due to C—H stretching (3000–2850 cm^{-1}), C—H bending (1470–1450 cm^{-1}) and C—H vibrations in compounds bearing carbon chains with more than four CH_2 groups (710 cm^{-1}) (Silverstein, Webster, & Kiemle, 2004). The phosphate group is characterized by a band around 1220 cm^{-1} corresponding to the P=O bond, a shoulder around 950 cm^{-1} corresponding to P—OH bond and bands around 1010 cm^{-1} and 815 cm^{-1} corresponding to P—O—C (Inagaki et al., 1976; Leone, Torricelli, Giardino, & Barbucci, 2008a; Suflet et al., 2006). Compared to PE, the spectra of phosphorylated fibers indicated the absorption bands assigned to phosphate features whereas the bands assigned to the alkyl chain C—H stretching is missing.

The intensity of the peak at 3330 cm^{-1} corresponding to hydrogen-bonded OH stretching broadens after phosphorylation. This can be explained by the contribution of the carbamate group, namely NH_2 and HN—C=O stretching, which is formed by a side reaction between cellulose and urea (Klemm et al., 2004a; Klemm et al., 2004b; Knill, 2000). The contribution of this side product was also observed at 1710 cm^{-1} which corresponded to carbonyl stretching (Amaral, Granja, & Barbossa, 2005; Klemm et al., 2004a;



(a) (b) (c)

Fig. 2. SEM images of fibers: (a) Unmodified KF; (b) KF modified with PEC8; (c) KF modified with PEC18. Top: 250× magnification; bottom: 1000× magnification.

Klemm et al., 2004b; Knill, 2000). The decrease in the absorbance of the peak at 1315 cm^{-1} ascribed to CH_2 coupled with OH deformation was a sign of the phosphorylation of hydroxyl groups (Roeges, 1994). Moreover, comparing the spectra of phosphorylated fibers before and after acid wash, as seen in Fig. 3B, the characteristic peak of ammonium phosphate present at 1440 cm^{-1} (Roeges, 1994) was significantly decreased after acid treatment indicating that initial reaction products were in the ammonium form.

3.4. NMR characterization

Solid state ^{13}C-NMR spectra of fiber samples were all dominated by peaks assigned to carbons from the glucosidic units of cellulose. NMR results were in accordance with FTIR. The signal assigned to alkyl chain carbons, which should be present at chemical shifts between 10 and 70 ppm, was not observed in modified fiber spectra. This observation constitutes another evidence that the alkyl chain was not grafted to KF using the PE-urea system.

^{31}P-NMR spectra of PE reagents and phosphorylated fibers (Fig. 4) show resonances that are related to phosphate functionalities (PO_4 tetrahedra, phosphate-like structure) with a chemical shift observed near 0 ppm (Canet, 1996). As expected, no peak corresponding to phosphorus was present in the spectrum of unmodified KF. There was a small difference between PEC8 and PEC18 spectra. Only one narrow peak was arising for the phosphate ester with the longer chain, while a small shoulder peak appeared in the case of phosphate ester with the shorter chain. Unlike PEC18 which was determined to be a single monoester (mono-alkyl phosphate), PEC8 contained mono- and a small portion of diester (di-alkyl phosphate) after purification, which can be responsible for the second signal in the spectrum.

Compared to narrow bands shown for the initial PE, both modified fibers spectra displayed a single but broadened peak. The chemical shift was in the −10–10 ppm range. It was noted that the NMR spectra of solids are generally characterized by

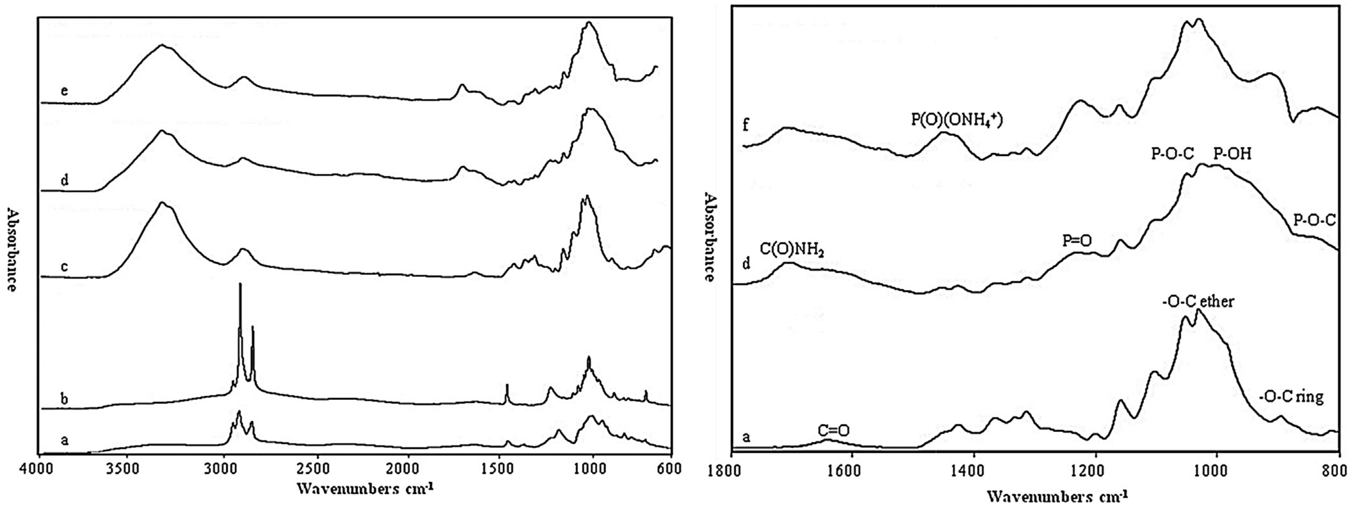


Fig. 3. (A) FTIR spectra of: (a) PEC8; (b) PEC18; (c) KF; (d) KF treated with PEC8; (e) KF treated with PEC18 and (B) KF (a); KF treated with PEC8: after acid wash (d); before acid wash (f).

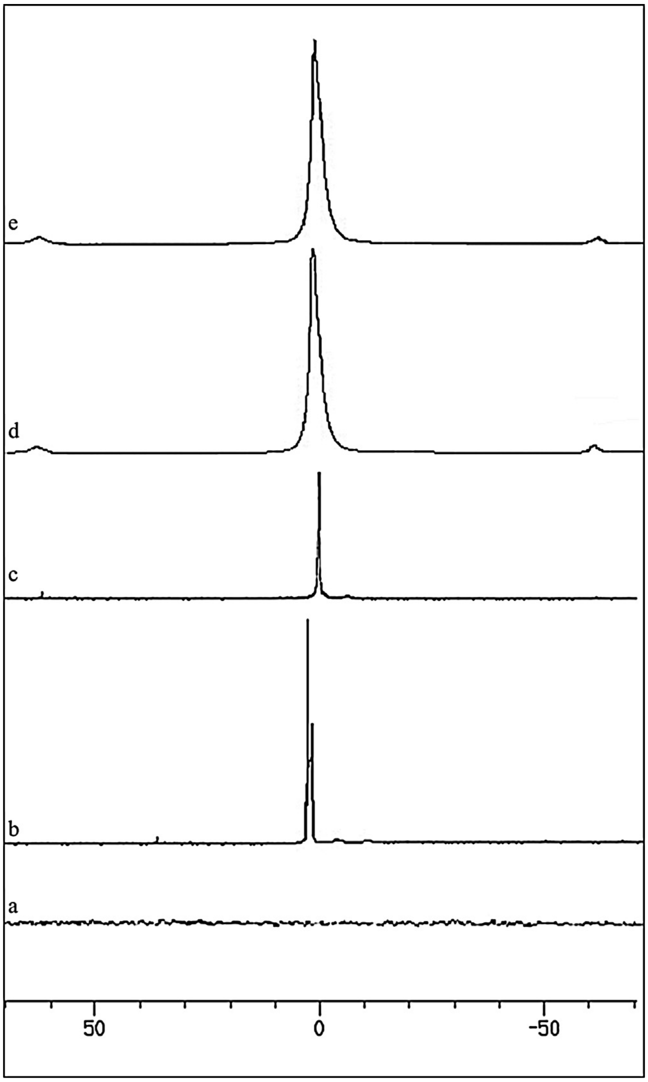


Fig. 4. ^{31}P NMR spectra of: (a) KF; (b) PEC8; (c) PEC18; (d) KF modified with PEC8; (e) KF modified with PEC18.

broad, resonances. A large contribution to the broadening arises from static dipolar interactions. The structural information, principally chemical shifts, is masked by line broadening effects (Canet, 1996; Kolowith, Clark, Ingall & Benner, 2001). However the broad peaks recorded for phosphorylated fibers spectra suggest that these signals were the result of multiple overlaps of phosphate-like moieties. Several possible chemical structures could be present in the products. According to published ^{31}P NMR data, the observed resonance in this region was corresponding to different types of P-esters: phosphate monoesters (0–10 ppm), orthophosphate (0–5 ppm), phosphate diesters (−5–0 ppm) and pyrophosphates (−10–−5 ppm) (Bovey et al., 1988; Sannigrahi & Ingall, 2005; Young & Ingall, 2010). Symmetrical side bands found at ±60 ppm were rotational side bands resulting from solid sample anisotropy (Granja, Pouységu, De Jéso & Baquey, 2001).

3.5. X-ray photoelectron spectroscopy (XPS)

3.5.1. Low resolution

XPS survey spectra of KF confirmed the presence of two major elements: carbon (285 eV) and oxygen (531 eV). Significant differences were observed between the calculated O/C atomic ratio obtained by XPS (0.65) and the theoretical O/C value of polysaccharides like cellulose (0.83). Gustafsson et al. (2003) used XPS to record the O/C ratio evolution of Kraft pulp during cooking and bleaching. They found that the ratio (0.65) was always lower than the theoretical (0.83) value when lignin and extractives were present at the fiber surface. The presence of these substances was conceivable since the fibers for this study were used as received from the pulp mill. Moreover, KFs were bleached, so the measured XPS O/C ratio was influenced by the presence of oxidized carbons and extractives rather than lignin whose concentration in such cases is very low. The O/C ratio increased significantly after phosphorylation: 1.04 for KF-PEC8 and 0.87 for KF-PEC18 compared to 0.65 for the unmodified pulp. This was expected since each grafted phosphate group adds three new oxygen atoms to each glycosidic unit. This result demonstrates once again that the alkyl chain was missing from the structure of phosphorylated KF.

Table 2
Effect of acid treatment on fiber surface composition determined by XPS.

Sample	Before acid wash			After acid wash		
	P (at%)	*N* (at%)	*P*/*N*	*P* (at%)	*N* (at%)	*P*/*N*
KF–PEC8	9.99	4.93	2.03	10.36	1.22	8.49
KF-PEC18	5.94	3.69	1.61	6.09	1.11	5.49

After phosphorylation, two new peaks appeared: the peak at 133 eV corresponding to phosphorus and another at 400 eV corresponding to nitrogen. The P/N atomic ratio can be roughly seen as the fiber propensity to be phosphorylated (main reaction) or carbamylated (side reaction). The nitrogen content was rather high in modified fibers (see Table 2), creating a false impression that the side reaction was in the same order of magnitude as the main reaction. However, after the acid treatment, the nitrogen content decreased significantly suggesting that nitrogen was predominantly present in fibers in the ammonium salt form, easily replaced by protons. In fact, FTIR spectra previously shown at Fig. 3 confirmed this hypothesis. Since the P/N ratio after acid treatment was very high and the detection of nitrogen in that case correlated almost entirely with the carbamate moiety, it can be concluded that the reaction conditions were much more suitable for phosphorylation than carbamylation.

3.5.2. High resolution

Table 3 presents data extracted from high resolution XPS spectra for deconvoluted C1s, O1s, P2p and N1s peaks for KF samples before acid wash.

3.5.2.1. C1s spectrum. The C1s spectra of modified and unmodified KF are deconvoluted to four components, which in terms of BE represents C_1 assigned to C—H and C—C in aliphatic and aromatic species (Rupper, Gaan, Salimova, & Herberger, 2010); C_2 assigned to C—O—C, C—O—H in ether and alcohols and/or the C—O—P linkage in hydrocarbonated phosphate which overlaps in the same BE region (Gustafsson et al., 2003; Ly, Bras, Sadacco, & Belgacem, 2010; Roeges, 1994)); C_3 assigned to O—C—O of acetal and C=O of carbonyl (Istone, 1995)); C_4 attributed to carboxyl and/or carbamate moieties (Ly & Brouillette, 2013).

As the alkyl chain was not present in modified fibers, the phosphorylation reaction did not interfere significantly with carbon linkages in the cellulose structure, so the carbon distribution from the deconvoluted C1s did not show significant changes either. The only noticeable modification was the slight increase of the C_4 component accompanied with a small chemical shift of the BE compared to carboxyl due to the carbamylation side reaction (Ly & Brouillette, 2013).

Table 3
High resolution XPS analysis of KF samples (before acid treatment).

Region	Assignment	KF		KF-PC8		KF-PEC18	
		BE (eV)	at%	*BE* (eV)	at%	*BE* (eV)	at%
C1s	C—C; C—H	285.00	12.00	285.00	16.61	285.00	16.82
	C—O—C; C—O—H; C—O—P	286.71	67.66	286.66	62.21	286.69	61.79
	C=O; O—C—O	288.10	18.17	287.99	16.27	288.05	17.03
	O—CO; N—C(=O)—O	289.34	2.17	289.68	4.89	289.70	4.31
O1s	C=$\underline{O}$, P=$\underline{O}$	530.89	0.83	531.44	22.78	531.49	14.36
	C—$\underline{O}$—C, C—$\underline{O}$—H, P—$\underline{O}$—C	533.00	99.17	533.00	73.54	533.06	83.73
	P—$\underline{O}$—H	–	–	534.57	3.68	534.49	1.91
P2p	Pentavalent phosphorus	–	–	134.56	–	134.67	–
N1s	$\underline{N}$—C(=O)—O, $\underline{N}H_2$	–	–	400.18	25.53	400.20	39.71
	$\underline{N}H_4{}^+$	–	–	402.09	74.47	402.05	60.29

Table 4
Distribution of phosphorus and nitrogen in phosphorylated KF after acid treatment.

Samples	Bulk (elemental analysis)		Surface (XPS)		Surface/bulk ratio	
	P (wt%)	*N* (wt%)	*P* (wt%)	*N* (wt%)	*P*	*N*
KF-PEC8	7.23	0.52	20.37	1.08	2.82	2.08
KF-PEC18	5.17	0.77	12.67	1.04	2.45	1.35

3.5.2.2. O1s spectra. The O1s spectra were fitted to three peaks corresponding in ascending order of BE values to: O_1 – double bonded oxygen in O=C (identified in carboxyl, carbonyl and carbamate moieties) and/or O=P from phosphate esters; O_2 – single bonded oxygen in O—C and O—H (identified in the cyclic hemiacetal structure of cellulose glycoside units) and/or O—P linkage in phosphate esters; O_3 – assigned to single bonded oxygen in P—O—H function of phosphate like structure. Concerning the O1s deconvolution for unmodified KF, different opinions were suggested. Some authors (Ariza et al., 2000; Gustafsson et al., 2003) consider that the C—O—C and C—O—H XPS signals overlap, whereas others (Ly & Brouillette, 2013; Raj et al., 2010; Roeges, 1994) give a different BE level for C—O—H and C—O—C bonds hence the appearance of separated peaks for each. Since the O1s deconvoluted spectra in the case of KF showed only two peaks, the first hypothesis should be considered hereafter, that C—O—H and C—O—C signals are at the same BE.

The phosphorylation reaction produces significant changes at the O_1 and O_3 extremity peaks. The O_1 peak for both modified fibers showed the most important increase in intensity and a slight chemical shift to a higher BE value compared to unmodified KF. Non-bridging oxygen in the phosphate group (O=P) and oxygen double bonded to carbon (O=C) from carbamates contributed to these changes. Moreover, it seemed that the O=P bond was largely responsible for O_1 evolution since the carbamate moiety came from the less favored side reaction. A new peak – $O_{3,}$ assigned to single bonded oxygen in the P—O—H function, located at around 534 eV, appeared in the case of phosphorylated fibers. Even though the intensity of this peak in both cases was quite low, it confirmed the successful grafting of phosphate to KF.

3.5.2.3. P2p spectra. The P2p peak for both types of phosphorylated fibers was deconvoluted into one component, centered at around 134 eV. According to the available literature (Gustafsson et al., 2003; Ly et al., 2010; Puziy et al., 2008; Roeges, 1994), this peak was attributed to pentavalent phosphorus (PO_4 tetrahedron, phosphate-like structure). However, like for NMR results, it was impossible to establish the exact structure of the grafted function.

3.5.2.4. N1s spectra. The N1s spectra were fitted into two distinct peaks. The peak at lower BE was assigned to nitrogen covalent bonds in the carbamate moiety (N—C=O and NH_2), while the peak at higher BE was rather assigned to charged amino groups, i.e., ammonium ions ($NH_4{}^+$) (Ly et al., 2010; Roeges, 1994). As expected, before the acid treatment of modified fibers, the peak corresponding to the ammonium form was important, as seen in Table 3. The situation significantly changed after acid treatment. The peak attributed to the carbamate moiety reached almost 55% in area contribution for N1s. Nevertheless, the signal related to the ammonium form was still large, suggesting that washing the phosphorylated fibers with a hydrochloric acid solution created new charged amino groups by protonating the amine function of the carbamate moiety.

3.6. Bulk vs. surface phosphorus distribution

The chemical modification of cellulosic fibers in a heterogeneous environment leads to the anisotropic distribution of moieties between surface and bulk. This is due to the uneven accessibility of the fiber wall which in turn is subject to its supramolecular structure. Table 4 presents the phosphorus and nitrogen content of modified fibers as obtained from bulk and surface analyses. Both elements were detected in larger concentrations (2–3 times more) at the surface than in the bulk. Data confirm that phosphorylation occurred preferentially at the surface where the hydroxyl functional groups are more accessible. Significant differences in reaction efficiency were observed when the alkyl chain length of PE reagents was changed. For the same reaction conditions, the phosphorus content in modified fibers increased with decreasing chain length. This phenomenon can be attributed to the viscosity of PE. Increasing the chain length will increase the viscosity of the liquid PE, and therefore decrease its diffusion rate into the fibers.

The phosphorus percentage found at the surface of fibers treated with PEC8 could be equivalent to a nearly complete substitution of all three hydroxyl groups, considering the reaction involved only simple mono-phosphate structures. This situation is difficult to achieve in practical conditions. Most likely, such high surface phosphorus contents may be attributed to a different arrangement of phosphate groups onto cellulose. A simple explanation could involve the condensation of phosphate during phosphorylation to form pyrophosphate or even oligo-phosphate grafted cellulose. A detailed verification of this hypothesis and the determination of the properties of phosphorylated KF are currently being investigated and will be reported later.

4. Conclusions

Phosphorylation of Kraft fibers using phosphate esters in molten urea allowed important quantities of phosphorus to be grafted while the problem of substrate degradation associated with conventional phosphorylating reagents was largely overcome. The phosphorylation efficiency was influenced by PE alkyl chain length, higher phosphorus content being obtained in the case of KF treated with the shorter chain reagent. Analyses indicated that phosphorus was grafted as phosphate-like moieties. However, the particular behavior exhibited by modified fibers suggested a more complex condensed structure for the grafted phosphorus like pyro- or even oligo-phosphate. This aspect was further supported by the detection of higher amounts of phosphorus on the surface of modified fibers compared to the bulk. The obtained phosphorylated Kraft fibers have an excellent potential for flame-retardant and ion-exchange application. Finally, we are still studying the possibility to retain the aliphatic chain during the phosphorylation reaction. The resulting cellulose phosphate ester could be used in water and grease barrier and anti-adhesive applications.

Acknowledgements

The authors want to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC).

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