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# Applying the WAXS method to estimate the supermolecular structure of cellulose fibres after mercerisation

**Abstract**

*This study focuses on the changes in the supermolecular structure of cellulose of natural fibres after the mercerisation process by sodium hydroxide.*
*This process is the first step in the modification of the natural fibres' surface which is performed in order to remove waxes and fats, in consequence of which the fibre's surface becomes more accessible to chemical reagents. The strong influence of mercerisation on the crystal structure of cellulose consists in transforming cellulose I (native form, Cell-I) to cellulose II (Cell-II). The results obtained indicated that the WAXS method is a good tool for estimating the efficiency of the mercerisation process. It was found that the degree of cellulose conversion depends on the conditions of mercerisation, namely the concentrations of alkali and the time of treatment. We observed that at increasing concentrations of alkali (from 10% to 16%), the content of cellulose II increased; however at 25% of alkali, the amount of the polymorph Cell-II rapidly dropped as an effect of the molecular degradation of cellulose. The latter was manifested by a decrease in the degree of crystallinity (up to 35%). We also discovered the influence of mercerisation time on converting Cell-I into Cell-II. Up to about 10 minutes, the content of cellulose II rapidly grows, and after that time no structural changes were observed.*

**Key words:** *cellulose natural fibres, polymorphism, mercerisation, WAXS.*

## 1. Introduction

The application of natural fibres (NF) as a reinforcing agent for thermoplastic polymer is of considerable interest due to their attractive properties [1], because natural fibres such as flax, hemp, jute etc. are characterised by lower density, and their lower cost in comparison to materials such as glass, carbon or steel fibres [2,3]. On the other hand, the relatively high strength and tensile modulus are comparable to aramid fibres. natural fibres may also represent economic and ecological interest, because they are renewable sources and products available worldwide. The application of NFs as components of composites with engineering thermoplastics contributes to a reduction in pollution because of their biodegradability [4].

In general, the properties of composites depend on the type of fibres and on the thermoplastic matrices and adhesion between them. A very important role is also played by the morphology and crystal structure of interfacial regions. To achieve good adhesion between hydrophilic cellulose fibres and hydrophobic matrix such as polyolefins, the modification of the NF surface or matrix is required. The natural fibres are modified by grafting reactions of cellulose chains such as esterification, etherification and treatment with isocyanates or silanes [3,5-7].

On the other hand, in addition to cellulose, natural fibres contain hemicelluloses, lignin, waxes and fats, which diminish their reactivity. Therefore, the first step in chemically modifying the natural fibres is the mercerisation process by alkali (NaOH) treatment, which removes these natural impurities [8, 9]. However, during the alkali treatment of native cellulose, its crystal structure, named as a cellulose-I (Cell-I), is transformed into cellulose II (Cell-II) [10,11]. The geometry of both celluloses is monoclinic, having the following parameters: a=8.3, b=10.3, c=7.9 Å, β=84° (for cellulose I) and a=8.1, b=10.3, c=9.1 Å, β=62° (for cellulose II). According to the literature [8], the transformation of cell-I into cell-II is realized by intermediate products such as alkali cellulose and hydratocellulose. The polymorphic transformation of Cell-I ⟶ Cell-II depends on alkali concentrations and the time of treatment [13,14]. In the literature various conditions of mercerisation are described, in which the concentration of NaOH solution oscillates from 6% to 25% [1,7,11,12,14,15], but polymorphic effects are reported qualitatively only.

The aim of the presented work was to establish a relationship between the conditions of mercerisation (concentration of NaOH solution and treatment time) and the degree of conversion Cell-I ⟶ Cell-II by the WAXS method.

## 2. Experimental

In our study we have used crude, unmodified flax fibres. The term 'crude' refers to the fact that the fibres were retted and then the shives removed. Before our experiments the flax fibres were neither washed nor extracted.

*Chemical treatment:*
The fibres were immersed in NaOH with different concentrations of solution: 10%, 12%, 16% and 25%. The samples were mercerised for 1, 2, 3, 4, 5, 7.5, 10, 15 and 30 minutes for each concentration.

After the alkali treatment, the fibres were washed with water to remove the excess of NaOH, and then dried in the air at a high temperature (ca. 110°C).

*Structural investigations:*
The supermolecular structure of cellulose fibres was analysed by means of wide-angle X-ray scattering (WAXS) using Cu K α radiation. The X-ray diffraction pattern was recorded in an angle range of 10-30° 2Θ. The deconvolution of peaks was performed by the method proposed by Hindeleh & Johnson [16], and improved and programmed by Rabiej [17]. After the separation of X-ray diffraction lines, the amount of cellulose II after chemical mercerisation was calculated on the basis of the separated area under the peaks of cellulose I and cellulose II. The degree of crystallinity ($X_c$) was determined by comparing the areas under crystalline peaks and the amorphous curve. The changes in the supermolecular structure of respective polymorphic forms of cellulose were analysed as a function of concentration of alkali at time of mercerisation process.

## 3. Results and discussion

The diffraction pattern of unmodified flax fibres is shown in Figure 1a, where three peaks at 2Θ = 15°, 17° and 22.7° confirmed that only cellulose I is present in crude fibres (Fig 1).

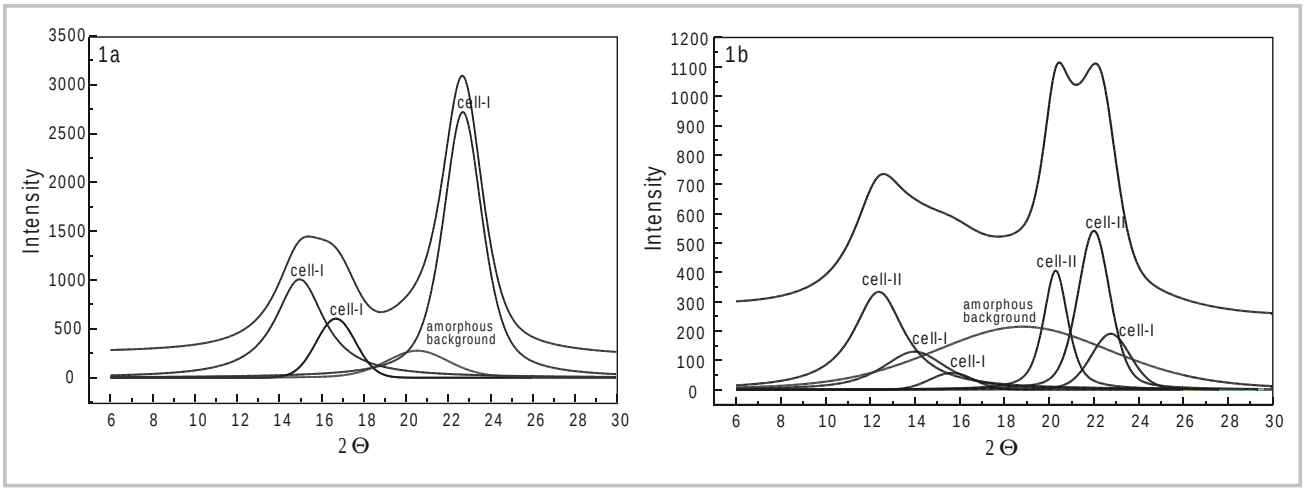


***Figure 1.*** *X-ray diffraction pattern of natural flax fibres: a) crude fibres; b) mercerised fibres (16% NaOH, 10 min.).*

On diffractograms of samples after mercerisation, three additional peaks ($2\Theta = 12.5^o$, $20^o$ and $22^o$) from cellulose II were registered. In Fig. 1b, the X-ray diffraction of fibres after mercerisation in 16% NaOH for 10 minutes is shown as an example. It is worth emphasising that on all x-ray diffraction patterns, six maxima with various intensity were noticed, which indicated that the conversion degree of cellulose I into cellulose II was differentiated, and depended on the conditions of the chemical treatment.

The amount of cellulose II as a function of time of mercerisation for various concentrations of NaOH solution is shown in Fig. 2.

The diagrams in Fig 2. show the significant influence of concentration of NaOH solution as well as the time of reaction on supermolecular structure of natural fibres. With the increase in concentrations of alkali (from 10% to 16%), the amount of cellulose II increases. The highest growth of cellulose II content took place up to 7.5 minutes, and subsequently only insignificant differences in growth of the amount of these polymorphs form were observed. The greatest efficiency of polymorphic transition of cellulose was noted in the 16% NaOH solution, where about 75% of Cell I was transferred into Cell II.

Unexpectedly, the mercerisation at 25% NaOH caused a rapid decrease of the Cell II phase after only 2 min. of treatment. Most probably the reason for this situation was the formation of alkalicellulose II which does not transform into Cell II [18]. Nor can we exclude partial degradation of the crystal structure.

The analysis of degree of crystallinity indicated that the mercerisation process caused a decrease in the total contents of the crystalline phase. The degree of crystallinity for unmodified NF fibres was 72%. Unexpectedly the highest fall in crystallinity (35%) was noted in samples after treatment with 16% NOH solution, where the greatest degree of Cell I⟶ Cell II transition took place (Table 1).

## 4. Conclusions

The alkali treatment of crude flax fibres causes the transformation of cellulose I into cellulose II.

The effectiveness of polymorphic transformation depends on the concentration of NaOH solution as well as on the time of chemical treatment.

The increase in NaOH concentration in the range from 10% up to 16% caused an increase in the amount of cellulose II; however, the application of 25% alkali solution causes the reverse effect after only 2 min.

The greatest effectiveness of structural phase transition is reached during the first 7.5 minutes of mercerisation, and after 10 min. reaches its maximal value (in the range of 60-76%, relatively).

***Table 1.*** *Changes of crystallinity of NF after mercerisation treatment.*

| Concentration of NaOH [%] | Drop of crystallinity degree in NF in relation to untreated samples [%] |
|---|---|
| 10 | 13 |
| 12 | 17 |
| 16 | 35 |
| 25 | 24 |

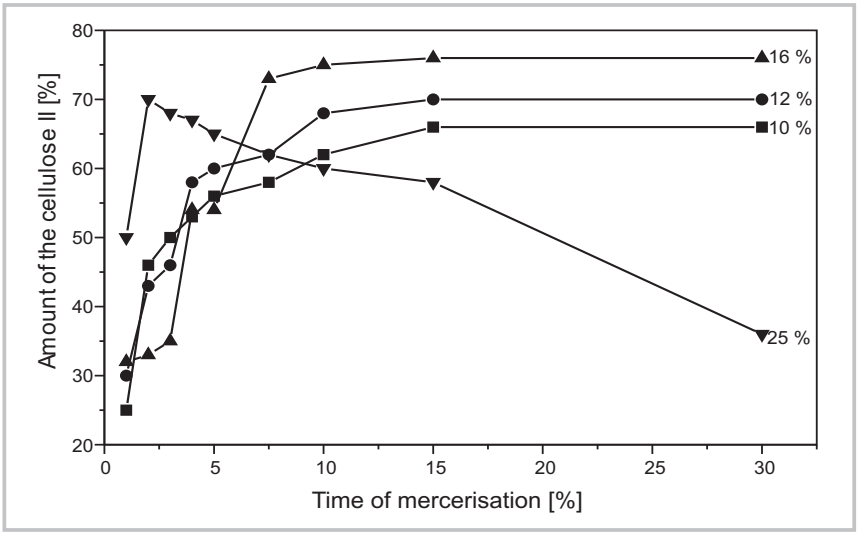


***Figure 2.*** *Amount of the cellulose II vs. time of mercerisation.*

After this time, the amount of Cell II remains on the same level.

The greatest efficiency of polymorphic transformation was in 16% NaOH solution, where more than 75% Cell II was formed.

The mercerisation also caused a significant fall in the contents of crystalline phase.

Finally, it is worth mentioning that the WAXS technique is a good tool for estimating the efficiency of the mercerisation process.

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# From the Polish Universities

The Polish State Accreditation Commission informed the Ministry for National Education & Sport and the Rector of the Technical University of Łódź, Professor Jan Krysiński Ph.D., D.Sc. by letters dated 21 February, 2003 that the Faculty for Engineering and Marketing of Textiles at the Technical University of Łódź had achieved a 'positive' opinion from the Commission's Council which had been considering the scientific and educational level of the Faculty in the specialisation of textile science and technique.

The Polish state educational and scientific authorities, with the intention of raising and maintaining a high level of education of Polish universities, organised the Accreditation Commission, which on the basis of reports from the Estimation Councils and the Specialist Group for Technical Specialisation Studies evaluates the individual faculties of Polish universities. To achieve a 'positive' opinion, a given Faculty must meet very high standards concerning staff, programming, organisation, and scientific equipment. The university staff must not only conduct the students' lessons and workshops, but must also carry out their own research work together with outstanding students at higher academic years. The list of individual requirements is long, and includes the number of students per professor and per other scientific researchers, a well-equipped library, post-graduate studies, the ECTS European estimation system, and realisation of the officially established programme requirements.

The Accreditation Commission awards a given faculty with accreditation for a period of two or five years depending on the estimation level achieved. The Faculty for Engineering and Marketing of Textiles at the Technical University of Łódź has achieved accreditation for five years. The next evaluation should be carried out in the academic year 2007/2008. It should be also emphasised that the Faculty was the first which has been rewarded by such an accreditation. Hitherto, the individual specialisations of the Technical University of Łódź had achieved a Certificate of Educational Quality from the University Accreditation Commission of the Rectors' Council of Polish Universities.