



Effect of chemical treatments on the chemical composition and properties of flax fibers

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Abstract: Flax fibers were modified with NaOH and NaClO₂ under different conditions in order to not only clarify the effects of hemicelluloses and lignin removal on the morphology and properties of flax fibers, but also to improve the fiber quality. The quality of flax fibers was characterized in terms of chemical composition, fineness, whiteness, and mechanical and sorption properties. Both treatments, alkali treatment leading to hemicelluloses removal (up to 72 %) and chlorite treatment leading to lignin removal (up to 96 %), induce a modification of the morphology and properties of flax fibers. For 5 % NaOH treatments, as well as all NaClO₂ treatments, an increase in the crystallinity was observed, while for higher NaOH concentrations, the mercerization phenomenon induced a slight decrease in the crystallinity. Modification with NaClO₂ resulted in fiber fibrillation while modification with NaOH at boiling temperature resulted in smoother fiber surfaces. Both treatments cause a decrease in tensile strength and water retention values, with the maximal decrease obtained with NaOH treatment at boiling temperature. Chlorite treatment resulted in finer fibers having a higher whiteness index compare to the alkali-modified fibers.

Keywords: bast fibers; alkali treatment; chlorite treatment; chemical composition; fiber properties.

INTRODUCTION

In order to reach high values for textile and technical applications (detailed considerations are presented in the Supplementary material to this paper), flax

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fibers have to be specially prepared or modified regarding homogenization and improvement of the fiber structure and properties, since as a crop-based material, their structure and properties depend on the growing conditions, including growth duration and procedures involved in the fiber extraction from the plant. The chemical structure of raw flax fibers is very heterogeneous and includes about 70 % cellulose and the rest are various non-cellulosic substances, such as hemicelluloses, lignin, pectin, small amounts of fats and waxes, pigments and residual ash (some details are presented in the Supplementary material).^{1–3} These non-cellulosic substances have a negative influence on the processing of flax material (spinning, weaving, dyeing, printing and finishing), affect their whiteness, sorption and adhesion properties and restrict the application of flax fibers.^{4–8} Therefore, for many applications, it may be necessary to further process the fibers to reduce the contents of non-cellulosic substances and/or improve some fiber properties (degrees of elementarization and degumming, degree of crystallization, surface roughness, mechanical and sorption properties, *etc.*).

Traditionally, chemical treatments have been used to remove non-cellulosic substances and improve the bast fiber quality, although many of these treatments give rise to environmental pollution. In spite of many efforts made to replace chemical processes in the processing of flax and other bast fibers by biological or physical processes,^{5,9–12} to date, alkali and chlorite treatments are still the most direct and efficient way to remove non-cellulosic substances and improve fiber quality. Furthermore, both treatments have been used for years as important tools for studying structure–properties relationship of natural cellulose fiber. The effect of lignin and hemicelluloses removal on the structure and properties of other fibers, such as jute,¹³ hemp^{6,14} and agave¹⁵ fibers, have been studied in detail, while such studies of flax fibers are still limited.

In this paper, these two chemical treatments of raw flax fibers, *i.e.*, treatments with sodium hydroxide and sodium chlorite solutions under different conditions, are performed not only to increase the refinement quality, and improve the properties of flax fibers, but also to clarify the effect of lignin and hemicelluloses removal on the morphology and properties of flax fibers, considering the limited resources in current literature dealing with this topic. The quality of unmodified and modified flax fibers was characterized by determining their chemical composition, fineness, whiteness, and mechanical and sorption properties. The results obtained in this study should provide comprehensive knowledge that would allow the refinement quality to be increased and the properties of flax fibers to be altered in a defined manner.

EXPERIMENTAL

Chemical treatment of flax fibers

Flax fibers (the details about materials used are given in the Supplementary material) were modified by two chemical treatments, *i.e.*, alkali treatment with sodium hydroxide and

oxidation with sodium chlorite solutions. Flax fibers were treated with sodium hydroxide solutions (5, 7, 10 and 18 %), at room temperature (20 °C) and with sodium hydroxide solutions (5, 7 and 10 %) at boiling temperature at 1 g:30 mL solid/liquid ratio, with constant stirring for different periods of time (30, 60 and 120 min), followed by neutralization with 1 % acetic acid solution, washing with distilled water until neutral (checked by multi-strip pH paper) and overnight drying in air. In the other chemical treatment, flax fibers were treated with sodium chlorite solutions (5, 10, 15 and 20 g L⁻¹), at pH 4–4.5 (pH adjusted by the addition of acetic acid), at boiling temperature, 1 g:30 mL solid/liquid ratio, under constant stirring for different periods (30, 45 and 60 min), followed by washing with distilled water and overnight drying in air. The chemical treatment scheme and a list of the samples are given in Table S-I of the Supplementary material.

The influences of the chemical treatments on features of flax fibers were evaluated by determination of the chemical composition (α -cellulose content, hemicelluloses content, value of copper number, lignin content expressed as Kappa number), iodine sorption, water retention, whiteness index, fineness and tensile strength of the unmodified and modified flax fibers.

Determination of weight loss and chemical composition

The loss in weight, as a result of chemical treatment, was determined by the direct gravimetric method described by Koblyakov.¹⁶ The chemical composition of the unmodified sample and each of the modified samples was determined according to the scheme of Soutar and Bryden¹⁷ by successive removal of water soluble substances, fats and waxes, pectin, lignin and hemicelluloses.

The residual lignin content in flax fibers was further estimated by the Kappa number determined by the micro Kappa number method.¹⁸ The weight of the unmodified and modified samples subjected to the micro Kappa number determination was up to 1.0 g depending on the residual lignin content to approximately equalize the permanganate consumption.

Methods for the characterization of the flax fiber properties

Determination of the copper number. The copper number of the unmodified and modified flax fibers, as a measure of the fiber quality (*i.e.*, a measure of the reducing end groups and cellulose degradation) was determined according to the standard method.¹⁹

Surface morphology. The fiber morphology was observed using a scanning electron microscope (SEM) JEOL JSM 6060LV, at 12 kV after sputtering with gold.

Determination of fineness. The fineness in tex was determined as per standard method²⁰ by dividing the mass of fibers by their known length.

Determination of iodine sorption and water retention values. The Schwertassek method was used for an evaluation of the sorption properties of flax fibers.^{21,22} According to Schwertassek, absorption occurs in the amorphous phase. A ratio of iodine sorption value (*ISV*, per 1 g cellulose) to 412 (mg iodine absorbed per 1 g of methylcellulose) determines the amorphous fraction. The crystallinity index (*CrI* / %) was calculated using the equation:²⁰

$$CrI = 100 - \left(100 \frac{ISV}{412} \right) \quad (1)$$

The water retention of the flax fibers was determined by the standard centrifuge method.²³

Determination of tensile strength. The tensile strength of single flax fibers were determined as the average of at least ten measurements, on tester type AVK-Budapest (Hungary)

with clamps spaced at 100 mm and with strain rate (bottom clamp rate) of 150 mm min⁻¹, by following the usual procedure described elsewhere.¹⁶ As flax fibers vary greatly in fineness, as well as the fact that raw fibers still stick very much together into bundles and modified fibers are mainly separated into single elemental cells (fibers), the tensile strength was expressed as tenacity – a specific value related to fineness (force per unit fineness). For this, the fineness of each single fiber was determined before the tensile testing.

Determination of whiteness index. Whiteness index of flax fibers was determined by using an Elrepho reflectometer (OPTON RFA 2, Germany) equipped with a D65 illuminant following the standard procedure.²⁴

RESULTS AND DISCUSSION

Influence of chemical treatment on the chemical composition of flax fibers

The effects of various chemical treatments and modification conditions on the removal of non-cellulosic components, as well as the decomposition of impurities and natural pigments in flax fibers, are generally characterized by weight loss. The effect of modification conditions on the weight loss of the modified flax fibers is shown in Fig. 1, while the chemical compositions and copper number of the unmodified and chemically modified flax fiber samples are given in Table S-II of the Supplementary material.

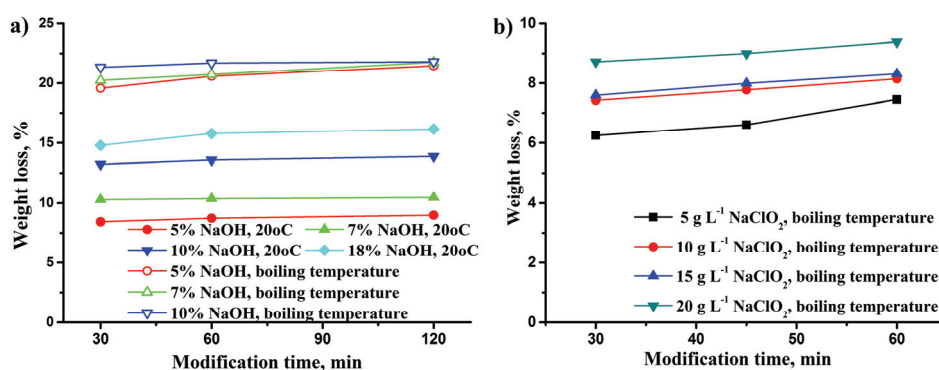


Fig. 1. Effect of modification conditions on the weight loss of flax fibers modified with: a) NaOH and b) NaClO₂.

The severity of treatment is generally characterized by weight loss, which is largely the result of solubilization/removal of hemicelluloses and/or lignin (and other minor constituents) from flax fibers. It is evident from Fig. 1 that with increasing concentration of modification agent (NaOH or NaClO₂), the weight loss of the flax fibers increased, whereas increasing the treatment time had a smaller influence on the weight loss. An exception was the treatment with boiling NaOH, when the concentration of NaOH had almost no influence on the weight loss of flax fibers, especially for a treatment time of 120 min. In addition, due to severity of modification conditions, treatments with NaOH at boiling temperature resulted

in the largest weight loss (21.46–21.80 %) in comparison with the treatments of flax fibers at 20 °C (8.97–16.14 %). Treatments of flax fibers with NaClO₂ (6.24–9.39 %, Fig. 1b) resulted in the removal of different degrees of non-cellulosic substances (Table S-II).

The obtained results clearly showed that treatment with NaOH leads to a significant removal of hemicelluloses and treatment with NaClO₂ leads to a significant removal of lignin from flax fibers, which is in agreement with literature data.^{6,14} The presence of some quantity of hemicelluloses and lignin in the fibers after various methods of flax processing could be explained, according to the literature,²⁵ by their location in fiber structure, *i.e.*, the fact that they are not only a part of intercellular layers, but also located in the fiber walls. Additionally, hemicelluloses are strongly tied to cellulose fibrils by hydrogen bonds, which could explain certain amount of residues of hemicelluloses in the structure after modification.^{5,26,27} The obtained results show that even in the case of the most severe treatment (2 h alkali treatment at boiling temperature) about 70 % of hemicelluloses were removed, *i.e.*, the hemicelluloses content was reduced from 7.84 % for the unmodified flax fibers to 2.22 % for the modified fibers. Moreover, for flax fibers modified with 5 % NaOH, at room temperature, and all chlorite-modified fibers, it seemed that the hemicelluloses were not affected by these treatments since their content even increased after the treatments. This was only initially, since if the obtained data was considered carefully together with the weight loss data (Fig. 1), it is clear that this was because of the simultaneous removal of hemicelluloses and other non-cellulosic components, which affected the ratio of the components in the modified fibers.

Generally, there was an evident tendency that the level of residual hemicelluloses decreased with increasing severity of the treatment, *i.e.*, on increasing the NaOH concentration, temperature or/and duration. For example, during 2 h treatment of flax fibers with 18 % NaOH at room temperature, the hemicelluloses content dropped to 2.93 %, while in the case of treatment with 5 % NaOH but at boiling temperature, only 30 min was required to obtain a similar hemicelluloses content (3.11 %). This means that through selection of the modification conditions, significant savings of chemicals or time could be achieved.

It is very difficult to remove the lignin in the fibers by the alkali process, because lignin has a strong chain of C–C bonds and aromatic groups and the effect of alkali processing for its removal is limited,^{27–29} but treatment with NaClO₂ leads to a significant removal of lignin from flax fibers. The highest degree of lignin removal (lignin content <0.15 %) was achieved in the sample FC20B60 that was treated with 20 g L⁻¹ solution of NaClO₂ at boiling temperature for 60 min and for which the value of Kappa number was 1.07 (Table S-II). Although the flax fibers were modified by the NaClO₂ solutions, significant removal of hemicelluloses does not occur. This can be explained by a selective oxi-

dative effect of sodium chlorite, which is also very important for preserving the α -cellulose content. Thus, if the treatment conditions are properly adjusted, sodium chlorite oxidizes only the reducing end-groups (aldehyde) of cellulose macromolecules to carboxylic groups, while the degree of polymerization of cellulose is not reduced.^{28,30}

All the modified flax fibers had a higher α -cellulose content (85–96 %) compared to the unmodified fibers (75.81 %), due to removal of non-cellulosic constituents. The high concentration of α -cellulose in all the modified fibers, together with the decrease in the copper number, is evidence that the fiber cellulose remained unimpaired (Table S-II). The observed decrease in the copper number was more pronounced for the flax fibers modified with NaOH. This could be explained by the removal of hemicelluloses under alkaline conditions, as well as low molecular weight fractions of cellulose, both being rich in reducing end groups. The modification temperature had the largest effect on the decrease in the copper number, followed by the NaOH concentration, while the duration of treatment had the smallest effect. In the case of flax fibers modified with NaClO₂, the observed decrease in the copper number could be explained by the removal of low molecular weight fractions of cellulose and oxidation of the reducing end groups of cellulose to carboxyl ones. However, the small increase in the copper number obtained for flax fibers modified under severe conditions, *i.e.*, with the higher concentrations of NaClO₂ (15 and 20 g L⁻¹), could be ascribed to cellulose chain scission.³¹

Morphology and fineness of the modified flax fibers

The removal of non-cellulosic substances from the middle lamella, which links elementary flax fibers, leads to disintegration and separation of technical flax fibers (Fig. 2). On the images obtained by SEM, shown in Fig. 2, changes in surface morphology and fiber separation between unmodified (Fig. 2a) and samples modified under different conditions (Fig. 2b–e) can be seen. The unmodified fibers (diameter range 60–80 μ m) still seem to be gathered into bundles, without visible separation of the fibers. The presence of a surface layer containing numerous debris originating from non-degraded cortical tissues, waxy substances, or peptic cements was noticed (Fig. 2a). After alkali treatment, the surface topography was entirely modified; the surface was free of impurities and a good separation of fibers was observed (Fig. 2b–d). The divided fibers exhibited a considerably cleaner surface, which indicates that most of the fiber junctions were dissolved. In the case of flax fibers modified at room temperature and lower alkali concentrations, some residual non-cellulosic components or precipitate of the dissolved lignin could occasionally be observed on the surface of the flax fibers (Fig. 2b). In addition, modification with 10 and 18 % NaOH at room temperature and under mild conditions resulted in textured flax fibers (Fig.

2b and c). Good fiber disintegration and separation, suggesting relative freedom from hemicelluloses and lignin, were observed in the case of fibers modified with NaOH and NaClO₂ under the most severe conditions (Figs. 2d and e). Furthermore, modification with NaClO₂ resulted in fiber fibrillation while modification with boiling NaOH results in smoother fiber surfaces.

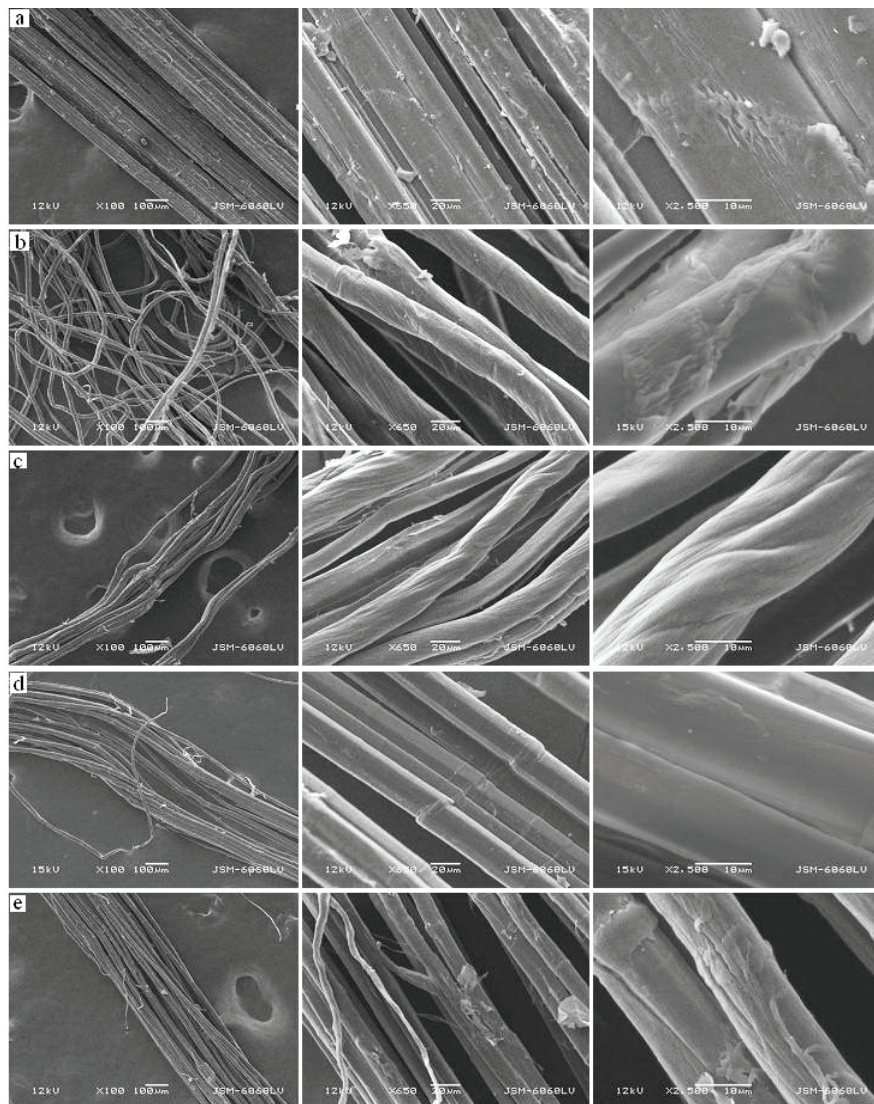


Fig. 2. SEM micrographs of flax fibers: a) unmodified fibers, b) fibers modified with 10 % NaOH, room temperature, 120 min, c) fibers modified with 18 % NaOH, room temperature, 120 min, d) fibers modified with 10 % NaOH, boiling temperature, 120 min and e) fibers modified with NaClO₂, boiling temperature, 60 min.

The separation of the flax fibers significantly increased their fineness, *i.e.*, finer fibers were obtained. The changes in fineness of the flax fibers after modification are shown in Fig. 3. After removal of the non-cellulosic substances in the modification process, the values for fineness of modified fibers was reduced about 4-fold, from 11.23 tex for the unmodified sample to 2.76 tex for the FC20B60 sample, which may have positive influence on the processing of flax fibers. Consequently, the increased aspect ratio, surface area of the fibers and the amount of cellulose exposed on the fiber surface may improve fiber–matrix interfacial bonding in case of composites, and/or cellulose interaction with functionalizing agents in case of further modification.

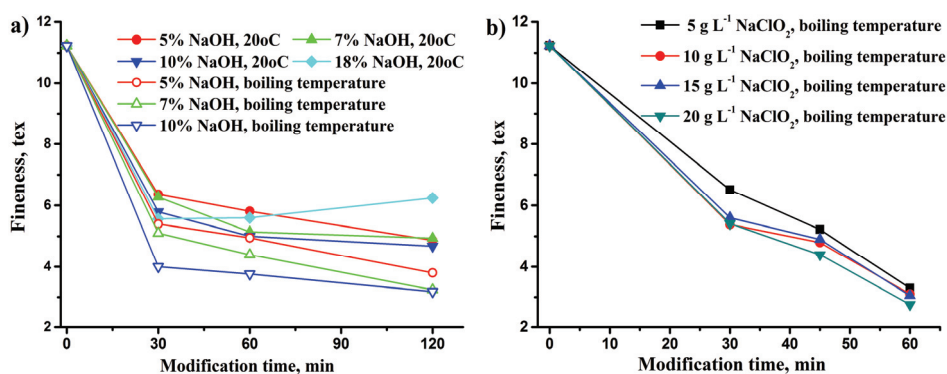


Fig. 3. Effect of the modification conditions on the fineness of flax fibers modified with: a) NaOH and b) NaClO₂.

Prolonging the modification time and increasing the concentration of the modification agent lead to decreased values for fineness, *i.e.*, the fineness of modified fibers were in the range from 6.36 tex (sample FH5R30) to 2.76 tex (sample FC20B60). The exception of this is the treatment with 18 % NaOH at room temperature, when the fineness value initially decreased (30 min treatment) and then increased. This could be explained by modification under mild conditions and the removal of hemicelluloses accompanied by swelling and shrinkage of the ultimate cells, which result in some disorientation of the fibrils (Fig. 2c). The duration of treatment had the largest effect on fiber fineness, followed by the modification temperature (in the case of alkali treatment), while concentration had the smallest effect. Since the concentration and modification temperature had higher effects on hemicelluloses and ligin removal than the treatment time (Table S-II), the obtained results could be explained not only by the prolonged time required for fiber swelling and shrinkage, as well as polymorphic transformation of cellulose, but also by the positive effect of prolonged stirring, *i.e.*, mechanical treatment, on fiber separation. The modified flax fibers were soft to the hand, unlike the unmodified fibers that are coarse and stiff.

Influence of chemical treatment on sorption properties of flax fibers

Changes in the chemical composition of flax fibers (*i.e.* the removal of hemicelluloses and lignin), as well as changes in the fiber structure (*i.e.* fiber fibrillation, disorientation of the fibrils, changes in the ratio of amorphous and crystalline regions, polymorphic transformation of cellulose I to cellulose II) during the chemical treatment cause changes in the sorption properties of flax fibers that were evaluated by determination of iodine sorption value and water retention value. The iodine sorption value (*ISV*) and crystallinity index (*CrI*) for the unmodified and modified flax fibers are presented in Table S-III of the Supplementary material. Iodine sorption value is a measure of the accessibility of fibers to aqueous solutions in the amorphous area and is inversely proportional to the fiber crystalline phase, expressed by the crystallinity index. As could be seen from the obtained *ISV* and *CrI* values (Table S-III), the NaOH and NaClO₂ treatments differently influenced the accessibility of the flax fibers and the ratio of amorphous and crystalline regions. Generally, the chlorite treated flax fibers have lower *ISV* values (from 88.2 to 97.2) and higher *CrI* values (from 76.4 to 78.6) compared to the unmodified flax fibers (*ISV*, 118.1; *CrI*, 71.3), while in the case of the NaOH treatments, a decrease in fiber accessibility was observed only for the lowest employed concentration (5 %). These lower iodine sorption values, *i.e.*, increased crystallinity, are the consequence of the removal of easily accessible non-cellulosic adsorbing material (*i.e.*, hemicelluloses and lignin), which is in agreement with results obtained for sodium chlorite-modified hemp fibers⁶ and alkali-modified flax^{12,32} and *Agave americana* L. fibers.¹⁵ For higher NaOH concentrations (>10 %), the observed increase in the iodine sorption value (up to 154.6), *i.e.*, a slight decrease in the crystallinity (*CrI* values up to 62.5), could be explained by the polymorphic transformation of cellulose I to cellulose II, as was reported by Ben Sghaier *et al.*¹⁵ During this process, the alkali penetrates into the flax fibers and they swell disrupting the crystalline regions, the cellulose chains rearrange from the native cellulose I to cellulose II; the amount of less ordered material in the fiber increases, while the crystalline part contracts. Under the same treatment time and temperature, the crystallinity index decreased with any increase in NaOH concentration since higher NaOH concentrations induce a considerable increase in swelling of cellulose microfibrils and dissociation of hydrogen bonds in cellulose I polymorph, and a portion of this during transformation to cellulose II misaligned leading to a decrease in cellulose crystallinity. On the other hand, under the same treatment time and NaOH concentration, the crystallinity index increased with increasing treatment temperature due to more intensive removal of non-cellulosic material, such as hemicelluloses and lignin, at higher temperatures.

Flax fibers–water interactions could be explained as a competition of hydrogen-bond formation between the hydroxyl groups of the cellulose polymer (but

also non-cellulosic materials, mainly hemicelluloses and lignin) and between that of the polymer and a water molecule or a water cluster. The water penetrates inside the fiber, breaks the secondary interactions between cellulose macromolecules and is adsorbed into the fiber by hydrogen bonds, which causes swelling of the fibers. Furthermore, after immersing flax fibers in water, they swell and imbibe considerably more water than they are capable of holding. The total water holding capacity of a fiber could be estimated by determining the water retention values. Water retention values of flax fibers modified with NaOH and NaClO₂ are presented in Fig. 4.

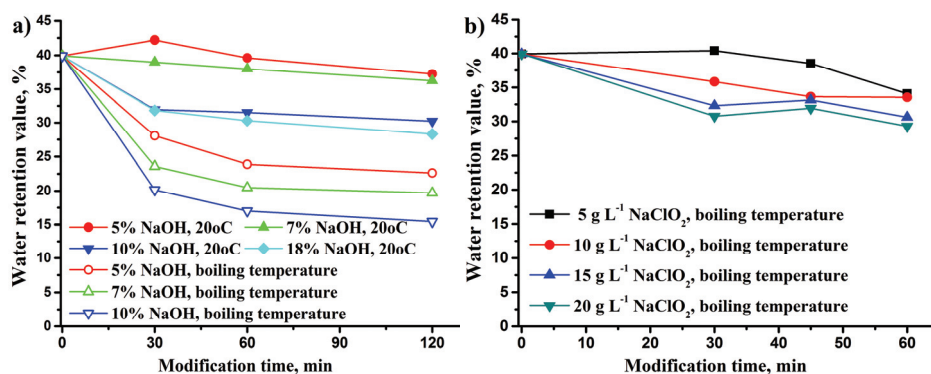


Fig. 4. Effect of the modification conditions on the water retention of flax fibers modified with: a) NaOH and b) NaClO₂.

Water retention capacities of fibers modified with NaOH and NaClO₂ were lower in comparison with initial fiber (39.91 %), except for the fiber samples FH5R30 (42.23 %) and FC5B30 (40.41 %), which showed small increases in the water retention capacity.

As shown in Fig. 4, the water retention capacity of the alkali-modified fibers decreased with increasing concentration of NaOH and modification time. Although treatment with NaOH removes fats and waxes (*i.e.*, the hydrophobic layer on the fiber surface),⁷ the modified fibers were incapable of keeping water molecules in their structure during centrifugation due to the simultaneous removal of hemicelluloses (Table I), which were situated in the interlamellar layers and amorphous areas. A similar decrease in water retention capacity of alkali-treated fibers was also observed during the alkali scouring of flax fibers,^{5,7} as well as alkali-treated hemp fibers.²⁷

The decrease in water retention capacity of flax fibers modified with NaClO₂ was not large compared to the unmodified fibers because NaClO₂ mainly removes lignin without significant removal of hemicelluloses (Table S-II) that are the main water holding components in flax fibers. For this reason, fibers with

progressively removed lignin and slightly increased crystallinity (Table S-III) are capable to retain more water than the alkali-treated flax fibers.

Evaluation of tensile properties of unmodified and modified flax fibers

Since the modification of flax fibers leads to changes in their chemical composition, crystallinity and fineness, changes in the mechanical properties of modified fibers were also to be expected. The effect of both chemical treatments on fiber tensile strength can be seen in Fig. 5.

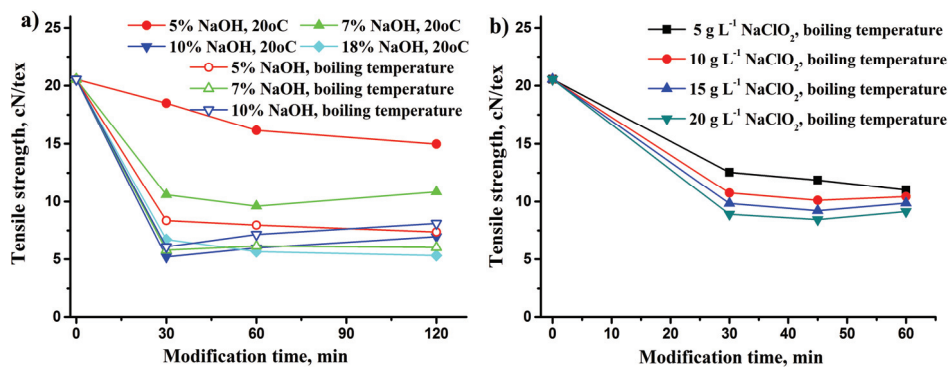


Fig. 5. Effect of modification conditions on the tensile strength of flax fibers modified with: a) NaOH and b) NaClO₂.

The tensile strength of all modified fibers was reduced, with maximal decrease obtained after 30 min of modification. The tensile strength of the alkali- and the chlorite-modified flax fibers decreased with increasing concentrations of modification agents, while over time, the tensile strength initially decreased and then increased. The loss in tensile strength could be ascribed to increased hemicelluloses and lignin removal (Table S-II) and/or fiber damage during treatment, *i.e.*, kick band (Fig. 2d), fiber fibrillation (Fig. 2e), *etc.*, while the observed slight increase in tensile strength with prolonged treatment could be ascribed to the fact that after removal of a large quantity of lignin, the middle lamella became more homogeneous, while the hemicelluloses removal caused less dense and rigid interfibrillar areas, both of which lead to an increased capacity for restructuring and orientation of the new fibrils. Furthermore, with prolonged treatment, fiber refinement, cleansing of the fiber surface from non-cellulosic components and fibrils detachment from the fiber surface were more pronounced. In the same manner, Muenstri *et al.*³³ reported a decrease in tensile strength of chlorite-modified coconut fibers to a minimum and then an increase with increasing amounts of lignin removal.

Exception of such behavior showed flax fibers modified with the lowest concentration (5 % NaOH and 5g L⁻¹ NaClO₂) and fiber modification under texturing conditions (18 % NaOH, under mild conditions), for which a slight tensile

strength decrease was observed with further prolongation of the treatment. In the case of fibers modified under texturing conditions (18 % NaOH, under mild conditions), the observed drop in tensile strength could be explained by the fact that during removal of hemicelluloses, swelling, shortening, and disorientation of the fiber fibrils occurred (Fig. 2c) since fibers were modified without tension. The same decrease in tenacity of chemically textured fibers was also observed during chemical texturing of juta fibers by Mukherjee and coworkers³¹ and hemp fibers by Kostic and coworkers.²⁷

Influence of chemical treatment on the whiteness index

The values of the whiteness index of unmodified flax fibers and the flax fibers modified with NaOH and NaClO₂ are presented in Fig. S-1 of the Supplementary material.

The removal of non-cellulosic components containing chromophore groups (Table S-II) increases the degree of whiteness of the modified flax fibers compared with the degree of whiteness of unmodified fibers, which was 22.4 %. Much higher degrees of whiteness were achieved in the samples treated with NaClO₂ compared with the samples treated with NaOH, as was expected due to the oxidative nature of NaClO₂ and removal of lignin to a higher extent (up to 96 %).

In the case of fibers modified with NaOH at 20 °C, the highest degree of whiteness (50.6 %) was achieved with treatment with 7 % NaOH for 120 min. If interest lies in decreasing treatment time, this could be achieved by increasing the sodium hydroxide concentration 10 %, when a similar effect could be achieved in 60 min. A further increase in the concentration and prolongation of the treatment time did not significantly increase the degree of whiteness.

The degrees of whiteness of fibers modified at the boiling temperature were lower compared with the samples modified at 20 °C and decreased with increasing NaOH concentration and treatment time. This could be explained by oxidation of hydroxyl groups under alkaline conditions to the aldehyde and keto groups and the formation of conjugated carbonyl structures, which provides a yellow color to cellulose. Furthermore, the addition of water, *i.e.*, wetting of the fibers, was followed by the disappearance of the yellow color due formation of tautomeric enols or hydrates, non-conjugated carbonyl structures that absorb in the near UV at around 270–280 nm.³¹

The degrees of whiteness of flax fibers modified with NaClO₂ were significantly higher compared with that of the unmodified flax fibers and increased with increasing NaClO₂ concentration and prolongation of the treatment time. During chlorite treatment, intensive oxidation of the chromophore groups, which are carriers of fiber color, occurred with the removal of accompanying substances. The highest degree of whiteness was achieved for the flax fibers modified with 20 g L⁻¹ NaClO₂ for 60 min (FC20B60).

CONCLUSIONS

The obtained results indicate that the chemical treatments undoubtedly change the chemical composition, *i.e.*, alkali treatment leads to hemicelluloses removal (up to 72 % of hemicelluloses removed) and chlorite treatment leads to lignin removal (up to 96 % of lignin removed), and induce a modification of the structure and properties of the flax fibers. Increases in the crystallinity were observed for the 5 % NaOH treatments, as well as all the NaClO₂ treatments, while for higher NaOH concentrations, the mercerization phenomenon induced a slight decrease in the crystallinity.

Analyses of obtained results showed that the modification of the flax fibers induced a high level of fiber separation. After removal of the non-cellulosic substances in the modification process, the values for the fineness of the modified flax fibers were reduced from 11.23 tex for the unmodified fibers to 2.76 tex for the FC20B60 sample. Images obtained by SEM showed that modification with NaClO₂ results in fiber fibrillation while modification with NaOH at boiling temperature resulted in smoother fiber surfaces. In contrast to coarse and stiff unmodified fibers, the modified fibers are soft to the hand.

The tensile strength of all treated fibers was reduced, with the maximal decrease being obtained after 30 min of modification. The loss in tensile strength could be ascribed to hemicelluloses and lignin removal and/or fiber damage during treatment, *i.e.*, kick band, fiber fibrillation, *etc.* The water retention values of the modified flax fibers were lower than the value of the untreated flax fibers. The progressive removal of hemicelluloses had a more significant influence on the water retention ability of flax fibers than the removal of lignin. Applied chemical treatments have a considerable influence on whiteness index of flax fibers. Flax fibers modified with NaClO₂ have a higher whiteness index (59.9–71.1 %) than alkaline modified fibers (50.6 %).

The gained comprehensive knowledge enables increased refinement quality and alteration of the properties of flax fibers in a defined manner.

SUPPLEMENTARY MATERIAL

Details concerning the flax fibers, their applications, chemical treatment scheme, the chemical composition and copper number, list of samples, iodine sorption values, crystallinity index values and whiteness index value of untreated and treated flax fibers are available electronically from <http://www.sbd.org.rs/JSCS/> or from the corresponding author on request.

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ИЗВОД
УТИЦАЈ ХЕМИЈСКОГ МОДИФИКОВАЊА НА ХЕМИЈСКИ САСТАВ И СВОЈСТВА
ВЛАКАНА ЛАНА

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Модификовање влакана лана растворима натријум-хидроксида и натријум-хлорита, при различитим условима, извршено је у циљу разјашњавања ефеката уклањања хемицелулоза и лигнина на морфологију и својства влакана лана, али и побољшања квалитета влакана. Квалитет влакана лана окарактерисан је одређивањем њиховог хемијског састава, финоће, степена белине, механичких и сорпционих својстава. Оба третмана, третман алкалијама којим се прогресивно уклањају хемицелулозе (до 72 %) и третман хлоритом којим се прогресивно уклања лигнин (до 96 %), проузроковала су значајне промене у морфологији и својствима влакана лана. Третман 5 % NaOH, као и сви третмани са NaClO₂, довели су до повећања кристалности влакана лана, док је третман са раствором NaOH већих концентрација, услед процеса мерцеризације, узроковао смањење кристалности. Модификовање влакана лана NaClO₂ имало је за последицу фибрилизацију влакана, док је модификовање алкалијама на температури кључања довело до чишћења површине влакана и добијање влакана са глатком површином. Оба третмана праћена су смањењем јачине на кидање и способности задржавања воде модификованих влакана, при чему је ово смањење најизраженије код влакана модификованих алкалијама на температури кључања. Веће повећање финоће и степена белине добијено је код влакана модификованих са NaClO₂.

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