

Chemical Modification of Kraft Cellulose Fibres: Influence of Pretreatment on Paper Properties

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Chemical modifications of cellulose fibres (kraft pulp) in NaOH/H₂O and NaCl/H₂O systems were investigated. Handsheets were prepared that contained 25% of the modified fibres. Changes in the modified samples were examined by measuring their mechanical and optical properties and comparing them to those made with unmodified fibres. The observed differences were explained and supported by structural analyses, by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was found that the NaOH/H₂O pretreatment led to a significant deterioration of optical and strength properties of the handsheets. These modifications affected both the inner part of the crystalline cellulose (change from cellulose I to cellulose II) and the morphology of the fibers. Conversely, these properties slightly improved after propargylation, due to the propargyl functional groups. For the NaCl/H₂O system, a significant enhancement of the mechanical properties of the handsheets was noted, such as an increase of up to 108% of the tear index. The propargylation further increased the tear index (by 157%). These enhancements were not accompanied by significant changes at both the micrometric and nanometric scales, except for the increase of the crystallinity index after propargylation.

Keywords: Kraft pulp; Propargylation; New material; Polysaccharides

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INTRODUCTION

Society is more and more concerned about safety and health issues, while working towards sustainability. Green chemistry represents an innovation area that not only preserves resources, but also contributes to the progress of the chemical industry. In this context, advances in fine chemical synthesis have been mostly oriented toward the use of renewable feedstocks, new reaction conditions, and the development of less-toxic and more biodegradable compounds (Kerton and Marriott 2009).

Cellulose fibres are the most abundant of the renewable, biodegradable, and biocompatible natural polymers. They can be derivatized to yield various useful products (Awada *et al.* 2012, 2014; Mohanty *et al.* 2012). Furthermore, the potential to prepare different functionalized and grafted polymers is of great interest for industrial and medical applications, *e.g.*, polysaccharide modifications using “click chemistry” reactions (Elchinger *et al.* 2011, 2012; Faugeras *et al.* 2012a). Propargylyed cellulose has been used to prepare numerous cellulose derivatives since the development of Huisgen’s 1,3-dipolar

azide-alkyne cycloaddition reaction catalyzed by copper (Kolb *et al.* 2001; Tornøe *et al.* 2002; Rostovtsev *et al.* 2002). For this reason, previous work by the authors focused on the propargylation of cellulose in an aqueous medium (Faugeras *et al.* 2012b). A pretreatment step, which was to cool the cellulose fibres to $-18\text{ }^{\circ}\text{C}$ in a NaOH solution, was used to improve the propargylation reaction in water. It has been demonstrated that the use of NaOH modifies the structure and the morphology of the fibres (Gonzalez *et al.* 1999; Mohanty *et al.* 2000; Elchinger *et al.* 2014). In addition, alkali treatment leads to fibre fibrillation, *i.e.* breaking down of the fibre bundles into smaller fibres (Siregar *et al.* 2010). To avoid this problem, the present work considers replacing NaOH with NaCl during the pretreatment step.

A comparison between the two methods will be the main goal of this study. XPS analysis allows the study of the chemical modification of the pretreated fibres. SEM and EDX were also used to study the influence of the pretreatment steps on the fibres' morphologies and structures. Finally, the influence of pretreatment on the mechanical properties of papers was studied.

EXPERIMENTAL

Materials

All solvents and chemicals were obtained commercially, and unless otherwise stated, were used as received without further purification. NaOH micropearls and NaCl were purchased from Acros Organics. Propargyl bromide (80%) in toluene was purchased from Alfa Aesar. Bleached softwood kraft pulp, which was the cellulose fibre source, was acquired from a local pulp and paper mill (Kruger Wayagamack, Trois-Rivières, Canada)

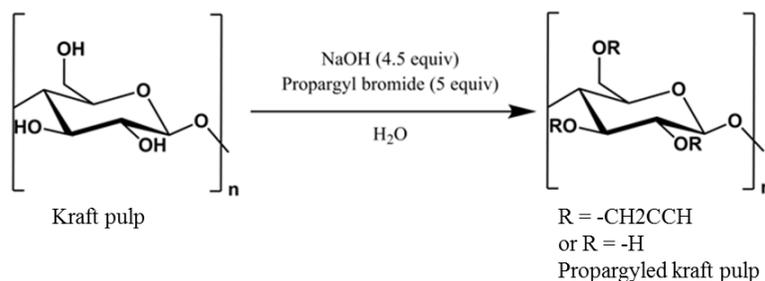
Pretreatment of Cellulose Fibres

Cellulose fibres (100 g) were suspended in 2.69 L of deionised water, to which NaOH (250 g) or NaCl (360 g) was added. Afterwards, the mixture was shaken to dissolve the NaOH or the NaCl at room temperature, which resulted in a dispersion of the cellulose fibres in a NaOH or a NaCl solution. The dispersion was cooled to $-78\text{ }^{\circ}\text{C}$ and held at that temperature until complete solidification (typically 24 h). The frozen solid was allowed to thaw at room temperature. Then, deionised water (2.06 L) was added to the mixture. The resulting dispersion contained 2% of the cellulose fibres in a 5% aqueous NaOH or in a 7.2% aqueous NaCl solution.

Propargylation of Cellulose Fibres

Propargylation of cellulose fibres (Scheme 1) was achieved by adding to the suspended fibres (4.75 L; 620.0 mmol NaOH or NaCl; 100 g fibers) propargyl bromide (368 mL; 3.1 mol CHCCH₂Br; 5 equiv/AGU).

After 7 days under continuous mechanical stirring at room temperature, the reaction mixture was filtered and washed with hot water (10 L) and hot ethanol (EtOH; 5 L). The resulting product was dried at $50\text{ }^{\circ}\text{C}$ in an oven.



Scheme 1. Kraft pulp propargylation in NaOH

X-Ray Photoelectron Spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy (XPS) experiments were carried out using a Kratos Axis Ultra spectrometer that provided elemental composition information, as an atomic percentage, for the surface layer (a few nanometers) of the tested materials. A 225-W monochromatic aluminium X-ray source (Al $K\alpha$) was used. Survey scans were taken with 1.0-eV steps and 160-eV analyser pass energy, while the high-resolution regional spectra were recorded with 0.1-eV steps and 40-eV pass energy. The vacuum pressure was typically 1×10^{-9} Torr. An area of 2 mm² at three different spots was analysed to obtain an average over the sample and to avoid any bias arising from surface heterogeneity. The position of the detector was at an angle of 90° to the sample surface. Deconvolution analysis was performed with a SUN Sparc Station IPX computer (Vision 2). The spectrum analysis was done with Casa XPS 2.3.9 software.

Handsheet Process

Unmodified and modified cellulose fibres (20 g) were separately disintegrated in 2 L of deionised water for 10 min. Then, a mixture containing 25% and 75% of the modified and unmodified fibres, respectively, was prepared and dispersed in deionised water at 0.15% consistency. A set of five handsheets with a grammage of 60 g/m² each was made in a British sheet-mould according to TAPPI Standard T 205 (1995). All handsheets were pressed respectively for 5 min on one side and 2 min on the other side with 345 kPa of pressure. Then, the handsheets were conditioned overnight in a conditioning room at 23 °C and 50% relative humidity (according to TAPPI Standard T 402 (2003)) prior to characterization and testing. A set of handsheets, from unmodified cellulose fibres (control handsheets), was prepared for comparison. Each experimental condition was replicated three times.

Handsheet Characterization

Brightness and opacity

The brightness and opacity measurements were performed using a Color Touch PC apparatus according to TAPPI Standard T 452 os75 (1998).

Tear index

The tear index measurement was performed using a ProTear Elmendorf tear tester from Thwing-Albert according to TAPPI Standard T 414 os65c (2004).

Elongation and breaking length

The elongation and the breaking length were measured using an Instron 4201 tensile tester according to TAPPI Standard T 494 os70 (2001). Two strips (15 mm wide ×

150 mm long) from each handsheet were prepared. In total, 10 specimens were tested from each handsheet set.

Scanning electron microscope (SEM) analysis

Scanning electron microscope (SEM) analysis was performed using a JEOL JSM-5500 SEM with a voltage of 15.0 kV. The top side of the handsheet was analysed. Three different locations on the sample surface were analysed. Two different magnifications are presented for each location.

X-ray diffraction (XRD) measurements

X-ray diffraction (XRD) measurements were performed using a homemade goniometer (Zerrouki *et al.* 2004; Medhioub *et al.* 2007). The X-ray pattern was obtained with $K\alpha_2$ -filtered Cu $K\alpha_1$ radiation (Si 111 crystal monochromator) using a Seifert X-ray generator operating at 35 kV and 35 mA. Scans ranged from 3° to 40° with sampling at 0.02° increments.

RESULTS AND DISCUSSION

XPS Analysis

The propargylation of the fibres was followed by XPS. In general, the surface of the cellulose fibres consisted mostly of carbon and oxygen. The O and C percentage, obtained from the low-resolution XPS spectrum (also called a survey spectrum), made it possible to measure the O/C Ratio after the propargylation. Table 1 summarizes the data extracted from the survey XPS spectra and the O/C Ratio.

Table 1. Atomic % of the C and O Present at the Fibre Surfaces Before and After Chemical Modification and the Value of the O/C Ratio.

	C	O	O/C
Untreated fibres	59.89	40.11	0.67
Propargylation (NaOH/H ₂ O system)	71.02	28.97	0.41
Propargylation (NaCl/H ₂ O system)	65.44	34.56	0.53

According to the survey spectra (*c.f.* data in Table 1), the fibres, before and after the chemical modification, consisted mostly of carbon and oxygen. Moreover, it was apparent that after the chemical modification, the O/C ratio decreased because of the presence of the propargyl group. In fact, the propargyl moiety mostly contains C atoms. On the other hand, comparing the O/C ratio between the two pretreatment systems, it is clear that the NaOH/H₂O pretreatment system resulted in a lower O/C ratio. This difference can be related to the increased efficiency of the reaction in the NaOH/H₂O system.

Carbon signal check

After the propargylation, the percentage of the different classes of carbons, which appeared at different peaks, was changed. These changes were influenced by the propargyl group, which contained mostly C atoms. According to the literature data for lignocellulosic fibres (Dorris and Gray 1978a,b; Belgacem *et al.* 1995; Montplaisir *et al.* 2008), and from

our experimental spectra, it is possible to separate the various carbons into four main classes:

C1: Carbon-Carbon or Carbon-Hydrogen bonding (C-C, C-H, peak at 285.00 eV).

C2: Carbon having a simple bond with only one oxygen (C-O, peak at 286.48 eV).

C3: Carbon that bonds only one oxygen carbonyl or two oxygen atoms, non-carbonyl (O-C-O, C=O, peak at 288.04 eV). The carboxylate groups (COO⁻) appear also at the same energy.

C4: Carbon that bonds an oxygen carbonyl and an oxygen non-carbonyl (COOH, peak at 288.94 eV).

Figure 1 represents three typical high-resolution spectra of the C1s for the untreated fibres, the propargyld fibers using the NaOH/H₂O system, and the propargyld fibers using the NaCl/H₂O system. From the high-resolution XPS spectrum, the percentage of each class of carbon was measured. These values are presented in Table 2.

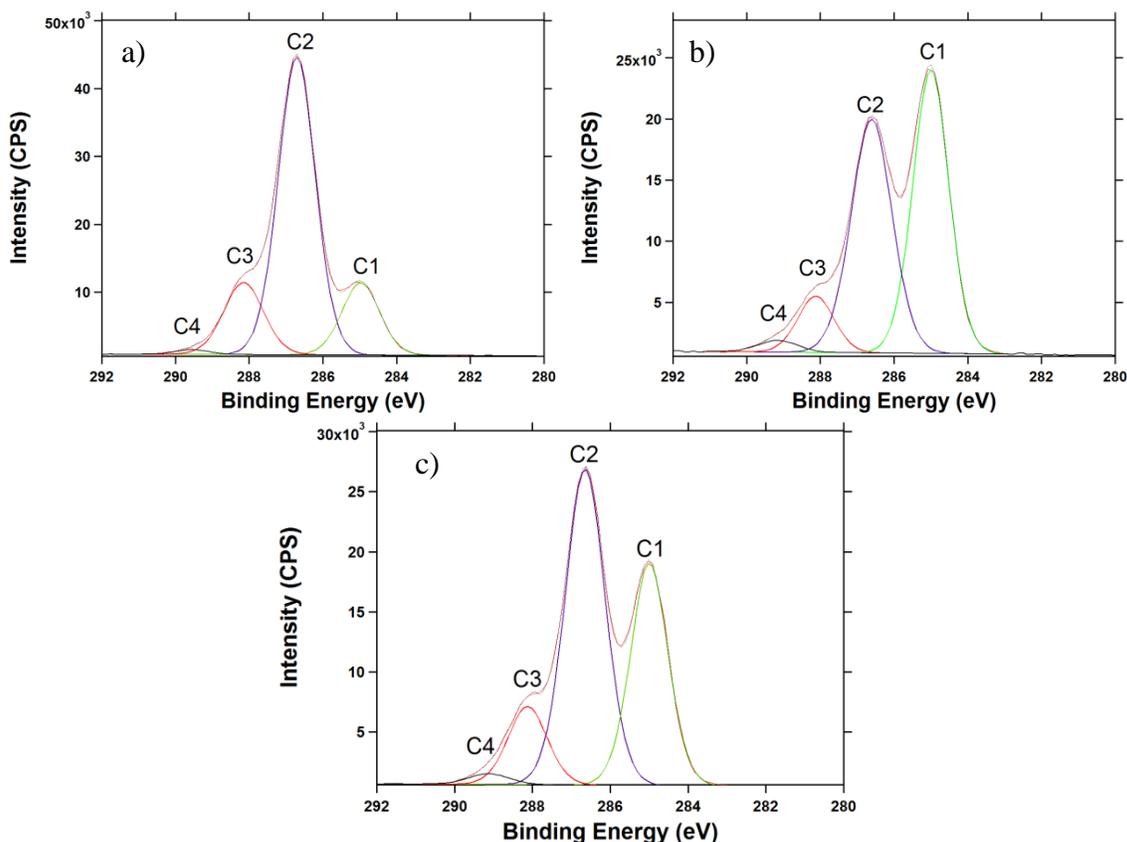


Fig. 1. High-resolution XPS spectrum of a) the C1s for the untreated fibres, b) the C1s for the fibres propargyld using the NaOH/H₂O system and c) the C1s for the fibres propargyld using the NaCl/H₂O system

Table 2. Atomic % (At. %) of Each Class of Carbon Present at the Fibre Surfaces

Name	Pos. (eV)	Untreated fibres	Propargyled fibres (NaOH/H ₂ O system)	Propargyled fibres (NaCl/H ₂ O system)
		At. %	At. %	At. %
C1	285.00	16.21	45.97	34.06
C2	286.6	65.774	42.74	51.58
C3	288.12	17.02	9.18	12.56
C4	289.16	0.991	2.10	1.81

The C1 peak at 285 eV should not be present in the cellulose structure. It can be associated with the presence of some aliphatic and/or aromatic impurities, such as lignin, extractive substances, and fatty acids. After the chemical modification using the two systems, an increase in this peak was clearly observed. This increase can be related to the presence of the grafted propargyl group (which mostly contains aliphatic and alkyne carbons). Accordingly, the percentage of the other peaks (C2, C3, and C4) was changed. The chemical modification using the NaOH/H₂O system induced a significant relative increase in the C1 peak (from 16.21% to 45.97%), proving the high grafting yield of the propargylation reaction when NaOH was used during fibre pretreatment.

Optical and Mechanical Properties of Handsheets

The effect of the pretreatment and propargylation reaction on the optical and mechanical properties of handsheets was investigated. The values are presented as a percentage of the control handsheet values in Table 3. The values of the control handsheets are also presented for comparison.

Table 3. Optical and Mechanical Properties of the Different Handsheets. Values for Untreated Fibres and Percentage of Change of These Property Values After Each Treatment

	Untreated fibres	Pretreated fibres (NaOH/H ₂ O)	Propargyled fibres (NaOH/H ₂ O)	Pretreated fibres (NaCl/H ₂ O)	Propargyled fibres (NaCl/H ₂ O)
Opacity	79.5%	-2.6%	+0.7%	+1.8%	+2.5%
Brightness	78.1%	+0.9%	-4.5%	+4.5%	+3.6%
Tear index	4.04 mN·m ² ·g ⁻¹	-23.9%	+13.2%	+108.4%	+157.4%
Breaking length	2.38 km	-31.0%	-3.4%	-21.0%	+0.4%
Elongation	1.68%	-29.1%	-0.6%	+2.6%	+31.7%

Both the alkali and NaCl pretreatments of the fibres modified both the optical and the mechanical properties of the handsheets. For the optical properties, only slight modifications were observed with both pretreatment cases. In contrast, the modifications of the mechanical properties clearly depended on the pretreatment and on the presence of the grafted propargyl group. Indeed, just the alkali pretreatment of the cellulose fibres resulted in a significant decrease in the mechanical properties when compared to the control samples (*i.e.*, untreated fibres). These decreases in mechanical strength can be related to the degradation of the fibre because of the action of NaOH on cellulose. Conversely, just

the NaCl pretreatment of the fibres led to a significant improvement of these properties, except for the breaking length, when compared to the control samples. In addition, the comparison between the NaOH and the NaCl pretreatment indicated that the use of the NaCl was more interesting. For example, the tear index increased by 108.4% with the NaCl pretreatment and decreased by 23.9% with the NaOH pretreatment. The increase in the mechanical strength values with NaCl can be related to the insertion of Na⁺ ions between polysaccharide chains. The presence of positive ions should increase the interaction between the fibres.

On the other hand, the propargylation of the pretreated kraft fibres led to a significant improvement in the mechanical properties. For example, with the propargylated NaOH/H₂O pretreatment system, an increase in the tear index by 13.3% was observed while the breaking length and the elongation at rupture decreased only by 3.4% and 0.6%, respectively. Finally, the propargylated NaCl/H₂O pretreatment system led to the most meaningful improvements in both the mechanical and optical properties of the handsheets. These results are sufficiently encouraging to consider propargylation reactions with kraft fibres pretreated by the NaCl/H₂O system.

With the NaCl/H₂O pretreatment system, regardless of the amount of propargyl bromide used, the O/C Ratio was about 0.53 and the mass yields were around 128% (Table 1). The O/C Ratio obtained was higher than those achieved with NaOH. Nevertheless, the use of NaCl remains interesting, as it avoids the degradation reaction caused by NaOH attacking cellulose; furthermore, it considerably enhanced the fibre strength. These results are sufficiently encouraging to consider propargylation with the NaCl/H₂O system.

Structural Characterization

SEM analysis

To explain the evolution of the mechanical and strength properties of kraft pulp after propargylation, it was assumed that chemical changes responsible for these variations affected the microstructure of fibres. Accordingly, scanning electron microscopy (SEM) analysis was carried out to examine the structural modification resulting from both NaOH/H₂O and NaCl/H₂O treatments, as well as the subsequent propargylation.

Representative SEM images are shown in Figs. 2 and 3. Figure 2 illustrates the obvious differences, where native kraft fibres seem flattened, while NaOH/H₂O-treated fibres appeared swollen and present a rougher surface. SEM pictures of propargylyed fibres show a surface more like that of the kraft pulp treated with NaOH. In contrast, the NaCl/H₂O treatment did not degrade the fibres, as there were no obvious difference between the SEM photographs (Fig. 2). This first comparative structural analysis explains, in part, the differences observed in the mechanical and optical properties of the modified kraft fibres (in the two systems considered).

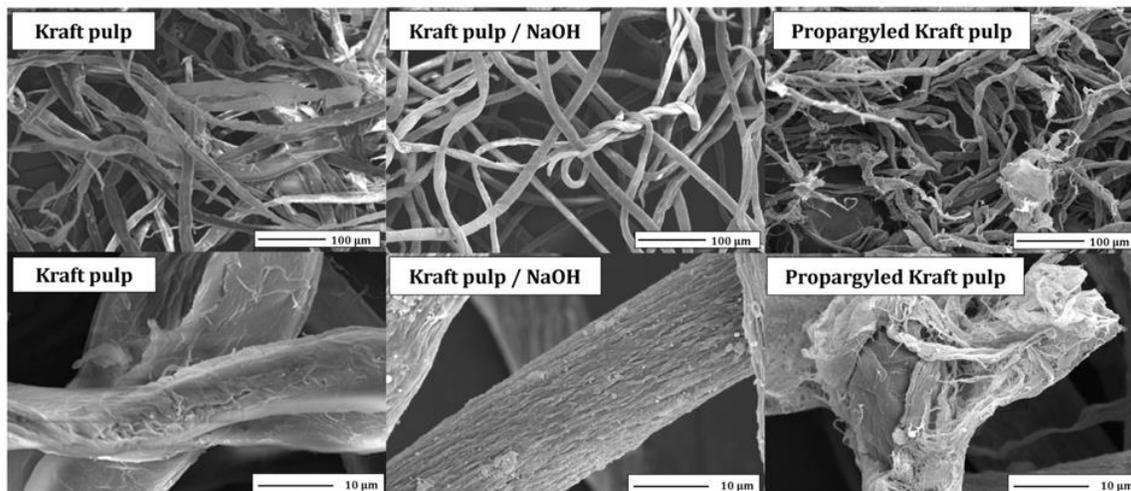


Fig. 2. SEM images of kraft pulp, NaOH/H₂O treated kraft pulp, and propargyld kraft pulp. Two different magnifications, for the same sample location, are presented.

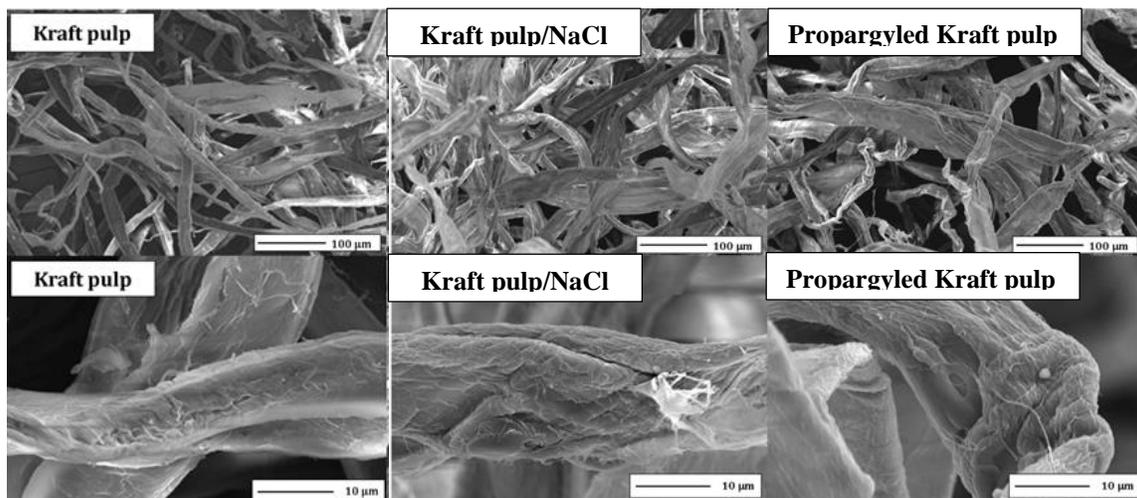


Fig. 3. SEM images of kraft pulp, NaCl/H₂O treated kraft pulp, and propargyld kraft pulp. Two different magnifications, for the same sample location, are presented.

Further information was obtained by X-ray diffraction measurements to characterize the nanometric domains of the kraft pulp microstructure.

XRD analysis

The X-ray diffraction (XRD) technique was used to investigate changes in the microstructure of kraft fibres, as a consequence of the chemical pretreatments and modifications. Figure 4 shows the diffractograms of untreated samples, samples pretreated with NaOH, and propargyld kraft pulp samples. The pattern of native cellulose is also presented as a reference.

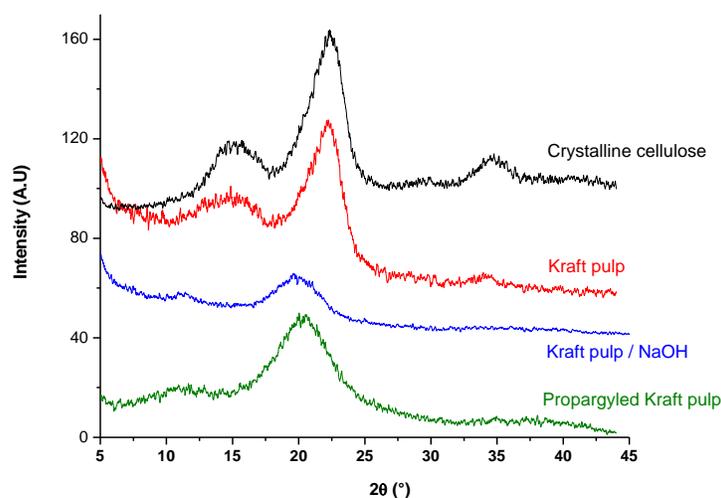


Fig. 4. XRD diffractograms of kraft pulp sample, sample pretreated with NaOH/H₂O, and propargyld sample. Crystalline cellulose pattern is also added for comparison. For more clarity, patterns are shifted along the ordinate.

For the unmodified kraft fibres, the spectrum revealed a shape similar to that of cellulose I, while the diffractogram of samples pretreated with NaOH/H₂O showed a shift of the principal peak towards smaller angles. As explained in a previous study (Elchinger *et al.* 2014), this pretreatment leads to the cleavage of the cellulose crystallite and thus to a change of cellulose type, from I to II. In contrast, the change due to propargylation concerns only the crystallinity index of fibres.

The degree of crystallinity (or crystallinity index), estimated by measuring the mean diffraction peak intensity and the amorphous phase contribution, decreased slightly with NaOH pretreatment, from 52% ± 1% to 46% ± 2%; afterwards, it increased up to 57% ± 2% after propargylation (Table 3). Compared to NaOH treated kraft pulp, the effect of propargylation on cellulose microstructure appeared primarily on the crystallite size (estimated from the Debye-Scherrer equation), where a decrease of 16% was observed (Table 3). In addition, a slight shift of the 101 diffraction peak toward higher 2θ values (Fig. 3) indicated that the inter-reticular plane spacing was reduced by 4%. These results, coupled with the SEM analysis, showed that the NaOH/H₂O medium modified both the inner part of the crystalline cellulose and the interfibre bindings, which inevitably affected the strength properties of the original kraft fibres. The increase in the crystallinity index for the propargyld kraft pulp to reach a value comparable to that of untreated kraft pulp, indicates that fibres functionalization is probably at the origin, at least in part, of the observed enhancements of its mechanical properties.

The same XRD analysis was performed on the NaCl/H₂O modified kraft pulp to examine the impact of NaCl/H₂O when compared to NaOH/H₂O treatment. The diffractograms of the untreated kraft pulp sample, sample pretreated with NaCl/H₂O, and propargyld sample are presented in Fig. 5.

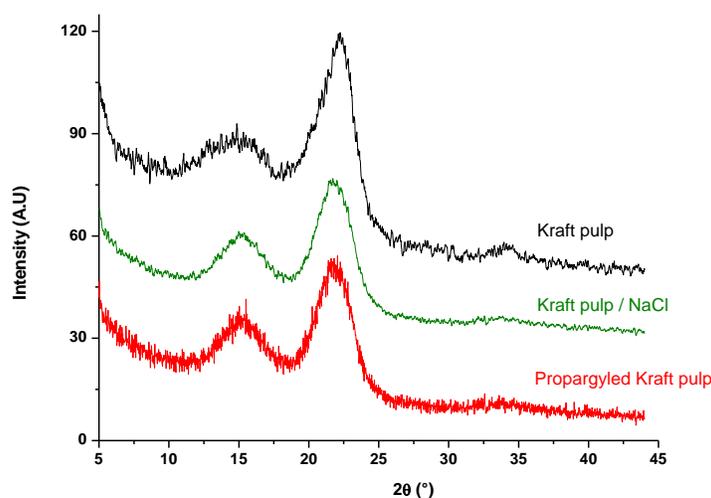


Fig. 5. XRD diffractograms of kraft pulp sample, sample pretreated with NaCl/H₂O, and propargylyed sample. For more clarity, patterns are shifted along the ordinate.

In contrast to NaOH/H₂O treatment, all the patterns revealed a shape similar to that of cellulose I, which showed that the NaCl/H₂O medium only weakly affected the crystalline nature of the kraft pulp. The XRD results are presented in Table 4.

The crystallinity increased slightly, from 52% ± 1% to 55% ± 1%, under NaCl/H₂O treatment and up to 61% ± 2% after propargylation (Table 3). The crystallite size (for 002 Miller indexes) decreased by 14% after NaCl/H₂O treatment, and then it remained constant after propargylation. A slight shift of the 002 diffraction peak towards lower 2θ values (Fig. 5) indicated that the inter-reticular plane spacing increased by only 2% after NaCl/H₂O treatment and remained constant after propargylation (Table 4). Similar to previous results and those obtained by SEM, it was concluded that the NaCl/H₂O system favoured soft modifications to the micro-fibril surfaces without notably changing the microcrystalline structure of the kraft pulp fibers; the only exception observed was the increase in the crystallinity index after propargylation.

Table 4. XRD Results for the Untreated Fibres, Pre-treated Fibres (in NaOH/H₂O and NaCl/H₂O systems), and Propargylyed Fibres

	Untreated fibres	Pretreated fibres (NaOH/H ₂ O)	Propargylyed fibres (NaOH/H ₂ O)	Pretreated fibres (NaCl/H ₂ O)	Propargylyed fibres (NaCl/H ₂ O)
Crystallite size (nm)	2.8 ± 0.1	1.8 ± 0.1	1.5 ± 0.1	2.4 ± 0.1	2.5 ± 0.1
Crystallinity Index (%)	52 ± 1	46 ± 2	57 ± 2	55 ± 1	61 ± 2
d-spacing* (nm)	0.399 ± 0.001	0.451 ± 0.001	0.431 ± 0.001	0.408 ± 0.001	0.406 ± 0.001

According to the structural analysis, the mechanical strength properties of the kraft pulp samples were closely related to the micro/nano-structure of the considered materials, namely, the crystallite dimensions, the crystallinity index, the cellulose type at the

nanometric scale, and the fibre size, their arrangements, and their integrity in the micrometric domain.

The combined effect of the inter-reticular plane spacing and the crystallinity index seems to have had a predominant role in increasing mechanical properties. Indeed, propargylation of NaOH/H₂O treated kraft pulp, showed an enhancement of tear index as consequence of about 24% crystallinity index augmentation and 4% of d-spacing reduction (compared to NaOH/H₂O treated fibres). For NaCl/H₂O treated kraft pulp, where the inter-reticular plane spacing remained constant (within uncertainties), the improvement of crystallinity index (+17% and +11% compared to untreated kraft pulp and to NaCl/H₂O treated one, respectively) may explain the noticeable increase of tear index.

CONCLUSIONS

1. The chemical modification of kraft pulp was investigated with two different aqueous freezing pretreatment systems: NaOH/H₂O and NaCl/H₂O. For the first treatment, a significant deterioration of the optical and mechanical properties was observed. These properties were, however, slightly improved after propargylation. For the NaCl/H₂O system, a significant enhancement of the mechanical properties of the kraft fibre samples was noted: up to a 108% increase for tear index. The propargylation slightly increased the tear index (+157%).
2. XPS analyses confirmed the chemical modification of the fibres. The propargylation was more efficient in the NaOH/H₂O system.
3. Finally, SEM and XRD analyses were performed to explain the observed differences in the mechanical properties of kraft pulps modified by the two systems. The results clearly showed that using NaOH/H₂O caused changes in both the inner part of crystallite cellulose (which change from cellulose I to cellulose II) and the fibres. In contrast, the NaCl/H₂O system did not produce significant changes at either the micrometric or nanometric scales, except for the increase in the crystallinity index after propargylation.
4. These results were sufficiently encouraging to envisage various applications of functionalized and modified propargylyed kraft pulp by additional reactions with the NaCl/H₂O system.

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