

The Properties of Phosphorylated Kraft Fibers

Ying Shi,^a Dan Belosinschi,^a François Brouillette,^{a,*} Ahmed Belfkira,^b and Bruno Chabot^a

The properties of phosphorylated kraft fibers, including their flame retardancy and behavior in water, such as electrical charge and swelling capacity, were investigated in this study. Two different phosphorus contents and three forms of phosphorylated fibers (ammonium, acid, and sodium) were analyzed. All types of phosphorylated fibers exhibited high char formation and limiting oxygen index (LOI) values, indicating good flame retardancy. In particular, the ammonium form exhibited the best flame retardancy behavior and the highest LOI value. The charge density and swelling capacity of the kraft fibers were significantly increased by phosphorylation. Alkaline treatment following the phosphorylation reaction further increased the water retention value (WRV) and surface charge of the kraft fibers. Compared to unmodified kraft fibers, the phosphorylated fibers had lower absolute values of the negative zeta potentials, and these values were less affected by conductivity.

Keywords: Kraft fibers; Phosphorylation; Flame retardancy; Charge density; Swelling

Contact information: a: Lignocellulosic Materials Research Centre (CRML), Université du Québec à Trois-Rivières, C.P. 500 Trois-Rivières, QC G9A5H7 Canada; b: Bioorganic and Macromolecular Chemistry Laboratory (LCBM), Université Caddi Ayyad, Faculté des Sciences et Techniques, Av. Abdelkarim Elkhatabi, B.P 549 Marrakesh, Morocco;
* Corresponding author: francois.brouillette@uqtr.ca

INTRODUCTION

Cellulose phosphorylation, usually yielding anionic cellulosic phosphate, endows cellulosic materials with novel properties that make them useful in many applications. The first and most important property of phosphorylated fibers is their durable fire-retardancy, which is widely exploited by the textiles industry (Klemm 1998). This characteristic can be achieved not only by physically mixing the substrates with flame retardant (FR) compounds but also by forming chemical bonds between them. According to recently issued environmental regulations, the production and use of once-prevalent halogenated FRs are now restricted. Thus, phosphorus-containing compounds are regarded as a convenient, suitable alternative. They can act both as mixing additives and reactive chemicals (Horrocks *et al.* 2005; Horrocks 2011; van der Veen and de Boer 2012). However, several issues must be addressed before phosphorus FRs can become widely used, including their permanency, toxicity, environmental friendliness, harmlessness to substrates, and others. Developing a convenient cellulose phosphorylation pathway with low add-on chemicals is a pertinent field of study. This type of material has a high value in durable, fire-proofing cellulosic products manufacturing and could help overcome the environmental issues caused by the gradual release of traditional FRs (Lewin and Sallo 1984).

The chemical linkage of phosphorus atoms to cellulose chains significantly decreases the formation of flammable volatiles. It has been proposed that dehydration and

dephosphorylation occur during the thermal degradation of cellulose with the formation of an unsaturated C=C bond in the glucopyranose ring. This action prevents the cleavage of the $\beta(1\rightarrow4)$ glycosidic linkage and imparts flame retardancy to the cellulose fibers (Inagaki *et al.* 1976; Jain *et al.* 1985; Blanchard and Graves 2003; Gaan and Sun 2007a,b).

The second important application of phosphorylated fibers is in the production of ion-exchangers. Several cellulose sources, ranging from agriculture residues to virgin lignocellulosic materials, such as wheat grass (Wilson and Harris 1968), cotton linters (Nada *et al.* 2006), bagasse (Eid *et al.* 2007), banana leaves (Nada *et al.* 2010), and wood pulp (Nada *et al.* 2009b), have been considered for this purpose. By introducing anionic phosphate groups, cation exchange properties are imparted to the cellulosic material, which could be in the form of a powder, wadding, sheet (Nifant'ev 1965), or hydrogel (Granja *et al.* 2001). This diversity of forms makes phosphorylated cellulosic products suitable for several ion-exchange processes such as water treatment (removal of color and metal ions) (Nada *et al.* 2009a); chromatography of proteins and vitamins in bioseparation processes (Peterson and Sober 1956; Firth *et al.* 1968); and osteogenic activity as a nucleating center by attracting and sequestering Ca^{2+} in the design of biomimetic materials (Leone *et al.* 2008).

In a previous work (Shi *et al.* 2014), a pathway to produce highly phosphorylated, non-degraded kraft fibers was described. In this paper, the properties of these modified fibers were investigated with a focus on their flame retardancy and aqueous behavior. The influence of acid or alkali treatments on the phosphorylated fibers' properties was also evaluated. The potential value of the phosphorylated kraft fibers in fire-proofing of composite materials and cation-exchangers is discussed.

EXPERIMENTAL

Preparation of Phosphorylated Kraft Fibers

Phosphorylation of kraft fibers

The phosphorylated kraft fibers (KFP) used in this study were synthesized according to the procedure described previously *via* reaction between cellulosic fibers and phosphate esters (PE) in molten urea (Shi *et al.* 2014). The phosphate esters were derived from two linear fatty alcohols with chain lengths of 8 (C8) or 18 (C18) carbons. The modified fibers had high phosphorus content: more than 7% for PEC8-treated fibers (KFP7) and 5% for PEC18-treated fibers (KFP5). No significant fiber degradation was observed, despite the fact that kraft fibers (KF) were submitted to a harsh reaction environment (*i.e.*, high temperature and acidity).

Pretreatment of the phosphorylated kraft fibers

The phosphorylated fibers were obtained in their ammonium salt (KFP-NH₄⁺) form. To study the effect of pH on fiber properties, further acid and alkaline treatments were conducted. The modified fibers in their acidic form (KFP-H) were obtained using treatment in a 0.1 N aqueous HCl solution, and the basic form (KFP-Na) was obtained after a second treatment with 0.1 N NaOH, as shown in Fig. 1. After these treatments, the fibers were washed thoroughly with deionized water to remove trace acid or alkali. The pH of the treated, modified fiber suspensions was found to be slightly acidic for KFP-H and weakly basic for KFP-Na.

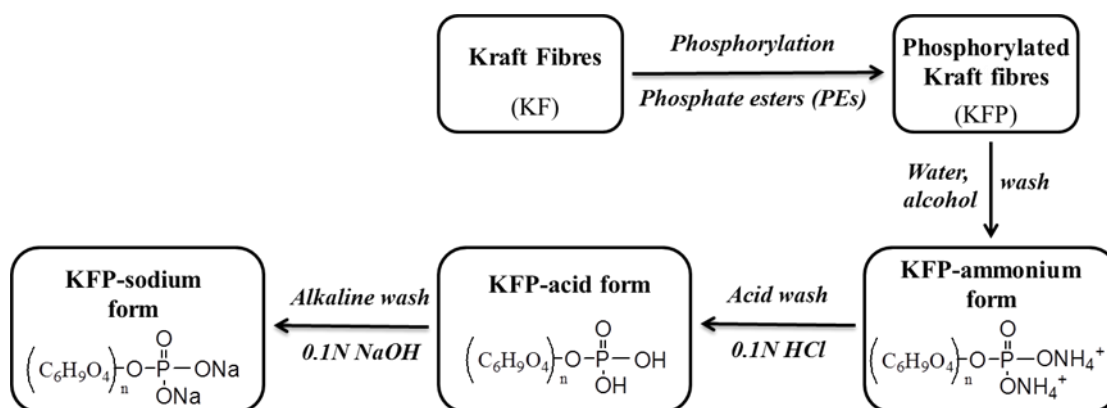


Fig. 1. Post-treatment of phosphorylated fibers

Evaluation of the Properties of Phosphorylated Kraft Fibers

Thermal properties

Thermogravimetric analyses were performed using a Perkin-Elmer (USA) Diamond TG/DTA analyzer. Samples were heated at a scan rate of 5 °C/min from room temperature to 575 °C under a nitrogen atmosphere. This low heating rate was used to prevent the formation of a temperature gradient between the surface and the inside of the fiber sample. Then, nitrogen was replaced with oxygen and the scan rate was increased to 10 °C/min until the temperature reached 1000 °C.

The limiting oxygen index (LOI) is a standard value for characterizing the combustion properties of materials. LOI measurements were conducted according to ASTM standard method D2863-00 (2013). This test provides the minimum concentration of oxygen in a flowing oxygen/nitrogen mixture that can support combustion. The LOI value is the volume fraction of oxygen in the gas mixture when burning occurs. For untreated cellulose fabrics, the LOI is reported to be approximately 19 (Tesoro 1978).

Electrostatic properties

The total charge of the phosphorylated fibers was determined by conductometric titration using a Thermo (USA) Orion conductometer (Model 150) and a Metrohm Brinkmann (USA) automated titrator (Dosimat 765) under an inert nitrogen atmosphere. An appropriate amount of acid-washed fibers was dispersed in a 1 mM aqueous sodium chloride solution and titrated with 0.1 N NaOH.

Polyelectrolyte titration was performed to detect the surface charge of the phosphorylated fibers in their ammonium, acid, and sodium forms. Two standard polyelectrolytes, polydiallyldimethylammonium chloride (poly-DADMAC, positively charged) and poly(vinyl sulfate) potassium salt (PVSK, negatively charged) were used for the titrations. Approximately 0.15 g of sample was allowed to absorb the positively charged polyelectrolyte from an excess poly-DADMAC solution to neutralize the anionic charge at the fiber surface. The suspension was stirred for 30 min to ensure that adsorption reached equilibrium. The fibers were separated by filtration and dried completely before the sample weight was recorded. The filtrate was subsequently titrated with the negatively charged polyelectrolyte to determine the excess poly-DADMAC. This titration was performed on a Müttek (Germany) PCD-03 particle charge detector combined with a PCD-T3 automatic titrator that uses the streaming potential technique to detect the titration end-point. The surface charge density of the fiber samples was

calculated as the ratio of the amount of poly-DADMAC adsorbed to the dried fiber weight (Cadena *et al.* 2009).

The zeta potential of the fiber samples was measured with a Müttek SZP 04 zeta potential meter using the streaming potential technique. Because the zeta potential is conductivity-dependent, the measurement was conducted under various conductivities obtained by adding specific amounts of 1 mM KCl solution as the background electrolyte.

Water retention value (WRV)

According to the SCAN test method, the WRV describes the capacity of cellulose fibers to hold water (SCAN 2000). The procedure was carried out by centrifuging a pad of moist fibers in a centrifuge tube with a wire screen at its base. A test pad consisting of pulp fibers was formed by dewatering a pulp suspension on the wire screen. The centrifuge was accelerated at a relative centrifugal force of 3000 g for 15 min to eliminate all water that can be removed by mechanical forces. Subsequently, the weight of the moist sample was determined and the sample was reweighed after drying at 105 °C. The ratio of the wet mass after centrifugation to the dry mass of the fiber sample is the WRV. Four successive swelling/drying cycles were conducted within each experimental series to evaluate the hornification phenomenon.

RESULTS AND DISCUSSION

Thermal Behavior of Phosphorylated Fibers

Cellulosic materials undergo a single-stage pyrolysis reaction when heated in a nitrogen atmosphere, as shown in Fig. 2. The main reactions are dehydration, desaturation of the C₂-C₃ bond of the anhydroglucose unit, and breakage of the β(1→4) glycosidic linkage. This results in the formation of a levoglucosan intermediate that readily decomposes into volatile compounds at temperatures below 400 °C (Gaan and Sun 2007a; Aoki and Nishio 2010). The decomposition of the unmodified kraft fiber sample occurred between 280 and 375 °C, and the weight loss reached almost 85%.

Phosphorylated fibers also exhibited monomodal weight loss curves under a nitrogen atmosphere, regardless of their chemical form (ammonium, acid, or sodium). Their thermal behavior was totally changed by introducing the phosphate moiety. The onset of the pyrolysis of phosphorylated cellulose was strongly shifted to lower temperatures (T_{d1}) compared to that of unmodified kraft fibers, as can be seen in Table 1. A significant quantity of char was obtained after pyrolysis under the nitrogen atmosphere. As is well known, earlier thermal degradation and char formation are responsible for the flame retardant character of phosphorylated cellulose.

A mechanism for the thermal stabilisation of phosphate-grafted cellulosic materials has previously been proposed based on empirical evidence (Gottlieb 1956; Kandola and Horrocks 1996; Aoki and Nishio 2010). Dephosphorylation was proposed as the first step of the thermal decomposition. Dephosphorylation was proposed to take place mostly by dehydration and desaturation of the glucopyranose ring in cellulose and by the formation of a phosphoric acid species, which creates a char layer, protecting the matrix from atmospheric oxygen (Green 1992; Aoki and Nishio 2010; van der Veen and de Boer 2012). As a result of dehydration, unsaturated C=C bonds are formed in the glucopyranose ring. A keto-enol tautomerism can take place if the C=C bond is located

between the C₂ and C₃ atoms. Another C=C bond can be formed by dephosphorylating the C₆ atom. This latter action allegedly prevents the cleavage of the β(1→4) glycosidic linkage and the subsequent generation of highly volatile levoglucosan (Aoki and Nishio 2010).

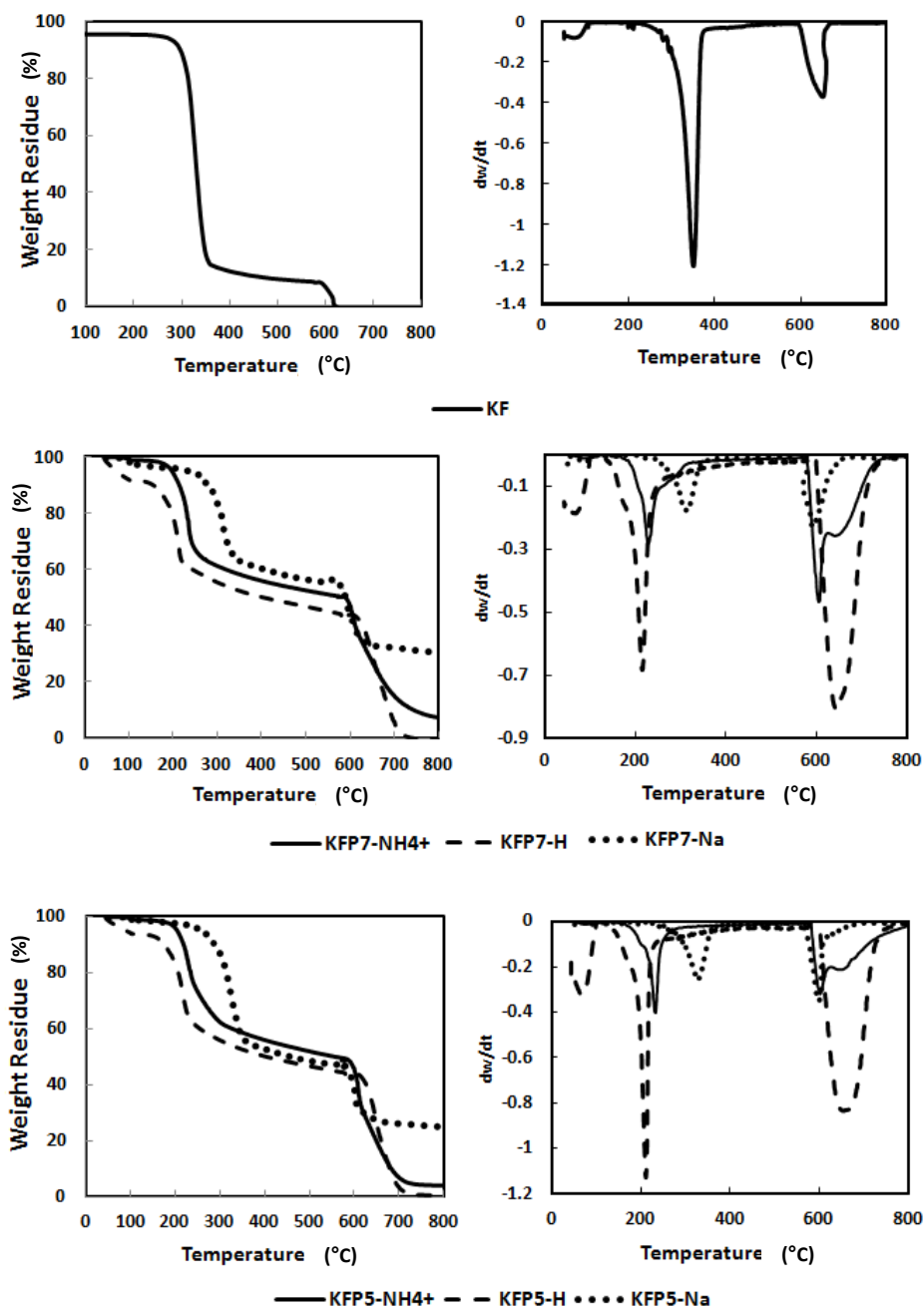


Fig. 2. Thermal stability of fiber samples determined by TGA and DTG

The lowest onset temperature for the thermal degradation of phosphorylated fibers was obtained with the acid form, followed by the ammonium and sodium forms. Compared with kraft fibers, the sodium form exhibited the smallest T_{d1} decrease (Table 1). As described previously, the onset of thermal degradation corresponds to the dephosphorylation temperature rather than the pyrolysis of cellulose chains. Hence, variation in the onset temperature among all forms of phosphorylated fibers is related to

the chemical structure of grafted moieties. The decomposition temperature of phosphoric acid and disodium phosphate is broadly linked to the onset degradation temperature of phosphorylated fibers in the acid and sodium forms. It appears easier to dephosphorylate the acid form with the release of phosphoric acid than the disodium form with the release of phosphate salt. In the ammonium form, T_{d1} was 25 °C higher than in the acid form. As demonstrated by Gaan *et al.* (2008), ammonium phosphate undergoes a condensation reaction to form amide phosphate and water. This reaction could increase the onset temperature because it is endothermic.

Table 1. Relative Thermal Stability of Fiber Samples by TGA

Sample	T_{d1}^* (°C)	T_{d2}^* (°C)	Residue at T_{d2} (%)	Char Formation at 575 °C (%)
KF	280	375	16.38	10.57
KFP5-NH ₄ ⁺	170	260	68.16	49.60
KFP5-H	145	235	68.57	44.38
KFP5-Na	230	360	56.97	46.91
KFP7-NH ₄ ⁺	170	250	66.91	50.40
KFP7-H	145	245	68.92	44.33
KFP7-Na	220	345	64.39	56.06

* T_{d1} and T_{d2} represent the start and the end temperatures of decomposition determined by DTG; the weight loss is calculated as a percentage relative to the weight at T_{d1} .

As expected, grafting phosphate species greatly increased the char formation from kraft fibers. Increasing the phosphorus content from 5% to 7% did not influence char yields. It was expected that different phosphorylation levels would affect the amount of char generated by the combustion of the fibers. In another study, the char percentage was reported to increase with increasing phosphorus content (Aoki and Nishio 2010). However, in this study, phosphorylation took place under heterogeneous conditions and the phosphorus was confirmed to be mostly grafted at the fiber surface (Shi *et al.* 2014). According to the mechanism of cellulose flame retardancy, the phosphorus located at the C₆ position is primarily involved in the char formation process. It can be assumed that the C₆ position of the modified fibers was completely phosphorylated because this position is easier to substitute than C₂ or C₃ (Aoki and Nishio 2010). In addition, previous results obtained with phosphorylated fibers (Shi *et al.* 2014) indicate that the substitution degree at the fiber surface exceeded 2 for both KPF5 and KPF7. The modified fibers reached the same level of char formation, regardless of the total phosphorus content. Nevertheless, the mass residue seemed to increase with phosphorus content for the sodium form. This was because the amount of sodium retained by modified fibers increased with phosphorus content because it was directly bonded to the phosphate moiety. All sodium was found in the char because the TG analysis did not volatilize it. Comparing KFP-NH₄⁺ with KFP-H, the char yield always exceeded 5% in the ammonium form, regardless of the phosphorus content. Several other studies confirm the synergistic action between nitrogen and phosphorus in charring and imparting flame retardant behavior (Tesoro *et al.* 1969; Hendrix *et al.* 1970; Reeves *et al.* 1970; Kishore and Mohandas 1981; Lewin 1999, 2001). As mentioned, Gaan *et al.* (2008) proposed a mechanism for the P-N synergistic effect that begins by amide phosphate formation *via* the endothermic condensation of ammonium phosphate. During the burning process, the amide phosphate could further condense to form P-N-O complex polymers, creating a

protective coating layer at the fiber surface. This layer is believed to protect the cellulosic fibers from thermal degradation, as evidenced by the char yields and flame retardancy behavior.

Flame Retardancy of Phosphorylated Fibers

The combustible nature of cellulose is clearly shown by its thermal degradation behavior. In summary, when ignited, cellulose chains initially undergo endothermic depolymerization, and this is followed by decomposition to levoglucosan. In a second stage, fire propagation is promoted by the formation of combustible, volatile compounds such as alcohols, aldehydes, ketones, and hydrocarbons (Kandola *et al.* 1996; Kandola and Hull 2009).

Ammonium, hydrogen, and sodium phosphorylated fibers all exhibited good flame retardant properties, as can be seen from the LOI values listed in Table 2. Unlike the char yield, the phosphorus content seemed to influence the flame retardancy in that the LOI values increased with the phosphorus content. As explained above, phosphorus species created during the dehydration of glucopyranose rings can polymerize at the fiber surface. These oligophosphates act as a char barrier, protecting the organic matrix from atmospheric oxygen and retarding burning (Gaan *et al.* 2008). Obviously, this protective effect is enhanced by increasing the amount of phosphorus species found on the fiber surfaces. The behavior of the modified fibers obtained in this study was in agreement with this situation because the phosphorylation process used in this study promotes the grafting of phosphate moieties at the fiber surfaces.

Table 2. LOI Values for Different Types of Phosphorylated Fibers

Fiber type	LOI value (%)	
	KFP5	KFP7
Ammonium (NH ₄ ⁺)	30	57
Hydrogen (H)	27	35
Sodium (Na)	28	29

The P-N synergistic effect is exhibited clearly by the ammonium forms of phosphorylated fibers. They exhibited the highest LOI values at both phosphorus contents. The results are in agreement with the TG analyses, confirming that the presence of ammonium improves char formation. As previously reported (Gaan *et al.* 2008), the thermal degradation of ammonium phosphate yields a phosphoramidate, a product with a boiling point higher than that of the analogous phosphate species. This means that phosphoramidates are more likely to be present in the condensed phase and thus are more available for subsequent polymerization reactions. In addition, the polymerization of phosphate amides is more likely to occur than that of phosphoric acid upon fiber pyrolysis. During polymerization, nitrogen allows for the formation of several different bonds, such as phosphorus oxynitride, phosphoramidate, and phosphazene, whereas phosphoric acid poly-condenses only according to a P-O-P pattern (Gaan *et al.* 2008).

The presence of sodium is detrimental to the flame retardant behavior of phosphorylated fibers. However, their LOI values were high enough to maintain flame retardancy. In this case, the LOI value increased by only one unit when the phosphorus content increased from 5% to 7%. The dephosphorylation of the sodium form occurred at a much later stage, as can be seen from the onset temperatures (Table 2). This helps keep the phosphate species in the condensed phase, favoring a potential polymerization

reaction. In fact, the sodium form is as difficult to polymerize as it is to dephosphorylate because the phosphate metal salt is very stable. This feature leads to a less compact protective barrier and lower LOI values.

Electrostatic Properties

To evaluate the propensity of phosphorylated kraft fibers to act as a cation-exchange material, conductometric titration, cationic charge demand, and zeta-potential measurements were conducted. Only the modified fibers with the highest phosphorus content (KFP7) were tested because the ion exchange efficiency was expected to increase with increasing grafted phosphate.

Conductometric titrations were performed to determine the total charge of the phosphorylated fibers. Sodium hydroxide was used as the titrant because it reacts with all acidic hydroxyl groups of the phosphate moieties. Moreover, ionic species such as Na^+ and OH^- are able to reach the bulk region of the fibers otherwise inaccessible to larger species like polymers. Typical titration curves are shown in Fig. 3. As previously described (Fras *et al.* 2004; Zemljic *et al.* 2008), kraft fibers display a sharp, V-shaped curve that indicates very low acidic group content (sulfonate and carboxyl). On the other hand, the titration curve of modified fibers exhibited a large buffer segment, resulting from grafted phosphate moieties, before the final conductivity increase. The total charge, calculated from the conductometric titration (less than 100 $\mu\text{eq/g}$ for kraft fibers) was almost 40 times higher after phosphorylation (Table 3).

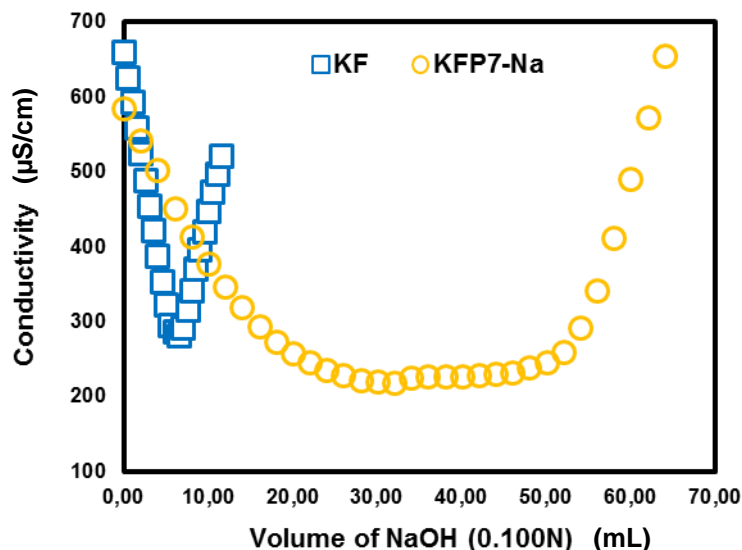


Fig. 3. Conductometric titration of kraft fibers and KFP7

Table 3. Distribution of Fiber Charge

Sample	Surface Charge ($\mu\text{eq/g}$)	Total Charge ($\mu\text{eq/g}$)	Charge Ratio (Surface/Total)
KF	12	91	0.132
KFP7-Na	473	3636	0.130
KFP7-H	255	-	-
KFP7-NH4+	273	-	-

The surface charge of the fiber samples was determined by polyelectrolyte titration. Cellulosic fibers, as well as phosphorylated fibers, become negatively charged when dispersed in water. Positively charged polyelectrolytes such as poly-DADMAC interact with the negative charges of the fibers and can be used for quantitative analysis. Polymer accessibility is restricted to the fiber surface because of their large molecular weight. According to previous results (Shi *et al.* 2014), the amount of grafted phosphorus was almost three times higher at the surface than in the bulk of the fibers. Hence, it was expected that the results of the polyelectrolyte and conductometric titrations would be similar. Table 3 shows a large difference between these two measurements because the cationic charge demand was very low compared to the total charge. The surface charge density was 7 to 15 times lower than the total charge, depending on the phosphorylated fiber form. These results show that the polyelectrolyte titration was more of a semi-quantitative measurement than a quantitative one. The main reasons for this difference are related to the isothermal adsorption of poly-DADMAC and to the phosphate distribution at the fiber surface. It seems that isothermal adsorption was limited by the conformation and electrostatic repulsion of the polymer chains. On the other hand, a number of phosphate moieties were inaccessible to the cationic polymer because they may have been located slightly beneath the fiber surface.

Despite this limitation, the cationic charge demand gives a good indication of the extent of kraft fiber phosphorylation. The surface charge density of the phosphorylated fibers in the ammonium and acid forms was approximately 20 times higher than that of the initial kraft fibers, whereas the sodium form had a charge density nearly 40 times higher. Another interesting fact is that the surface/total charge ratio did not significantly change before or after phosphorylation, as can be seen in Table 3. Comparing the different forms of phosphorylated fibers, the surface charge density of the sodium form was almost twice that of the ammonium and acid forms. This could indicate that the fiber wall accessibility to poly-DADMAC was greatly increased by the alkaline treatment. The WRV results will be useful to determine the effect of the alkaline treatment on fiber accessibility to poly-DADMAC.

The measurement of zeta potential is used to characterize the magnitude of unbalanced electrokinetic potential at the slipping plane. The results of the zeta potential measurements are presented in Fig. 4. As expected, the recorded zeta potentials were negative because the fibers bore negative charges in water. The zeta potential of kraft fibers decreased exponentially with increasing conductivity. This was related to the compression of the diffuse layer when the electrolyte concentration and the conductivity in the water phase increased (Horvath *et al.* 2005; Cadena *et al.* 2009). On the contrary, the conductivity had much less influence on the zeta potential of the phosphorylated fibers. Except for fibers in the acid form (whose zeta potential could not be measured at low conductivities because they generated, by themselves, a high electrolyte concentration in water), all the other forms exhibited low zeta potential across a wide conductivity range. It was concluded that the positive charges required to counterbalance the negative charges of the phosphorylated fibers were mostly located inside the slipping plane (*i.e.*, in the stationary layer region), as these fibers were shown to have high charge density and low absolute value of the negative zeta potential at low conductivities. The results demonstrate that phosphorylated fibers are good candidates for use in ion-exchange materials. They can form complexes with ionic species inside the slipping plane.

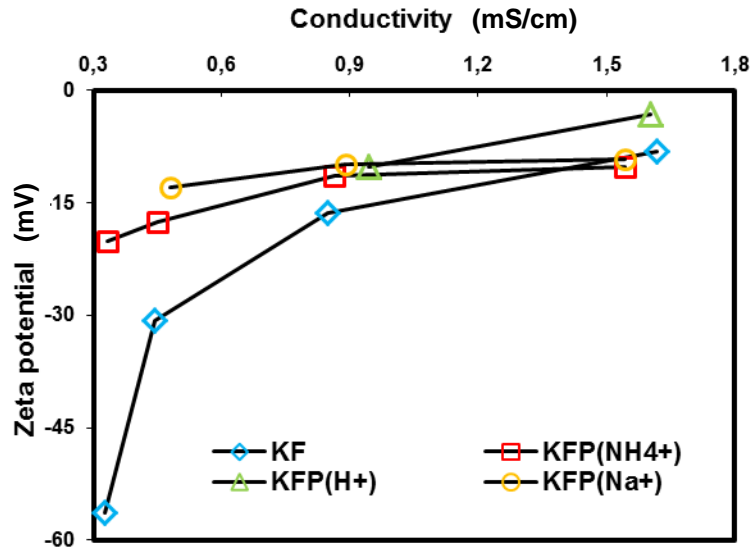


Fig. 4. Evolution of the zeta potential of fiber samples with conductivity

Water Retention Value

The capacity of cellulose fibers to retain water is closely related to their chemical composition, the mechanical treatments applied, and the drying history. For example, the presence of hydrophobic materials such as lignin reduces the WRV value, while hydrophilic materials, such as hemicelluloses, increase it. The beating process modifies the fiber structure by creating internal and external fibrillation, enhancing the capacity of fibers to hold water (Vainio and Paulapuro 2007). The drying process acts opposite to beating, causing hornification, a partially reversible phenomenon that decreases the WRV for dried fibers (Diniz *et al.* 2004).

As shown in Fig. 5, the water retention capacity of kraft fibers increased after phosphorylation because phosphate groups are hydrophilic (Saito *et al.* 1995) and the reaction predominantly occurred at the fiber surface.

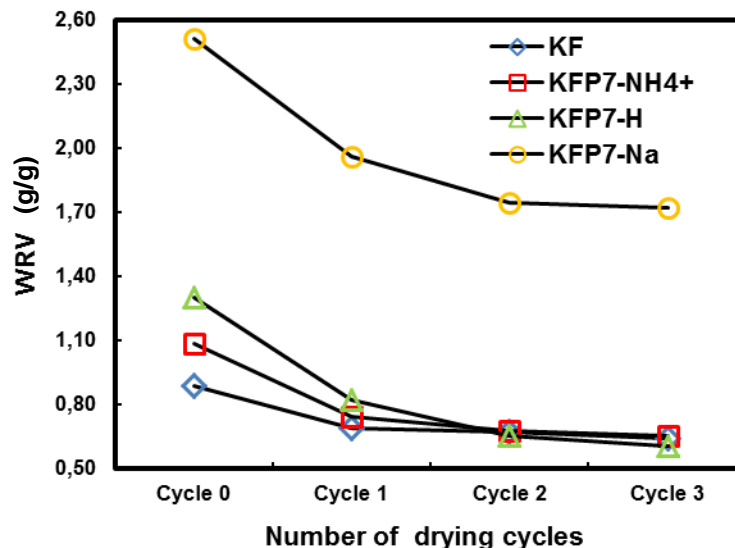


Fig. 5. Effect of phosphorylation on the capacity of kraft fibers to retain water

No significant differences in the WRV of kraft and phosphorylated fibers, in either the ammonium or hydrogen form, were observed between drying cycles. Hornification mostly reached a stable level after the first drying cycle, and the water retention capacity dropped to the same value, regardless of the fiber type. These results show that grafted phosphate groups in the ammonium or acid forms did not delay hornification. Considering the thermal degradation behavior of these two fiber samples, the drying process promoted dephosphorylation; consequently, the dehydration of glucose units and the formation of hydrophobic C=C bonds occurred at a lower temperature. For this reason, the swelling capacity dropped significantly after the first drying cycle and became the same as in the unmodified kraft fibers.

The phosphorylated fibers in the sodium form exhibited the highest swelling capacity. An explanation was given to explain how ionic groups such as Na^+ affect the swelling properties of cellulosic fibers using the Donnan theory (Donnan and Harris 1911; Grignon and Scallan 1980; Scallan 1983). Mobile ions are considered the main driving force of swelling by producing an osmotic pressure differential between the cellulosic fibers and the solution in which they are immersed. When the phosphorylated fibers are immersed in the aqueous NaOH solution, sodium ions adsorb to the acidic phosphate moieties. This process generates a concentration gradient: the charge density on the fibers is much higher than the ionic concentration in the solution. In this case, the fiber wall behaves like a semi-permeable membrane, allowing free passage of water and swelling until equilibrium is reached. The nature of the counter ions of the acidic groups plays an important role in this equilibrium because their dissociation state in solution controls the osmotic pressure. For example, the acidic groups in the hydrogen and ammonium form dissociate to a small extent, whereas the sodium form exhibits much higher dissociation ability (Grignon and Scallan 1980; Lindström and Carlsson 1982; Scallan 1983; Lindström 1992; Bäckström and Hammar 2010). The results shown in Fig. 5 are in agreement with this theory.

Figure 6 presents the WRV values of unmodified and modified kraft fibers after the alkaline treatment.

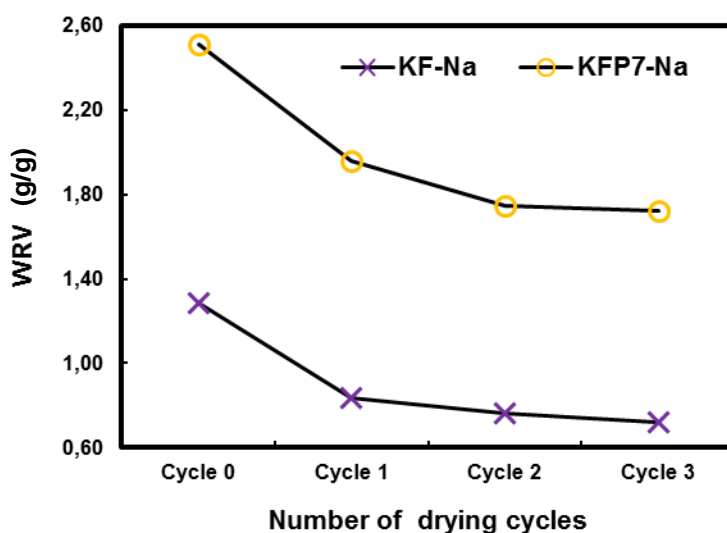


Fig. 6. Effect of alkaline treatment on the capacity of fibers to retain water

Fibers containing carboxyl and phosphate moieties behaved similarly in water. The WRV evolution with the number of drying cycles was the same, and the gap between them was due only to the different acidic group contents. The charge density of phosphorylated fibers was almost 40 times higher than in unmodified fibers containing only carboxyl groups. Overall, hornification was delayed to some extent in the phosphorylated fibers in the sodium form. This phenomenon can be attributed to the large quantity of sodium bonded to the phosphate moieties. The sodium ions increased the decomposition temperature of the phosphorylated fibers and retarded the dehydration of glucose units, as seen by TGA (Table 1). Moreover, the presence of sodium ions increased the osmotic pressure differential, the main driving force of fiber swelling. As a result, the swelling capacity of KFP7-Na remained twice as high as that of KF-Na, even after four drying cycles.

CONCLUSIONS

1. Phosphorylated kraft fibers exhibited good flame retardant properties, regardless of their phosphorus content and form (ammonium, hydrogen, or sodium). A considerable quantity of char was formed during the TG analyses, and the LOI significantly exceeded 21.
2. The LOI value increased with the quantity of phosphorus grafted to the fibers. Overall, the ammonium form of the phosphorylated fibers presented the best flame retardancy behavior, with a very high LOI value of 57.
3. The investigation of the electrical charge indicated that the phosphorylation reaction imparted a high charge density to fibers. This increased their swelling capacity in water.
4. An alkaline treatment further increased fiber wall accessibility. The WRV and surface charge of alkaline-treated fibers were almost two times higher than following acidic treatment. The combination of low absolute value of the negative zeta potential and high charge density make phosphorylated fibers a promising ion-exchange material.

ACKNOWLEDGMENTS

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support and Prof. Derek Gates (University of British Columbia, Vancouver, Canada) for performing the LOI tests.

REFERENCES CITED

- Aoki, D., and Nishio, Y. (2010). "Phosphorylated cellulose propionate derivatives as thermoplastic flame resistant/retardant materials: Influence of regioselective phosphorylation on their thermal degradation behaviour," *Cellulose* 17(5), 963-976. DOI: 10.1007/s10570-010-9440-8

- ASTM D2863-13 (2013). "Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (oxygen index)," ASTM International, West Conshohocken, PA.
- Bäckström, M., and Hammar, L. Å. (2010). "The influence of the counter-ions to the charged groups on the refinability of never-dried bleached pulps," *BioResources* 5(4), 2751-2764. DOI: 10.15376/biores.5.4.2751-2764
- Blanchard, E. J., and Graves, E. E. (2003). "Phosphorylation of cellulose with some phosphonic acid derivatives," *Textile Research Journal* 73(1), 22-26. DOI: 10.1177/004051750307300104
- Cadena, E. M., Garcia, J., Vidal, T., and Torres, A. L. (2009). "Determination of zeta potential and cationic demand in ECF and TCF bleached pulp from eucalyptus and flax. Influence of measuring conditions," *Cellulose* 16(3), 491-500. DOI: 10.1007/s10570-009-9275-3
- Donnan, F. G., and Harris, A. B. (1911). "The osmotic pressure and conductivity of aqueous solutions of congo-red, and reversible membrane equilibria," *Journal of the Chemical Society, Transactions* 99(0), 1554-1577. DOI: 10.1039/CT9119901554
- Eid, M. A., Mahdy, A. A., Eid, K. A., Hashem, H. A., and Nada, A. M. A. (2007). "Behaviour of chemically modified bagasse in sorption of rare earth elements," *Journal of Scientific and Industrial Research* 66(2), 162-169.
- Fernandes Diniz, J. M. B., Gil, M. H., and Castro, J. A. A. M. (2004). "Hornification—Its origin and interpretation in wood pulps," *Wood Science and Technology* 37(6), 489-494. DOI: 10.1007/s00226-003-0216-2
- Firth, R. A., Hill, H. A. O., Pratt, J. M., and Thorp, R. G. (1968). "Separation and identification of organocobalt derivatives of vitamin B12 on thin-layer cellulose," *Analytical Biochemistry* 23(3), 429-432. DOI: 10.1016/0003-2697(68)90234-0
- Fras, L., Laine, J., Stenius, P., Stana-Kleinschek, K., Ribitsch, V., and Doleček, V. (2004). "Determination of dissociable groups in natural and regenerated cellulose fibers by different titration methods," *Journal of Applied Polymer Science* 92(5), 3186-3195. DOI: 10.1002/app.20294
- Gaan, S., and Sun, G. (2007a). "Effect of phosphorus and nitrogen on flame retardant cellulose: A study of phosphorus compounds," *Journal of Analytical and Applied Pyrolysis* 78(2), 371-377. DOI: 10.1016/j.jaap.2006.09.010
- Gaan, S., and Sun, G. (2007b). "Effect of phosphorus flame retardants on thermo-oxidative decomposition of cotton," *Polymer Degradation and Stability* 92(6), 968-974. DOI: 10.1016/j.polymdegradstab.2007.03.009
- Gaan, S., Sun, G., Hutches, K., and Engelhard, M. H. (2008). "Effect of nitrogen additives on flame retardant action of tributyl phosphate: Phosphorus–nitrogen synergism," *Polymer Degradation and Stability* 93(1), 99-108. DOI: 10.1016/j.polymdegradstab.2007.10.013
- Gottlieb, I. M. (1956). "A theory of flame-retardant finishes," *Textile Research Journal* 26(2), 156-167.
- Granja, P. L., Pouységu, L., Deffieux, D., Daudé, G., De Jéso, B., Labrugère, C., Baquey, C., and Barbosa, M. A. (2001). "Cellulose phosphates as biomaterials. II. Surface chemical modification of regenerated cellulose hydrogels," *Journal of Applied Polymer Science* 82(13), 3354-3365. DOI: 10.1002/app.2194
- Green, J. (1992). "A review of phosphorus- containing flame retardants," *Journal of Fire Sciences* 10(6), 470-487.

- Grignon, J., and Scallan, A. M. (1980). "Effect of pH and neutral salts upon the swelling of cellulose gels," *Journal of Applied Polymer Science* 25(12), 2829-2843. DOI: 10.1002/app.1980.070251215
- Hendrix, J. E., Bostic, J. E., Olson, E. S., and Barker, R. H. (1970). "Pyrolysis and combustion of cellulose. I. Effects of triphenyl phosphate in the presence of nitrogenous bases," *Journal of Applied Polymer Science* 14(7), 1701-1723. DOI: 10.1002/app.1970.070140705
- Horrocks, A. R. (2011). "Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions," *Polymer Degradation and Stability* 96(3), 377-392. DOI: 10.1016/j.polymdegradstab.2010.03.036
- Horrocks, A. R., Kandola, B. K., Davies, P. J., Zhang, S., and Padbury, S. A. (2005). "Developments in flame retardant textiles – A review," *Polymer Degradation and Stability* 88(1), 3-12. DOI: 10.1016/j.polymdegradstab.2003.10.024
- Horvath, A. E., Lindström, T., and Laine, J. (2005). "On the indirect polyelectrolyte titration of cellulosic fibers. Conditions for charge stoichiometry and comparison with ESCA," *Langmuir* 22(2), 824-830. DOI: 10.1021/la052217i
- Inagaki, N., Nakamura, S., Asai, H., and Katsuura, K. (1976). "Phosphorylation of cellulose with phosphorous acid and thermal degradation of the product," *Journal of Applied Polymer Science* 20(10), 2829-2836. DOI: 10.1002/app.1976.070201017
- Jain, R. K., Lal, K., and Bhatnagar, H. L. (1985). "Thermal degradation of cellulose and its phosphorylated products in air and nitrogen," *Journal of Applied Polymer Science* 30(3), 897-914. DOI: 10.1002/app.1985.070300302
- Kandola, B. K., and Horrocks, A. R. (1996). "Complex char formation in flame-retarded fibre-intumescent combinations—II. Thermal analytical studies," *Polymer Degradation and Stability* 54(2-3), 289-303. DOI: S0141-3910(96)00054-7
- Kandola, B. K., and Hull, T. R. (2009). *Fire Retardancy of Polymers: New Strategies and Mechanisms*, Royal Society of Chemistry, Cambridge.
- Kandola, B. K., Horrocks, A. R., Price, D., and Coleman, G. V. (1996). "Flame-retardant treatments of cellulose and their influence on the mechanism of cellulose pyrolysis," *Journal of Macromolecular Science, Part C* 36(4), 721-794. DOI: 10.1080/15321799608014859
- Kishore, K., and Mohandas, K. (1981). "Mechanistic studies on the action of ammonium phosphate on polymer fire retardancy," *Combustion and Flame* 43(0), 145-153. DOI: 10.1016/0010-2180(81)90013-4
- Klemm, D. (1998). *Comprehensive Cellulose Chemistry*, Wiley-VCH, Weinheim, Toronto.
- Leone, G., Torricelli, P., Giardino, R., and Barbucci, R. (2008). "New phosphorylated derivatives of carboxymethylcellulose with osteogenic activity," *Polymers for Advanced Technologies* 19(7), 824-830. DOI: 10.1002/pat.1041
- Lewin, M. (1999). "Synergistic and catalytic effects in flame retardancy of polymeric materials - An overview," *Journal of Fire Sciences* 17(1), 3-19.
- Lewin, M. (2001). "Synergism and catalysis in flame retardancy of polymers," *Polymers for Advanced Technologies* 12(3-4), 215-222. DOI: 10.1002/pat.132
- Lewin, M., and Sallo, S. B. (1984). *Handbook of Fiber Science and Technology. Vol. II. Chemical Processing of Fibers and Fabrics. Functional Finishes: Part B*, Marcel Dekker, New York.
- Lindström, T. (1992). "Chemical factors affecting the behaviour of fibres during papermaking," *Nordic Pulp & Paper Research Journal* 7(4), 181-192.

- Lindström, T., and Carlsson, G. (1982). "The effect of chemical environment on fiber swelling," *Svensk Papperstidning-Nordisk Cellulosa* 85(3), 14-20.
- Nada, A. M. A., El-Wakil, N. A., Hassan, M. L., and Adel, A. M. (2006). "Differential adsorption of heavy metal ions by cotton stalk cation-exchangers containing multiple functional groups," *Journal of Applied Polymer Science* 101(6), 4124-4132. DOI: 10.1002/app.23569
- Nada, A. M. A., Mahdy, A. A., and El-Gendy, A. A. (2009a). "Spectroscopy and chemical studies of cation exchangers prepared from corn cobs," *BioResources* 4(3), 1017-1031. DOI: 10.15376/biores.4.3.1017-1031
- Nada, A. M. A., Moussa, W. M., Abd El-Mongy, S., and Abd El-Sayed, E. S. (2009b). "Physicochemical studies of cation ion exchange wood pulp," *Australian Journal of Basic and Applied Sciences* 3(1), 9-16.
- Nada, A. M. A., El-Gendy, A. A., and Mohamed, S. H. (2010). "Banana leaves as adsorbents for removal of metal ions from waste water," *Carbohydrate Polymers* 82(4), 1025-1030. DOI: 10.1016/j.carbpol.2010.03.004
- Nifant'ev, E. E. (1965). "The phosphorylation of cellulose," *Russ. Chem. Rev.* 34(12), 942-949.
- Peterson, E. A., and Sober, H. A. (1956). "Chromatography of proteins. I. Cellulose ion-exchange adsorbents," *Journal of the American Chemical Society* 78(4), 751-755. DOI: 10.1021/ja01585a016
- Reeves, W. A., Perkins, R. M., Piccolo, B., and Drake, G. L. (1970). "Some chemical and physical factors influencing flame retardancy," *Textile Research Journal* 40(3), 223-231. DOI: 10.1177/004051757004000304
- Saito, N., Aoyama, M., Shimizu, Y., Takai, M., and Hayashi, J. (1995). "Super absorbent materials prepared from lignocellulosic materials by phosphorylation. 7. Characteristics of water absorbencies and alkaline treatments," *Mokuzai Gakkaishi* 41(2), 179-185.
- Scallan, A. M. (1983). "The effect of acidic groups on the swelling of pulps: A review," *TAPPI Journal* 66(11), 73-75.
- SCAN-C 62:00 (2000). "Water retention value," Scandinavian Pulp Paper and Board Testing Committee, Stockholm, Sweden.
- Shi, Y., Belosinschi, D., Brouillette, F., Belfkira, A., and Chabot, B. (2014). "Phosphorylation of kraft fibers with phosphate esters," *Carbohydrate Polymers* 106, 121-127. DOI: 10.1016/j.carbpol.2014.01.070
- Tesoro, G. C. (1978). "Chemical modification of polymers with flame-retardant compounds," *Journal of Polymer Science: Macromolecular Reviews* 13(1), 283-353. DOI: 10.1002/pol.1978.230130106
- Tesoro, G. G., Sello, S. B., and Willard, J. J. (1969). "Nitrogen-phosphorus synergism in flame-retardant cellulose," *Textile Research Journal* 39(2), 180-190. DOI: 10.1177/004051756903900208
- Vainio, A. K., and Paulapuro, H. (2007). "Interfiber bonding and fiber segment activation in paper," *BioResources* 3(2), 442-458. DOI: 10.15376/biores.3.2.442-458
- van der Veen, I., and de Boer, J. (2012). "Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis," *Chemosphere* 88(10), 1119-1153. DOI: 10.1016/j.chemosphere.2012.03.067
- Wilson, A. M., and Harris, G. A. (1968). "Phosphorylation in crested wheatgrass seeds at low water potentials," *Plant Physiology* 43(1), 61-65. DOI: 10.2307/4261245

Zemljic, F. L., Persin, Z., Stenius, P., and Stana-Kleinschek, K. (2008). "Carboxyl groups in pre-treated regenerated cellulose fibres," *Cellulose* 15(5), 681-609. DOI: 10.1007/s10570-008-9216-6

Article submitted: February 5, 2015; Peer review completed: April 26, 2015; Revised version received and accepted: May 22, 2015; Published: May 28, 2015.
DOI: 10.15376/biores.10.3.4375-4390