Effect of hydrogen-peroxide treatment on the physico-mechanical properties of flax fibers

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Flax fibers contain cellulose and different impurities (hemicelluloses, lignin, pectin, waxes and fats, mineral salts, natural coloring matter and water soluble compounds). From the ecological and industrial aspect, hydrogen peroxide is the most acceptable component for modification of flax fibers. The aim of the modification of flax fibers is to remove non-cellulose components and improve the fiber quality without significant changing of the mechanical properties. Flax fibers were treated with hydrogen peroxide solutions at concentrations 1%, 2% and 4% at 50 °C, 80 °C and boiling temperature for time period of 60 min. With the removal of non-cellulosic substances from fibers, it has been achieved a high degree of fiber separation and a significant increase of modified fibers fineness. The value for fineness of modified fibers was reduced about 2-4-fold and the modified flax fibers were softer to the hand, unlike unmodified fibers that are very coarse and stiff. However, the weight loss and removal of lignin, which gives the fibers strength, as well as a partial damage of the cellulose itself during the severity of treatment, brought to reduction in the tensile strength of the modified fibers.

INTRODUCTION

Flax (Linum usitatissimum) is an ancient crops that has been cultivated in many regions as an important raw material for textile production, oil and food (Gordon Cook, J., 1984; Pasković, 1966). The oldest flax findings date from Kavkaz 35000 years ago (Kvavadze et al., 2009). It is fascinating that some of these fibres were coloured and cut, indicating "advanced" technologies in the dawning of mankind. Flax clothing dominated in warm regions of ancient Mesopotamia and Egypt, as it offered ideal skin protection. Lignin in flax fibres is an excellent absorbent of ultraviolet radiation (Zimniewska et al., 2012). Flax fibre (linen) can increase the alfa-immunoglobulin content in humans and result in lower miographic tension of muscles, lower body temperature and sounder sleep (Kozlowski, 2001; Zimniewska et al., 2004). Unfortunately, flax production in the Balkan region was discontinued in the 1960's when cheap synthetic fibres replaced natural ones. An extended list of scientific studies about linseed/flax curative traits confirms the importance of this crop, which has been neglected in Balkan region for half of one century (Kozlowski, 2001, Nozinic et al., 2013; Zimniewska et al., 2004). The renewed global interest in this crop has also turned the attention in Bosnia and Herzegovina to the importance of returning the flax production, especially considering rich tradition of growing and processing of this crop in the past (Lazić et al., 2017; Lazić, 2018; Lazic et al., 2021).

Today, flax is a multiuse, multifunctional crop that provides raw material to a large number of traditional and innovative industrial applications (Jhala & Hall, 2010). With the development of new processes for fibers separation from the plant stems, which became more economical and environmentally friendly, together with the adoptions of modern trends and consumer demands for the natural materials, flax fibers have become very appealing and profitable on the market (Lazic et al., 2017). As for the textile applications, flax fibers are increasingly used due to their excellent properties, *i.e.*, very high strength, specific luster and handle, high absorbency and hygroscopicity, good thermal and electrostatic properties, protection against UV radiation, lack of any allergenic effect, optimum conditions for the skin, possibility of use in blends with cotton and chemical fibers, as well as many different possibilities for fiber modification in order to impart special or modify existing fiber properties, such as hydrophilicity, hydrophobicity, sorption, antimicrobial and other properties (Zimniewska et al., 2004; Abdel-Halim et al., 2010; Belgacem & Gandini, 2005; Surina et al., 2013; Alix et al., 2009).

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Flax fibers again have become a very important textile raw material for the textile industry. However, the processing of flax fibres is presently limited, as the textile industry has not yet adapted to thus product. 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 (Buchert et al., 2001; Mustata et al., 2013). These non-cellulosic substances have a negative influence on the processing of flax and restrict the application of flax fibers (Abdel-Halim et al., 2010; Fakin et al., 2006; Kostic et al., 2010). Therefore, in order to reduce the contents of non-cellulosic substances and reach high values for textile and technical applications, flax fibers have to be specially prepared or modified regarding homogenization and improvement of the fiber structure and 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 (Cao et al., 2012; Fakin et al., 2006; Surina et al., 2013). From the ecological and industrial aspect, hydrogen peroxide is the most acceptable agent for modification of flax fiber (Farooq et al., 2013; Liu et al., 2018). In this paper, chemical treatment of raw flax fibers, *i.e.*, treatment with hydrogen-peroxide solution under different conditions, is performed to increase the refinement quality, and improve the properties of flax fibers.

MATERIALS AND METHODS

Materials. Domestic water-retted flax fibers obtained from the flax Venica variety (Czech Republic) grown at the experimental grounds in the vicinity of Banja Luka (the Republic of Srpska, Bosnia and Herzegovina) were used in this investigation. Chemical composition of used long flax fibers is water solubles–1.81%, fats and waxes–1.73%, pectin–6.97%, α-cellulose–75.81%, hemicelluloses–7.84% and lignin–4.03%. All used chemicals were of analytical grade.The dry extracts prepared in this way were stored in a dark place until the moment of use. The concentrations of used solutions were determined experimentally. The prepared dry extract of A. melanocarpa diluted to 45 mg/mL, and the extract of C. mas diluted to 22.5 mg/mL in 6% (v/v) ethanol and used for casing treatment. The duration of submersion was 24h for all casings.

Hydrogen peroxide treatment. Flax fibers (F) were treated with hydrogen peroxide (P) solutions (1%, 2% and 4% w/v H_2O_2), at pH 10, at different temperature (50 °C, 80 °C and boiling temperature), 1:30 liquor ratio, for 60 min (list of samples are shown in Table 1). Sodium silicate (10 g/L Na_2SiO_3) and magnesium sulfate (0.3 g/L $MgSO_4$) as stabilizers of the bath were used to protect cellulose from degradation and to improve the efficiency of H_2O_2. Thereafter, the treated samples were neutralized by 1% hydrochloric acid, washed with distilled water and dried. The influence of chemical treatments on features of flax fibers was evaluated by determination of weight loss, chemical composition, fineness and tensile strength.

Determination of weight loss and chemical composition. The direct gravimetric method described by (Koblyakov, 1989) was used to determine the weight loss which is result of hydrogen peroxide treatment of flax fibers. Chemical composition of control sample and each of treated samples was determined according to the procedure described by Soutar and Bryden (Garner, 1966), which is based on the successive removal of water soluble substances (extraction by boiling water, 30 min), fats and waxes (extraction with ethanol/benzol 2:1 mixture), pectin (boiling in 1% ammonium oxalate,

Table 1. The chemical treatment conditions and list of samples

Modification condition			Sample code
Concentration	Temperature	Time, min	
Unmodified sample-control			FC
1% H_2O_2	50°C 80°C Boiling temperature	60	FP1T50 FP1T80 FP1TB
2% H_2O_2	50°C 80°C Boiling temperature	60	FP2T50 FP2T80 FP2TB
4% H_2O_2	50°C 80°C Boiling temperature	60	FP4T50 FP4T80 FP4TB

1 h), lignin (0.7% $NaClO_2$, boiling temperature, 2 h) and hemicelluloses (17.5% NaOH, room temperature). The copper number of investigated fibers was determined according to the standard TAPPI T-430 (1998). Also, the micro Kappa number method (TAPPI UM 246, 1991) was used to estimate the residual lignin content in flax fibers.

FE-SEM analysis. Morphological features of fibers were examined by field emission scanning electron microscopy (FESEM, Mira3Tescan), after sputtering with gold.

Determination of fineness. The fineness in tex was determined as per standard method (SRPS F.S2.212, 1963) by dividing the mass of fibers by their known length.

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 (Koblyakov, 1989). As flax fibers very 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.

RESULTS AND DISCUSSION

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. The quality of unmodified and modified flax fibers was characterized by determining their chemical composition, weight loss, fineness and mechanical properties.

Influence of hydrogen peroxide treatments on the chemical composition of flax fibers. The effect of modification conditions on the weight loss of the modified flax fibers is shown in Fig. 1. 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., with the increase of both H_2O_2 concentration and processing temperature, the weight loss of the flax fibers increases. The highest weight loss (13.4%) has been registered for the flax fibers treated with 4% H_2O_2 solution at the boiling temperature (sample F4TB), while the smallest weight

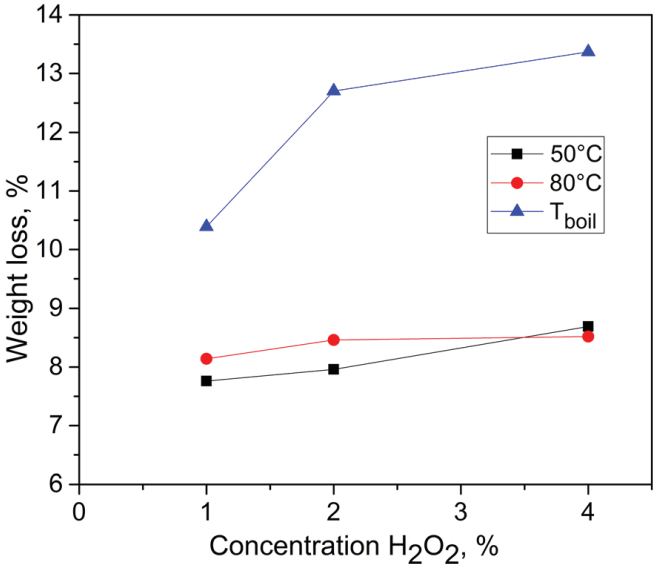

Fig. 1. Effect of temperature and H_2O_2 concentration on the weight loss of flax fibers

loss (7.8%) has been determined for the fibers treated under the mildest conditions, i.e. 1% H_2O_2 solution at 50 °C (sample FP1T50). The obtained results clearly showed that treatment with H_2O_2 leads to a significant removal of noncellulosic substances from flax fibers, which is in agreement with literature data (Milanovic et al., 2012). The chemical compositions of the unmodified and chemically modified flax fiber samples, i.e. effect of hydrogen peroxide treatment conditions on the chemical composition of flax fibers: content of a-cellulose, hemicelluloses and lignin (Kappa number), are given in Table 2. The data for copper number, as a measure of reducing end groups and cellulose degradation in flax fibers, are also presented.

The results in Table 2. show the value of Kappa number of treated flax fibers lower (10–15%) than the value of Kappa number of control flax fibers, which indicates that hydrogen peroxide treatment leads to the removal of lignin from the flax fibers. Accordingly, the highest degree of lignin removal (Kappa number 6.14) has been achieved for the sample treated with 4% H_2O_2 at the boiling temperature (FP4TB). Under these treatment conditions, the value of Kappa number has been even 4.5 times lower than the value of Kappa number of control flax fibers. Looking at the results of hemicelluloses content in Table 2 it seems that it content has increased after the treatment. However, if we carefully considered the data obtained for the Kappa number related to the lignin content (Table 2.) and weight loss (Fig. 1.) of the treated flax fibers, it is clear that the difference between the weight loss and the loss of lignin is accounted for other noncellulosic components (i.e. water solubles, fats and waxes, pectin and hemicelluloses), which are lost during the treatment. The higher content of a-cellulose in

Table 2. The chemical composition and copper number of control and treated flax fibers

Sample code	α -cellulose content, %	Hemicelluloses content, %	Kappa number	Copper number
FC	75,81	7,84	27,53	1,37
FP1T50	84,33	9,60	7,92	1,21
FP1T80	84,68	10,41	7,62	0,99
FP1TB	86,11	10,00	7,20	0,90
FP2T50	84,72	9,82	7,57	1,16
FP2T80	84,87	10,15	7,40	0,94
FP2TB	86,41	9,34	7,12	0,87
FP4T50	84,97	10,23	7,20	1,00
FP4T80	85,21	10,13	6,88	0,86
FP4TB	87,35	9,24	6,14	0,82

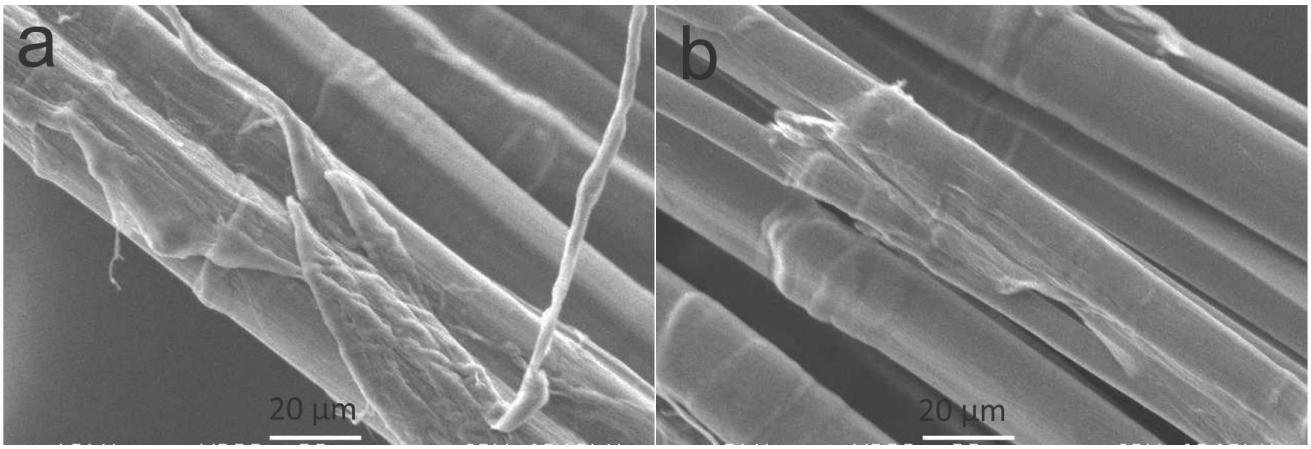

Fig. 2. SEM photographs of control (a) and flax fibers treated with 4% H_2O_2 at 50 °C (b)

all treated fibers (84.33–87.35%) compared to the control sample (75.81%), together with the decrease in the copper number, indicates that the fiber cellulose has remained unimpaired.

Morphology and fineness of the modified flax fibers. The hydrogen peroxide treatment leads to the removal of non-cellulosic substances from the middle lamella, which links elementary flax fibers, leads to disintegration and separation of technical flax fibers giving a relatively cleaner fiber surface. On the images obtained by SEM (Fig. 2.) changes in surface morphology and fiber separation between unmodified (Fig. 2a.) and modified samples (Fig. 2b.) can be seen.

After modification, the values for fineness of modified fibers was reduced about 4-fold, from 11.23 tex for the unmodified sample to 2.84 tex for the FP4TB sample, which may have positive influence on the further processing of flax fibers (Fig. 3.).

Increasing processing temperature and concentration of the modification agent lead to decreased values for fineness, i.e., the fineness of modified fibers were in the range from 4.54 tex (sample FP1T50) to 2.84 tex (sample FP4TB).

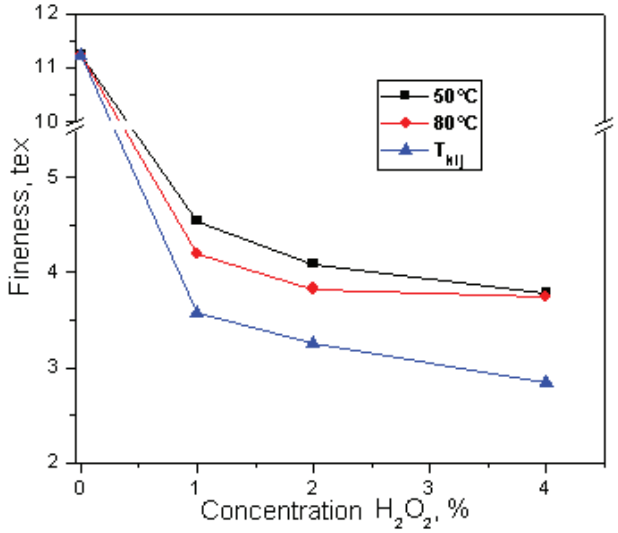

Fig. 3. Effect of the modification conditions on the fineness of flax fibers

Tensile properties of unmodified and modified flax fibers. The effect of hydrogen peroxide treatments on fiber tensile strength can be seen in Fig. 4., while in Fig. 5. is shown the relationship between weight loss and tensile strength.

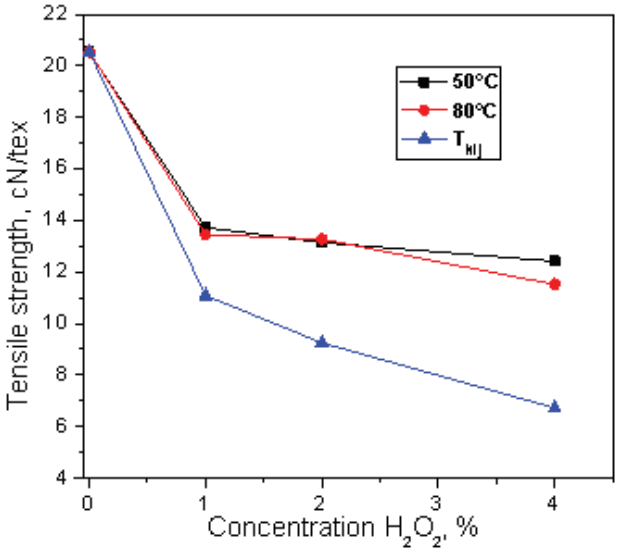

Fig. 4. Effect of modification conditions on the tensile strength of flax fibers modified with H_2O_2

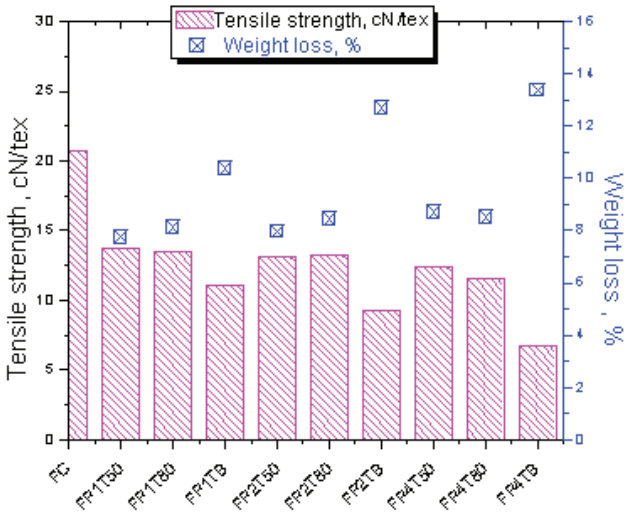

Fig. 5. Weight loss and tensile strength of the unmodified flax fibers and flax fibers modified with hydrogen peroxide

The tensile strength unmodified fibers was 20.53 cN/tex, while the tensile strength of all modified fibers was reduced and decreased with increasing processing temperature and concentrations of hydrogen peroxide in the range from 13.72 cN/tex (sample FP1T50) to 6.72 cN/tex (sample FP4TB).

The loss in tensile strength could be ascribed to weight loss (Fig. 5.), fiber damage during treatment, fiber fibrillation etc.

CONCLUSION

The obtained results indicate that the chemical treatment of flax fibers using hydrogen peroxide leads to removal of noncellulosic substances and induce a modification of the structure and properties of the flax fibers. With the removal of non-cellulosic substances from fibers, it has been achieved a high degree of fiber separation and a significant increase of modified fibers fineness. The value for fineness of modified fibers was reduced about 2-4-fold and the modified flax fibers were softer to the hand, unlike unmodified fibers that are very coarse and stiff. The values for the fineness of the modified flax fibers were reduced from 11.23 tex for the unmodified fibers to 2.84 tex for the FP4TB sample. Images obtained by SEM showed that modification with hydrogen peroxide results in fiber fibrillation and in smoother fiber surfaces. In contrast to coarse and stiff unmodified fibers, the modified fibers are soft to the hand. However, the weight loss, fiber fibrillation and removal of lignin, which gives the fibers strength, as well as partial damage of cellulose itself during the severity of treatment, brought to reduction in the tensile strength of the modified fibers.

The tensile strength of all treated fibers was reduced and the maximal decrease being obtained for sample FP4TB (6.72 cN/tex).

The established correlations between the structure and properties of flax fiber, obtained by selective removal of hemicellulose and lignin, allow the application of hydrogen peroxide for fiber modification, whereby the fiber structure can be altered in a wide range, with the possibility of obtaining the fibers of „desired" properties.

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