

I.I. Shamolina,  
A.M. Bochek\*,  
N.M. Zabivalova\*,  
D.A. Medvedeva\*,  
S.A. Grishanov\*\*

St. Petersburg State University  
of Technology and Design  
Bol'shaya Morskaya 18,  
191186 St. Petersburg, Russia

\*Institute of Macromolecular Compounds  
of Russian Academy of Sciences,  
St. Petersburg, Russia

\*\*De Montfort University  
The Gateway Leicester, LE1 9BH, UK

# An Investigation of Structural Changes in Short Flax Fibres in Chemical Treatment

## Abstract

The short fibre of oil-flax was studied by IR spectroscopy after fats, waxes and pectins were removed. The changes in the morphology of the fibre after various treatments were studied using SEM.

**Key words:** short flax fibre, IR-spectra, SEM method, fibre morphology.

## Introduction

It is known that among various cellulose-based materials produced from vegetable fibres flax-containing textiles are highly valued for their end-use properties. This is attributed to the fine features of flax fibre structure, morphology and presence of additional substances. Among the advantages of the flax-containing textiles are their high resistance in wear, high comfort, air permeability, good moisture sorption, and low electrical charge [1,2]. One of the problems with flax fibre processing in the textile industry is associated with the utilisation of wastes and short fibres remaining after the separation of long fibres. One method of utilising short flax fibres is the manufacture of flax-cotton blended yarn [3]. However, short flax fibres are different from cotton in their chemical composition because they contain more fats and waxes, lignin, hemicelluloses and pectins [1, 2, 4-7]. This affects the mechanical and end-use properties of flax fibres. Fats, lignin, hemicelluloses and pectins reduce contact angle in comparison with that of cotton fibres [8], which may cause variation in dye uptake. Removing the accompanying substances (pectins and other hemicelluloses) decreases moisture sorption [1] and increases the bio-stability of fibres [6,7]. The existing methods of flax fibre processing are based on the use of acids, alkali, and surfactants [4,9]. It should be noted that fibre treatment with solutions of acid or alkali is always accompanied with some destruction of macro-molecules of polymers (cellulose), and thus reduces the mechanical

characteristics of the fibre. It is therefore necessary to find methods of fibre treatment that would remove most of the fats, lignin and hemicelluloses, but would preserve high mechanical properties and moisture sorption.

The aim of the investigation is to study the influence of methods of fibre treatment on fibre structure and morphology.

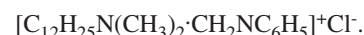
## Experimental

The fibre studied was that of seed-oil flax. The fibres were subjected to treatments aimed towards removing fats, waxes and pectins. The conditions of the treatments are presented in Table 1. As a control sample, bleached cotton fibres were used.

Fats and waxes were removed by treating the fibres with an 8:1 mixture of benzene and ethyl alcohol for 6 hours in a reflux condenser. Pectins were removed by a 0.03N solution of HCl using method [4]. The content of pectins is usually determined by treating fibres with a 1% solution of ammonium citrate [7,10]. However, not all the pectin can be removed by this method [11]. It was shown [12] that most

pectins can be removed from the flax fibres using a 0.03N solution of HCl. Therefore the residual pectins were removed by boiling fibres in the 0.03N solution of HCl for 30 minutes, followed by rinsing with hot and cold water until no reaction towards Cl<sup>-</sup> ions in the wash liquor solution was achieved using AgNO<sub>3</sub> as an indicator. It is interesting to note that hemicelluloses can be partly removed by this treatment; a diluted solution of acid or alkali is commonly used [13] to remove hemicelluloses from wood.

Fibre treatment with a surfactant was carried out in the same conditions as those of treatment with HCl. The surfactant used was dodecyldimethylbenzeneammonium chloride



After the treatment, the fibre samples were rinsed with distilled water and the presence of Cl<sup>-</sup> ions was checked. The samples were then dried at 105°C until constant weight was achieved.

The IR spectra of the samples in KBr tablets were obtained using a Bruker FS-88 IR Fourier spectrometer. Changes in fibre morphology were studied using SEM.

**Table 1.** Flax fibre treatments.

Sample	Description	Treatment	Substances removed	Crystallinity index, $I_{1372}/I_{2900}$
C1	Cotton	No treatment	-	0.67
F2	Flax	No treatment	-	0.39
F3	Flax	Benzene + Ethyl Alcohol	Fats and waxes	0.48
F4	Flax	Benzene + Ethyl Alcohol, 0.03N HCl	Fats and waxes, pectin, hemicellulose, oligosaccharides	0.66
F5	Flax	Water retting, 0.03N HCl	Pectin, hemicellulose, oligosaccharides	0.66
F6	Flax	Surfactant	Fats and waxes, pectin, oligosaccharides	0.61

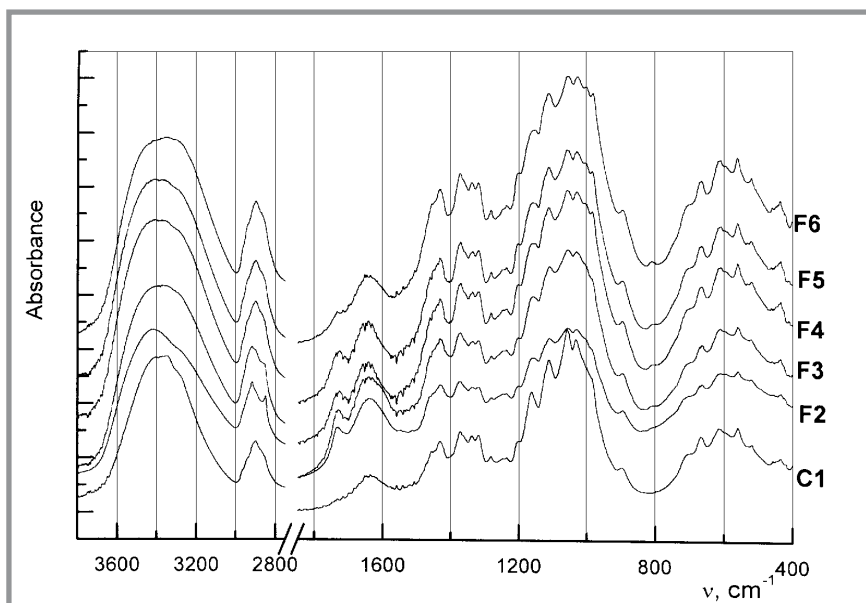


Figure 1. Infra-red spectra of cotton and flax fibres; C1 - cotton sample; F2 to F6 - flax samples (see Table 1).

## Results and Discussion

Figure 1 shows the IR spectra of cotton and short flax fibre treated according to the process described in Table 1. Cotton cellulose is usually characterised by two absorption bands: one wide band in the area of wave numbers 3000 to 3700  $\text{cm}^{-1}$  of free OH groups and intra- and intermolecular hydrogen bonds, and another at 2900  $\text{cm}^{-1}$  of  $\text{CH}_2$  and CH groups of the polymer. The latter at 2900  $\text{cm}^{-1}$  is symmetrical for pure cellulose [14].

Pectins are characterised by several bands: 1740  $\text{cm}^{-1}$  is characteristic of the free COOH groups of polygalacturonic acid, and those at 1410 and 1615  $\text{cm}^{-1}$  are of symmetrical and asymmetrical oscillations of ionised carboxyl groups respectively. In the area of 2850 to 2950  $\text{cm}^{-1}$ , one wide or two narrower bands at 2875 and 2925  $\text{cm}^{-1}$  can be observed which are attributed to the  $\text{CH}_2$  and CH groups of pectin [15].

Lignin of wood cellulose and flax cellulose is characterised by absorption bands at 1600, 1500 and 820-850  $\text{cm}^{-1}$  [14]. The presence of impurities in the cellulose can be identified using IR spectra, but only qualitatively.

In Figure 1, absorption bands at 1740  $\text{cm}^{-1}$  and at 1650 to 1600  $\text{cm}^{-1}$  can be observed in the spectrum of original flax fibres (sample F2) pointing to the presence of pectins. Additional bands at 2875 and 2925  $\text{cm}^{-1}$  also confirm this observation. It should be noted that  $\text{CH}_2$  and CH groups

of the fats and waxes could also contribute to the same bands. The presence of lignin can only be identified by comparing the spectra of original flax (sample F2) and cotton cellulose (sample C1). The absorption band at 1500  $\text{cm}^{-1}$  can be seen as a 'shoulder' in the spectrum of sample F2, which is characteristic of a wood cellulose and flax stems [14]. It should be noted that as fats and pectins are removed from flax, an absorption band at 820  $\text{cm}^{-1}$  appears in all IR spectra of flax samples, which points to the presence of lignin in the samples.

Fibre treatment with benzene and ethyl alcohol (sample F3) removes oily acids that affects the 2900  $\text{cm}^{-1}$  band and makes clearer those of lignin at 1500  $\text{cm}^{-1}$  and 820  $\text{cm}^{-1}$ . The band at 1500  $\text{cm}^{-1}$  can be seen as a 'shoulder'. Removing fats and pectins (sample F4) leads to the decrease in intensity of bands at 2875 and 2925  $\text{cm}^{-1}$  and, in comparison with samples F2 and F3, to a more symmetrical band at 2900  $\text{cm}^{-1}$  which is related to cellulose. The pectin bands at 2875 and 2925  $\text{cm}^{-1}$  can be seen as 'shoulders' symmetrical to the maximum at 2900  $\text{cm}^{-1}$ . It should be noted that after treatment with a 0.03N solution of HCl, absorption bands at 1740  $\text{cm}^{-1}$  related to pectins could still be seen in the spectra. This can be explained by the fact that treatment with HCl and ammonium citrate first of all removes pectins from the fibre surface. Pectins, however, are present not only in the wall of elementary flax fibres, but also in the in-

ter-fibre bonds. In order to remove pectin from inter-fibre bonds, a more intensive treatment is required which leads to fibre splitting and may cause destruction of the cellulose. The process of splitting flax fibre bundles into elementary fibres or filaments is called cottonisation, which was not the aim of this investigation.

Removing pectins by water retting followed by treatment with the solution of HCl (sample F5) did not cause any noticeable changes in the IR spectra.

Treatment with the surfactant (sample F6) significantly changed absorbance at 1740  $\text{cm}^{-1}$ , which can be associated with the removal of a substantial quantity of pectin. At the same time, the 850  $\text{cm}^{-1}$  band can be clearly identified in the spectrum and is attributed to lignin.

All the samples for IR-spectroscopy were prepared in the same standard conditions, which enabled an index of crystallinity of the cellulose to be evaluated using the spectra obtained. The index  $I_c$  is determined as a ratio of intensities of absorption bands at 1372 and 2900  $\text{cm}^{-1}$ ,  $I_{1372}$  and  $I_{2900}$ , respectively [16]:

$$I_c = I_{1372}/I_{2900} \quad (1)$$

The index usually shows good correlation with the degree of crystallinity determined by X-ray structure analysis. Therefore, changes in magnitude of the index follow the tendency in structural changes of cellulose which resulted from chemical treatments.

Table 1 gives the index of crystallinity of flax cellulose that was calculated using IR-spectra. It can be seen that the index is significantly lower for the original flax fibres in comparison with that of cotton. This can be explained by the fact that flax

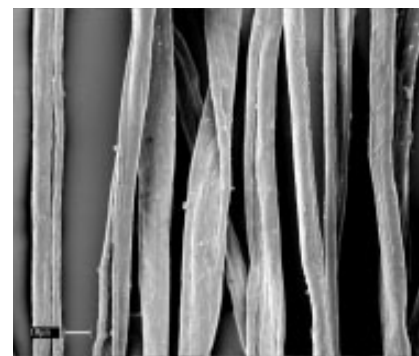


Figure 2. SEM image of cotton fibres (sample C1).

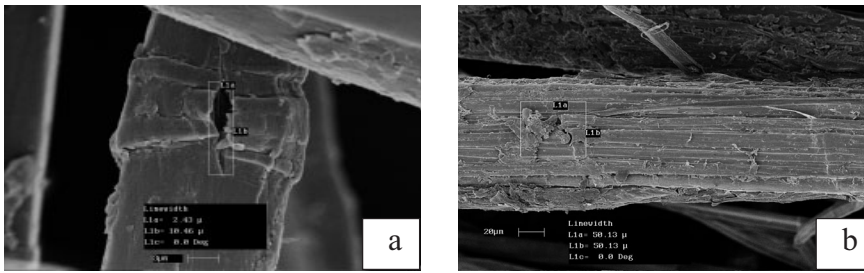


Figure 3. SEM images of original flax fibres (sample F2); a) individual fibre, b) fibre bundle.

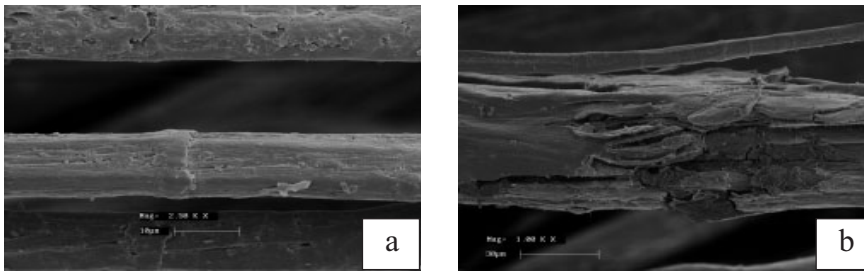


Figure 4. SEM images of flax fibres treated with benzene and ethyl alcohol (sample F3); a) individual fibre, b) fibre bundle.

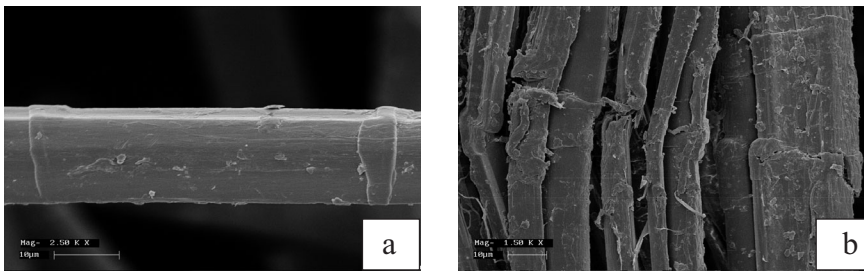


Figure 5. SEM images of flax fibres treated with benzene and ethyl alcohol and 0.03N HCl (sample F4); a) individual fibre, b) fibre bundle.

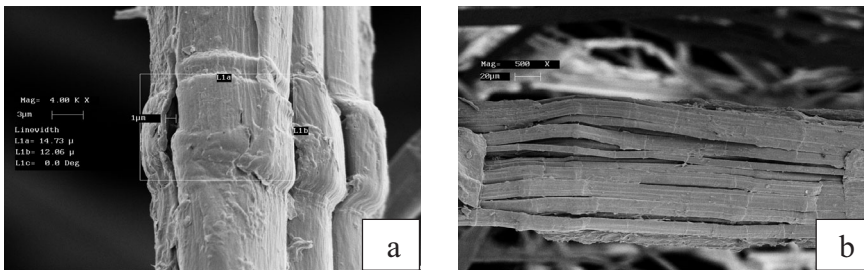


Figure 6. SEM images of flax fibres treated with 0.03N HCl after water retting (sample F5); a) individual fibre, b) fibre bundle.

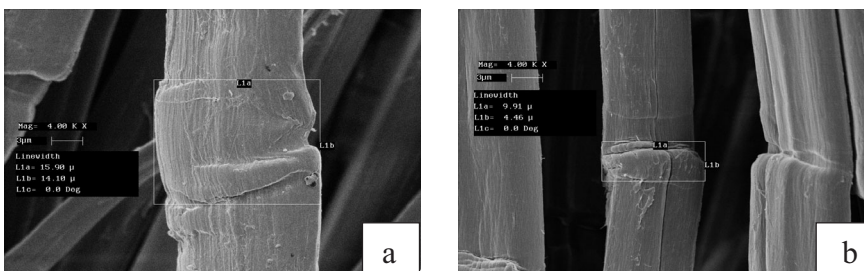


Figure 7. SEM images of flax fibres treated with surfactant (sample F6); a) individual fibre, b) fibre bundle.

fibres contain 10 to 15% of amorphous hemicelluloses and pectins; this contributes to the absorbance at  $2900\text{ cm}^{-1}$  which is related to covalent oscillations of CH groups. Deformational oscillations of CH groups at  $1372\text{ cm}^{-1}$  depend on the degree of orientation of macro-chains [16]. Therefore the index is lower for the non-treated samples. Removing fats and pectins leads to the decrease of the intensity at  $2900\text{ cm}^{-1}$ , and in turn to the increase in the index (compare samples F2 to F5).

The index of crystallinity of flax fibres treated with the surfactant (sample F6) was lower than that of the samples treated with HCl. This can be attributed to the smaller quantity of hemicelluloses and pectins removed by the surfactant.

Figures 2 to 7 present SEM images of flax fibres after the treatments mentioned in Table 1. Figures 2 and 3 demonstrate the differences in morphology of cotton and flax fibres. Residual substances can be seen on the surface of flax fibres after they have been extracted from the plant (Figure 3). These are small parts of parenchyma, pectins and other components of the outer layer of the plant's stem. Removing fats and waxes (Figure 4) made pectin residuals and imperfections on the fibre surface more visible. Figure 4 shows pectin components which bond elementary fibrils into bundles. Treating fibres with a benzene-alcohol mixture followed by a solution of HCl caused fibre bundle splitting and fibre surface cleaning (Figure 5). At the same time, a substantial quantity of non-cellulose substances can be observed on the fibre surface. Water retting followed by treatment with the HCl solution resulted in better cleaning and splitting of the fibre (Figure 6b). Microfibrils of cellulose oriented along the fibre axis can be clearly seen on the surface (Figure 6a). Fibre treatment with the surfactant (Figure 7) led to better fibre surface cleaning among all treatments considered. Comparing the SEM images of flax fibres, the contribution of each of the treatments towards fibre bundle splitting and fibre surface cleaning can be assessed. It can be seen that, to a certain extent, all treatments remove non-cellulose substances from the fibre surface.

## Conclusion

Flax fibres were treated with a mixture of benzene and ethyl alcohol, solutions of HCl, and surfactant with the aim of removing fats, waxes, pectins and hemicellu-



loses. Analysis of IR spectra and SEM images of flax fibres after various treatments showed that these substances could be removed by treating fibres with a surfactant. On one hand, using the surfactant instead of a benzene-alcohol mixture and solution of HCl decreases the destruction of cellulose macro-chains and enables the organic solvents to be dispensed with; on the other hand, it decreases the quantity of hemicelluloses removed from the fibre surface. In order to find a more appropriate surfactant that would substitute the benzene-alcohol mixture and solution of HCl in flax fibre processing, it is necessary to explore the ability of surfactants, for example non-ionic and ionic, cation-active and anion-active, to remove hemicelluloses and other accompanying substances from flax fibres.

### Acknowledgement

The authors would like to thank the NATO Science for Peace Programme for supporting the work reported as part of project no. 973658, entitled 'Improving the Performance of Flax Blended Yarns Produced on Cotton and Wool Spinning Systems'.

### References

1. L.N. Kuleshova, N.V. Komarova, N.N. Osipova, H.G. Taraskina, and V.N. Hodirev, 'The Influence of Accompanying Substances on Hydrophilicity of the Original Flax Cellulose', *Chemistry of Wood*, 1988, No 4, 92-94.
2. *Handbook on Flax and Chemical Fibres Spinning*. Ed. by L.B. Kariakin, L.N. Ginzburg. Leningrad, Legprombitizdat, 1991, 3-31.
3. N.N. Truevtsev, I.I. Shamolina, L.M. Asnis, S.E. Gladish, S.A. Grishanov, 'The Investigation and Improvement of Properties of Flax-Containing Textiles', *Fibres and Textiles in Eastern Europe*, 1999, 7, No 3(26), 28-30.
4. *Handbook on Chemical Finishing of Linen Fabric*. Ed. by G.I. Fridliand. Moscow, Legkaya Industriya, 1973, 14-33.
5. V.I. Popa, I.G. Breaban, 'Cellulose as a Component of Biodegradable Composites', *Cellulose Chemistry and Technology*, 1995, 29, No 5, 575-587.
6. T.V. Piven, V.I. Hodirev, 'Biodestruction of Linen and Cotton', *Chemistry of Wood*, 1988, No 1, 100-105.
7. T. V. Piven, V. I. Hodirev. *The Influence of Accompanying Substances on Linen Cellulose Resistance against Biodestruction*. *Chemistry of Wood*, 1988, No 1, 106-111.
8. J.M. van Hazendonk, J.C. van der Putten and J.T.F. Keurentjes. *A Method for the Determination of the Surface Tension of Cellulose Fibres in their Natural State and its Relation with Chemical Composition*. *Cellulose and Cellulose Derivatives: Physico-Chemical Aspects and Industrial Applications*. Ed. by J.F. Kennedy, G.O. Phillips, P.O. Williams, L. Pienlell. Woodhead Publishing Ltd, Cambridge, England, 1995, 107-114.
9. Y.S. Darevskiy, V.I. Hodirev, M.V. Latosh, M.A. Kushner, 'An Investigation of the Chemistry of Processes in Flax Cellulose Production', *Chemistry of Wood*, 1985, No 5, 38-42.
10. W.J. Meijer, N. Vertgert, B. Rutgers, M. van der Waart, 'The Pectin Content as a Measure of the Retting and Rettability of Flax', *Industrial Crops and Products*, 1995, 4, 273-284.
11. M.A. Sobolev, A.A. Krasivskaya, 'A Volumetric Method of Identifying Pectins', *Textile Industry*, 1954, No 7, 39-41.
12. I.I. Shamolina, L.M. Asnis, R.J. Harwood, S.A. Grishanov, A.M. Bochek, N.M. Zabivalova, 'Separation and Investigation of Properties of Flax Fibre Pectins', *Proc. of the 1st Central European Conference on Fibre Grade Polymers, Chemical Fibres and Special Textiles*, 3-4 October 2000, Łódź, Poland, 47-63.
13. *Experiments in the Chemistry of Wood*. Ed. by V. M. Nikitin. Moscow, Lesnaya Promishlennost, 1965, 50-158.
14. R.G. Zbankov, 'Infra Red Spectra of Cellulose and its Derivatives', *Minsk, Nauka i Tehnika*, 1964, 338.
15. G.B. Aimuhammedova, J.E. Alieva, N.P. Sheluhina, 'Properties and Applications of Pectin Sorbents', *Frunze, Ilim*, 1984, 131.
16. *Cellulose and its Derivatives*. Ed. by N. Bikales, L. Segal. Moscow, Mir, 1974, 1, 214-235.

Received 11.01.2002 Reviewed 08.10.2002

## The University of Bielsko-Biała - the Youngest Polish University with a Textile Faculty

**Rector:** Professor Marek Trombski, Ph.D., D.Sc.

**Dean of the Faculty of Textile Engineering and Environment Protection and Director of the Institute of Textiles and Polymer Materials:** Professor Stefan Boryniec, Ph.D., D.Sc.

The University of Bielsko-Biała (Akademia Techniczno-Humanistyczna w Bielsku-Białej) is a state university which was established by an act of the Polish Parliament of 19 July 2001. The basis for the new university was the Bielsko-Biała Branch of the Technical University of Łódź, which has been active since 1969. The University of Bielsko-Biała is the most important technical and humanistic university active in the Beskidian region. Young people who have completed their education at this University go on to join the technical and scientific staff of the textile industry, the machine construction industry, and the automobile industry; they are active in environmental protection, and offer their skills in questions of organisation and management. Information Technology specialists first graduated in 2002.

At present, there are four faculties which conduct research work and education. These are the Faculty of Machine Construction and Information Technology, the **Faculty of Textile Engineering and Environmental Protection** (which includes also the **Institute of Textiles and Polymer Materials**), the Faculty of Management and Information Technology, and the Humanistic-Social Faculty. All the faculties systematically update the educational study programmes to the economical conditions, and to the current needs of the regional and national industries. Their teaching considers modern trends in science, technology and economy. The University of Bielsko-Biała educates students to different levels: Master of Science degree studies (related to the German 'Dipl. Eng.'), higher branch studies (related to the 'bachelor' or 'engineer' degrees), post-graduate studies, and also different specialised studies and courses. The students can also obtain informational technology and pedagogic education independently of their professional major subject.

University of Bielsko-Biała  
Akademia Techniczno-Humanistyczna w Bielsku-Białej  
ul. Willowa 2, 43-309 Bielsko-Biała, Poland  
Tel. +48 33 82-274-00; 82-292-24  
Fax +48 33 815-16-10; 812-35-02