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Influence of Enzymatic Treatment on the Flax Fibre Morphological Structure, Physico-Chemical Properties and Metrological Parameters of Yarn

Abstract
The effect of enzymatic treatment with cellulolytic and pectinolytic enzymes on the morphological structure and properties of flax fibre and yarn has been examined. The enzymatic treatment has been introduced as a factor assisting the efficiency of the bleaching process. Attention has principally been concentrated on the application of such bleaching technologies which eliminate the chlorine compounds, and at he same time secure obtaining metrological indices and aesthetic values of yarn and physico-chemical properties of the fibres at the required level.

Key words: *flax fibres, enzymatic treatment, bleaching, morphological structure, physico-chemical properties, mechanical properties, whiteness.*

Introduction

The technical progress observed recently in the textile industry is intended to make manufacturing processes friendlier to the environment. Therefore, technologists and researchers are paying more and more attention to the possible use of enzymes in finishing processes, as these natural agents undergo complete degradation in effluents [1,2]. By using enzymatic agents in finishing processes, one can obtain textile goods with an improved comfort of use (a soft handle or feel, decreased fabric weight, reduced tendency to pilling) and increased lustre, as well as reduced shrinkage in the case of wool fabrics [3-8].

The major problem in using enzymatic agents is their correct selection from the point of view of the effects obtainable during treatment [9]. Chemically, enzymes are colloidal macromolecular compounds consisting exclusively of a homogeneous protein substance (monocomponent enzymes) or two or three components – protein and non-protein substances known as the prosthetic group (bi- or multi-component enzymes).

Enzymes are mostly classified on the basis of the reaction they catalyse. Similarly, the names of enzyme groups or particular enzymes are derived from the name of the reaction or the compound which undergoes enzymatic effects. Therefore, the group of enzymes which catalyse the hydrolysis of substrates into simpler compounds with water is called hydrolases, while the enzymes which decompose ester bonds are called esterases, the enzymes catalysing pectin hydrolysis are pectinases, cellulose hydrolysis - cellulases, etc. [10-11].

The large dimensions of enzyme molecules and their spatial arrangement reduce their abilities to penetrate the complex fibre structure. However, in the view of some authors, the action of enzymes on fibres results in the disturbance of fibre structure which, depending on the treatment intensity, assumes the form of partial fibrillation or superficial defibrillation, due to the enzymatic hydrolysis of the fibre material [12-16].

In the textile industry, flax fibres are mostly processed as technical or industrial fibres. The share of partly disintegrated complex fibre (cottonine) in textile processing is still relatively low. One should believe that the trends towards more ‘delicate’, thinner and softer fabrics, as well as towards extending the range of blended fabrics of flax and other fibres, will promote the introduction of higher amounts of complex and even elementary flax fibres into textile processing [17-20].

The quality of the final technical flax fibre (either complex or elementary) will be affected by all the processes used in its isolation, in addition of course to the specific features of the raw material resulting from the plant’s botanical variety and the conditions of its growth. The quality of the final technical fibre also depends on the structure of the elementary fibres, and their arrangement and combination in bunches and in the bundle of technical fibres [21-22].

Considering the effects of enzymatic treatments of cellulose fibres, one may assume that major changes will result from the removal of non-cellulose substances present in the fibres in various amounts as well as those resulting from cellulose decomposition and its partial elimination from fibres. These changes will be followed by the modification of the fibre’s morphological structure and properties (especially surface properties) which will be shown in different properties of the final products (above all, yarns).

The aim of the present study was to examine the effect of enzymatic treatment on the morphological structure and properties of flax fibre, and the metrological parameters of the yarn made of this fibre.

Experimental

Materials

Fibres and yarns
Flax roving with a sliver thickness of 750 tex and wet-spun carded flax yarn with the characteristics given in Tables 1 and 2 were used in the examinations.

Enzymes applied
Two enzymatic agents of a cellulolytic character and one enzymatic agent of a pectinolytic nature were used in the treatments:

Table 1. Characteristics of flax roving used.

Quantitative and chemical compositions	Unit	Value
Combed wet-spun flax 25 x 84	%	66.0
Combed retted flax 25 x 50	%	17.0
Combed retted flax 25 x 84	%	17.0
Hemicellulose content	%	16.0
Lignin content	%	4.5
Pectins content	%	1.5
Polymerisation degree of cellulose	-	3510

Table 2. Metrological parameters of yarn and its chemical constitution.

Parameter investigated	Unit	Value of index
Linear density	tex	120
Tensile strength	cN	1777.8
Tenacity	cN/tex	14.82
Flexural rigidity	$\mu N.m^2$	0.241
Whiteness degree	%	6.7
Polymerisation degree of cellulose	-	3220
Content of hemicellulose	%	12.6
Content of lignin	%	2,6
Content of pectins	%	1,36

- Tinozym CEL of Ciba Geigy A.G. [23],
- Cellulosoft Ultra L of Novo Nordisk [24],
- BioPrep L of Novo Nordisk [24].

Methods

Characteristics of the enzymatic agents activities

The activity of endo-1,4-β-gluconase indicates the enzyme capability to hydrolyse 1,4-β-glycoside bonds resulting in the formation of cellooligosaccharides which are decomposed by cellobiohydrolase and -β-glycosidase into polysaccharides and then to simple sugars (Table 3). According to the literature data, this results in the hydrolysis of 1,4-β-glucoside bonds of cellulose macromolecule in its middle fragments [3].

The activity of pectinolytic agent BioPrep L, according to its manufacturers, is given by the indicator 3000 APSU/g (Alkaline Pectinase Standard Unit). The activity of BioPrep L was determined in accordance with the standard EB-SM-0419.02 [24].

Application conditions of enzymatic agents

Table 4 shows the conditions of enzyme application as proposed by their manufacturers. The enzymatic treatment was run either before or after fibre bleaching with hydrogen peroxide carried out according to the following recipe: 5 ml/l of 35% H_2O_2, 2 ml/l of water glass, 1 g/l of NaOH, 0.5 g/l of Pretepon G, bath ratio 50:1 (samples 8, 11, 26), bath ratio 20:1 (samples 9, 12, 27), temp. 90°C, time - 1 hour, rinsing with water, neutralisation with a water bath containing 3 ml/l of CH_3COOH 50%.

Table 3. Activities of the cellulolytic enzymes.

Enzymatic agent	Activity of endo-1,4-β-gluconase, U/dm³
Tinozym CEL	542.5
Celluosoft Ultra L	500.0

The effects of enzymatic fibre treatments (treatment before the bleaching process - samples 8, 11, 26; treatment after the bleaching process - samples 9, 12, 27) were compared with those obtained in fibre bleaching without enzymes (sample 2 in Tables 5-10) and to the sample of raw fibres (sample 0 in Tables 5-10).

Testing the selected samples of flax fibre and yarn properties

The following properties of the flax fibre and yarn which were subjected to the preliminary treatments and bleaching process were determined:

- electron microscope observations of fibre cross-sections and longitudinal views to assess the degree of elementary filament separation, purification of their surface and the extent of possible fibre damage on a macro scale,
- determination of the average polymerisation degree to assess the extent of fibre destruction [25],
- quantitative determination of the fibre chemical composition (lignin, pectin and hemicellulose contents) to assess the degree of non-cellulose substance removal [26],
- fibre weight loss assessment, [27],
- tensile strength of yarn [28],
- yarn flexural rigidity [29],
- degree of fibre whiteness [30],
- fibre wettability in water [31].

Results

The results of the performed tests are given in Tables 5-10 and illustrated in Figures 1-4.

Discussion

Assessment of changes in the morphological structure of flax fibre

Based on the results illustrated in Figures 1- 4, concerning the cross-sections and longitudinal views of flax fibres subjected to various variants of preliminary treatment in the form of yarn, we may conclude that:

- The yarn treatments applied result in different degrees of fibre disintegration in the complexes of technical fibres forming the yarn, different degrees of fibre purification from lignin and pectin substances, and different degrees of changes in the fibre surface.
- The bleaching of flax fibre with hydrogen peroxide (with the use of the cellulolytic enzyme Tinozym CEL) leads to a good separation of fibres; there are no larger complexes of fibres; the fibre surface is well-purified, and a clear 'digestion' of the fibre surface is observed.
- The peroxide bleaching of flax fibre with the use of the cellulolytic enzyme Cellulosoft Ultra L causes the degree of fibre separation to increase; a low quantity of accompanying substances appears; changes are observed within the areas of the fibre knees, as is a clear 'digestion' of the fibre surface.
- The peroxide bleaching with the use of the pectinolytic enzyme Bio Prep L causes the fibre complexes to disintegrate; fibres in complexes are clearly separated; fibre surfaces are smooth, well-purified from non-cellulose substances.

The comparative analysis of the results from the point of view of the degree of fibre separation, surface purification and changes shows that the most advantageous variants of treatment include the peroxide bleaching with the use of enzymatic agents such as Tinozym CEL and Bio Prep L.

Assessment of changes in the quantitative chemical composition of the fibre

Based on the changes in the quantitative chemical composition of flax fibre (Tables 5 and 6) in terms of fibre purification from non-cellulose substances, we may conclude that:

- The most effective variant of flax fibre treatment is the one which uses pectinolytic enzyme Bio Prep L in the peroxide bleaching process, when the enzymatic treatment is used either before or after the bleaching process (samples 26 and 27).
- A similar degree of fibre purification from non-cellulose substances is obtained in the peroxide bleaching process preceded by the preliminary treatment with the cellulolytic enzyme Cellulosoft Ultra L (sample 12).
- The most extensive changes caused by the applied fibre treatments concern the hemicellulose content, while the content of the other substances is only slightly changed.
- The peroxide bleaching in the conventional version appears to be the least effective fibre treatment in terms of hemicellulose removal.

Assessment of the average polymerisation degree of cellulose

The results of the polymerisation degree of flax fibre cellulose given in Tables 5 and 6 indicate that these changes depend on the treatment variant.

- The average polymerisation degree of cellulose in the case of bleaching aided with the enzymatic treatment depends on the type of the enzyme used.
- The highest value of the average polymerisation degree of cellulose (DP=2900-2920), indicating the lowest fibre damage, is obtained in the peroxide bleaching with the use of BioPrep L.
- A slight decrease in DP to 2560-2620 is observed in the peroxide bleaching with the use of the Enzyme Tinozym CEL.
- The applied variants of fibre bleaching with the use of the enzymatic agent Cellulosoft Ultra L result in considerable decreases in the average degree of cellulose polymerisation (DP=1974-2093).

Assessment of changes in the physical properties of flax fibre and yarn

Linear density of yarn

Based on the data given in Tables 7 and 8, one can observe that:

- The fibre weight loss is strongly dependent on the type of fibre treatment.
- The highest weight losses, at levels of 20.7% and 23%, are observed in the peroxide bleaching aided with the cellulolytic enzyme Tinozym CEL.
- Weight losses at a level of 16% take place in the peroxide bleaching aided with the cellulolytic enzyme Cellulosoft Ultra L.
- The lowest weight losses (comparable to those in the conventional peroxide bleaching, i.e. 10-11%) are observed after the peroxide bleaching aided with the enzyme BioPrep L, irrespective of whether the enzymatic treatment is used before or after the bleaching process.

Table 4. The enzymes application conditions.

Trade name	Dosage	pH	Temperature, °C	Process duration, min
Tinozym CEL	1-2 g/dm^3	4.5 - 5.5	45 - 55	40 - 60
Cellulosoft Ultra L	0.2 - 0.8%	5 - 6	45 - 60	45 - 75
BioPrep L	0.3%	8 - 9	60 - 65	60

Table 5. Results of chemical composition, weight loss and average degree of cellulose polymerisation of flax fibre after bleaching with hydrogen peroxide aided with cellulolytic enzymes.

Sample No.	Content of lignin, %	Content of pectin, %	Content of hemicellulose, %	Weight loss, %	Average polymerisation degree of cellulose
0	2.6	1.36	12.6	-	3220
2	1.5	0.44	4.9	10.0	2676
8	1.3	0.60	1.7	23.0	2560
9	1.5	0.49	2.8	20.7	2620
11	1.4	0.48	2.8	16.0	1974
12	1.2	0.54	1.5	16.2	2093

Table 6. Results of chemical composition, weight loss and average degree of cellulose polymerisation of flax fibre after bleaching with hydrogen peroxide aided with pectinolytic enzyme.

Sample No.	Content of lignin, %	Content of pectin, %	Content of hemicellulose, %	Weight loss, %	Average polymerisation degree of cellulose
0	2.6	1.36	12.6	-	3220
2	1.5	0.44	4.9	10.0	2676
26	1.7	0.59	1.2	10.9	2900
27	1.6	0.40	0.7	11.4	2920

Table 7. Results of metrological parameters of flax yarn after bleaching with hydrogen peroxide aided with cellulolytic enzymes.

Sample No.	Tensile strength, cN	Linear density, tex	Tenacity, cN/tex	Flexular rigidity, μN·m^2
0	1777.8	120.0	14.82	0.241
2	1580.5	108.0	14.63	0.125
8	1510.4	92.4	16.34	0.079
9	1540.3	95.1	16.19	0.094
11	1389.0	100.8	13.78	0.058
12	1412.0	100.6	14.04	0.065

Table 8. Results of metrological parameters of flax yarn after bleaching with hydrogen peroxide aided with pectinolytic enzyme.

Sample No.	Tensile strength, cN	Linear density, tex	Tenacity, cN/tex	Flexular rigidity, μN·m^2
0	1777.8	120.0	14.82	0.241
2	1580.5	108.0	14.63	0.125
26	1344.9	92.7	14.50	0.093
27	1281.0	106.0	12.08	0.087

Assessment of changes in the yarn tenacity

The results of yarn tenacity given in Tables 7 and 8 show that:

- The highest tenacity (over 16 cN/tex) is shown by the yarn after peroxide bleaching aided with the enzymatic agent Tinozym CEL.
- In the case of bleaching aided with the enzymatic agents Tinozym CEL

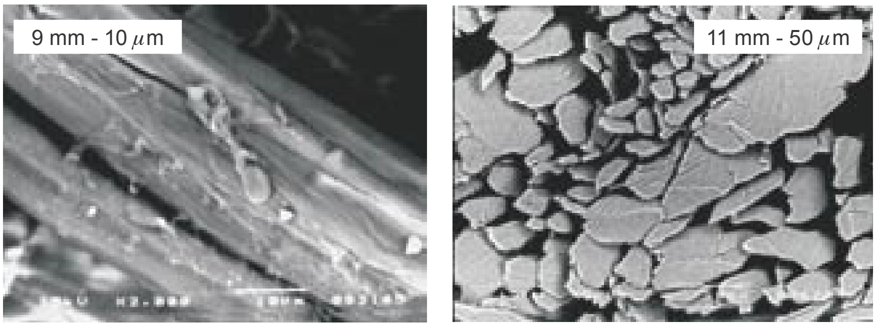

***Figure 1.** Longitudinal view and cross-section of raw flax fibre.*

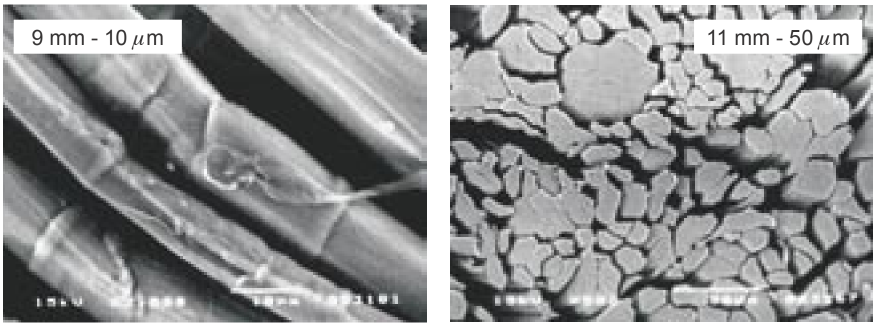

***Figure 2.** Longitudinal view and cross-section of flax fibre after conventional bleaching process.*

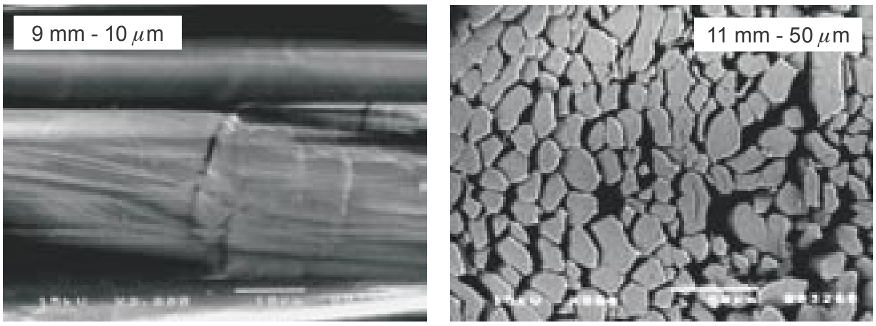

***Figure 3.** Longitudinal view and cross-section of flax fibre after enzymatic treatment with Tinozym CEL and bleaching process.*

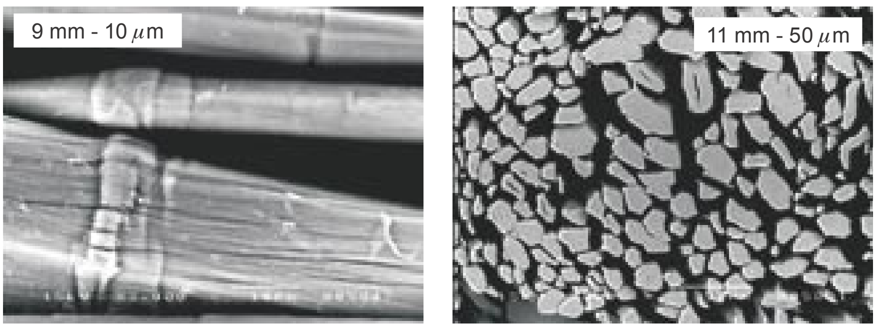

***Figure 4.** Longitudinal view and cross-section of flax fibre after enzymatic treatment with Cellulosoft Ultra L and bleaching process.*

and Cellulosoft Ultra L, the enzymatic treatment applied after the bleaching brings about no differences in the values of yarn tenacity.

- The enzymatic treatment with BioPrep L after the bleaching process causes the yarn tenacity to fall more (by about 2.5 cN/tex) than when the enzymatic treatment is used before the actual bleaching.

Changes in the flexural rigidity of flax yarn

From the data given in Tables 7 and 8 it follows that:

- The lowest values of yarn flexural rigidity are obtained after the peroxide bleaching aided with the cellulolytic enzymes. The most effective agent in decreasing the yarn flexural rigidity is Cellulosoft Ultra L (rigidity index: 0.058 $\mu N/m^2$), with the rigidity index of the initial yarn being at a level of 0.241$\mu N/m^2$. Less effective in these terms is the peroxide bleaching aided with the pectinolytic enzyme (0.087 - 0.093 $\mu N/m^2$).
- Using the enzymatic treatment with the cellulolytic enzyme Tinozym CEL before the bleaching with hydrogen peroxide, one can obtain flax yarn with a lower rigidity than when this agent is applied after the bleaching.
- The peroxide bleaching aided with the pectinolytic enzyme BioPrep L used after the bleaching allows a yarn to be obtained which is softer than when the enzymatic treatment is used before the bleaching.
- The least effective variant in decreasing the yarn rigidity is the conventional bleaching process.

Assessment of the whiteness degree of flax fibre and yarn

The results of the whiteness degree of flax fibre and yarn after the treatments according to the accepted variants, given in Tables 9 and 10 allow us to come to the following conclusions:

- The bleaching of flax yarn by the conventional peroxide process makes it possible to obtain a whiteness degree of 36%.
- The peroxide bleaching aided with the enzymatic treatment causes the whiteness degree of yarn to increase up to 45-53%.
- When the cellulolytic enzyme Tinozym CEL is applied before the peroxide bleaching, the whiteness degree of yarn obtained amounts to 52%; a similar effect is obtained with the use of the pectinolytic enzyme BioPrep L.
- In the peroxide bleaching followed by the treatment with the cellulolytic enzyme Cellulosoft Ultra L, the whiteness degree obtained reaches 53%.

Thus, we can conclude that practically all the variants of peroxide bleaching aided with the enzymatic treatment lead to comparative results of whiteness degree oscillating around 50% (according to standard PN-88/P-82456 - index 1/2 of whiteness degree).

Figure 5. *Longitudinal view and cross-section of flax fibre after enzymatic treatment with BioPrep L and bleaching process.*

The results of the yarn whiteness degree discussed above concern the single-stage bleaching process. To obtain a higher degree of whiteness, it is necessary to use an additional bleaching cycle.

Assessment of the yarn wettability

Based on the results of yarn wettability in water given in Tables 9 and 10, we can state that the peroxide bleaching processes aided with the enzymatic treatments with both cellulolytic and pectinolytic enzymes result in a considerable increase in the fibre wettability with water, as compared to those of raw flax fibre and fibre bleached by the conventional process.

Conclusions

The comprehensive assessment of the effectiveness of preliminary treatment and bleaching processes in terms of their effects on flax fibre and yarn properties leads us to the following conclusions:

Table 9. *Results of whiteness degree and fibre wettability in water after bleaching with hydrogen peroxide and aided with cellulolytic enzymes.*

Sample No.	Whiteness degree, %	Wettability, s
0	6.7	unwettable
2	36.2	5.8
8	52.0	1.2
9	45.3	1.0
11	49.2	1.0
12	53.0	1.0

Table 10. *Results of whiteness degree and fibre wettability in water after bleaching with hydrogen peroxide aided with pectinolytic enzyme.*

Sample No.	Whiteness degree, %	Wettability, s
0	6.7	unwettable
2	36.2	5.8
26	52.1	1.0
27	45.8	1.4

- The introduction of enzymatic treatment as an assisting factor in the hydrogen peroxide bleaching of flax fibre leads to a considerable increase in the fibre whiteness, especially when the enzymatic treatment is carried out before bleaching. This effect consists in increasing the degree of fibre purification from non-cellulose substances, which results in a considerable decrease in the yarn flexural rigidity, with the yarn tenacity remaining unchanged or just slightly reduced.
- In the case of cellulolytic agents, the fibre surface is changed and its smoothness is reduced, which may be considered a desirable effect in the system of fibre conversion into yarn (conventional technologies). In addition, there is good separation of fibres in the complexes of the technical fibres which form the yarn. It seems that, due to the changes mentioned concerning both technical and elementary fibres, the tensile strength of yarn is not lowered, whereas its weight is considerably reduced (an advantageous effect in terms of aesthetic values of the final textiles).
- The enzymatic agent of a pectinolytic character brings about different changes in flax fibres. Its effectiveness is particularly high in the purification of fibre surface and its smoothing. This effect may be reflected in a textile fabric in the form of increased lustre and 'coolness' to the touch.

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