X-ray Diffraction Study of Pine Wood Treated with NaOH

Abstract
The supramolecular structure of pine wood after mercerisation by sodium hydroxide was investigated by means of wide-angle x-ray scattering (WAXS). The relationship between the condition of mercerised pine wood (Pinus silvestris L.) and the degree of transformation from cellulose I to cellulose II were analysed.

It was found that the amount of cellulose II depends on the concentration of NaOH solution as well as on the time of chemical activation. The greatest efficiency of polymorphic transition of cellulose was noted in the highest concentration of sodium hydroxide solution (20 and 25%). Moreover, the rate of polymorphic conversion of cellulose by the decrease in the crystallinity of wood was estimated.

Key words: X-ray diffraction, supramolecular structure, pine wood, cellulose, mercerisation, sodium hydroxide.

Introduction

In recent years scientists’ high interest in investigating composites of wood and thermoplastic polymers has been observed. At present, there is a tendency to use mercerisation (treatment with a sodium hydroxide solution) to improve the compatibility between the hydrophilic wood fibre and hydrophobic polymer matrix. Natural fibres such as flax, hemp, jute, wood etc. treated in order to remove materials containing such as pectin, waxy substances and natural oils covering the external surface of the fibre cell wall. Moreover, the mercerisation process caused the fibrils to be revealed and gives a rough surface topography to the fibre [1], as well as causing the transformation of the native cellulose I into cellulose II [2-4].

The path from cellulose I to cellulose II goes by way of Na-cellulose I. If a cellulose sample is treated with an alkali solution, the cellulose swells to various extents depending on the type and the concentration of alkali, and also on the temperature [5]. At low concentrations, only the large pores in the cellulose structure are occupied. With increasing concentration, the smaller cation Na+ (Na+ = 0.276 nm) can advance more easily into smaller pores. Na+ seems to have a favourable diameter which is able to widen the smallest pores down to the space between the lattice planes and advance into them [6]. During intensive washing, the linked Na+ ions are removed and another lattice is formed, the cellulose II lattice. The geometry of both cellulosics is monoclinic, and has the following parameters: a=8.3, b=10.3, c=7.9A, β=84° (for cellulose I) and a=8.1, b=10.3, c=9.1A, β=62° (for cellulose II). Apart from a change in the dimensions of the space unit, the planes of the cellulose molecules are aligned approximately in the 101 direction. These changes are associated with a change in the hydrogen bonds [7,8]. From the thermodynamic point of view, the lattice of cellulose II is more stable than that of cellulose I [9].

The polymorphic transformation of cellulose I to cellulose II has been studied with various method and materials [4,10,11]. However, the mercerisation on wood has been less reported.

In this study we investigate the relationship between the condition of mercerised pine wood (Pinus silvestris L.) (concentration of sodium hydroxide solution and the time of activation) and the degree of transformation of cellulose I to cellulose II by the WAXS method.

Experimental

Alkali treatment:
The wood was dried at 70°C for 24 h in a vacuum oven, and was then immersed in NaOH with different concentrations of solution — 10%, 15%, 17.5%, 20%, 25%. The samples were kept immersed in the alkali solution for 15, 30, 45, 60 and 90 minutes for each concentration. The wood fibres were then washed several times with distilled water to remove excess sodium hydroxide. A final pH of 7 was maintained. The pine sawdust was then dried for 48 h at room temperature until a constant weight was achieved.

Structural investigations:
The supramolecular structure of wood cellulose was analysed by means of wide-angle X-ray scattering (WAXS) using Cu Kα radiation. The X-ray diffraction pattern was recorded within an angle range of 10-30° 2θ.

The deconvolution of peaks was performed by the method proposed by Hindle & Johnson [12], as improved and programmed by Rabiej [13]. After separation of X-ray diffraction lines, the amount of the 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 (Xc) was determined by comparing the areas under crystalline peaks and the amorphous curve. The changes in the supramolecular structure of the respective polymorph forms of cellulose were analysed as a function of concentration of alkali at the time of the mercerisation process.
Results and discussion

Figure 1 shows changes in the X-ray diffraction pattern of unmodified (Figure 1a) and mercerised (Figure 1b) pine wood.

The diffraction pattern of unmodified pine wood in Figure 1a showed only three peaks at 2θ = 15°, 17° and 22.7° which derived from cellulose I. On diffractograms of samples after mercerisation (Figure 1b), three additional peaks (2θ = 12.5°, 20° and 22°) from cellulose II were registered. In Figure 1b, the X-ray diffraction of pine wood after mercerisation in 25% NaOH for 45 minutes is shown as an example. It is worth underlining that on almost X-ray diffraction pattern, six peaks of various intensities were noticed. These results indicated that the polymorphic transformation of cellulose I into cellulose II depended on the conditions of chemical treatment, namely concentration of alkaline solution and time of treatment.

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

The amount of cellulose II increased with the increase in time of mercerisation, as well as of the concentration of NaOH solution. The greatest efficiency of polymorphic transition of cellulose was noted in the highest concentration of sodium hydroxide solution (20 and 25%) where above 60% of cellulose I was changed into cellulose II after only 45 minutes. When the pine wood was mercerised with 15% and 17.5% sodium hydroxide solution, the content of cellulose II was noticed to be lower. For example, the percentage of regenerated cellulose II after 60 minutes with 15% solution was 37%, and with the 17.5% solution it was 45%. Cellulose II was not observed on the X-ray diffraction pattern obtained from samples after mercerisation with 10% sodium hydroxide solution.

It is very interesting that pine wood is less susceptible to the crystal conversion of cellulose I into cellulose II, in comparison to natural fibres like flax and hemp [4]. A possible explanation for such a restraining effect is the presence of lignin in the wood. In agreement with the Okano & Sarko’s suggestion [16], mercerisation must proceed from the amorphous regions. Murase et al. [17] suggested that lignin hardly prevents the alkalii swelling of cellulose in wood. When wood is mercerised, the intermingling of chains will proceed through the micropore, and the anti-parallel chain arrangement will be produced. The chains in the anti-parallel arrangement will be crystallised to cellulose I when the wall is washed and dried. Moreover, earlier investigations indicated that hemi-cellulose is easily extracted by sodium hydroxide, and the effect of hemicellulose on mercerisation was considered to be relatively slight [18].

As the concentration of NaOH increases, X-ray diffraction results for alkalised pine sawdust (Figure 3) show an overall decrease in the degree of crystallinity. The degree of crystallinity of unmodified pine wood was 70%.

The fall of the degree of crystallinity of wood indicates the progress of the crystal conversion of cellulose I into cellulose II. The dependence of the decrease in this parameter vs. time mercerisation is similar for each concentration of hydroxide sodium solution.

The subject of our further investigations will examine different species of wood
(hardwood and softwood). The preliminary research has proved that the mercerisation of hardwood and softwood behaved similarly up to 30 minutes. The transformation of cellulose I into cellulose II over the range of mercerisation time of 45 to 90 minutes is more efficient for pine wood in comparison to beech wood.

On the basis of the obtained data, we can say that the ability of cellulose I to transform into cellulose II in wood depends not only on the conditions of the mercerisation process but also on the compositions of the wood.

**Conclusions**

The results obtained in this study lead us to the conclusions that:

- the polymorphic transformation of cellulose I into cellulose II in pine wood depends on the conditions of chemical treatment: concentration of alkaline solution and the time of treatments.
- The amount of cellulose II increased with the increase in mercerisation time as well as on the concentration of NaOH solution. The greatest efficiency of polymorphic transition of cellulose was noted in the highest concentration of sodium hydroxide solution (20 and 25%).
- The mercerisation process caused an overall decrease in the degree of crystallinity of pine wood.
- Pine wood is less susceptible to the crystal conversion of cellulose I into cellulose II in comparison to natural fibres such as flax and hemp.

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**References**


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take pleasure in inviting you to attend

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on

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in honour of

**Professor Andrzej Włochowicz**

on the occasion of his 75th birthday.

We believe that this scientific meeting will be the best way to show our appreciation of Professor Włochowicz’s excellent contribution to science in the field of fibre and polymer physics. It is our intention to arrange a meeting where outstanding scientists, his colleagues and friends will deliver top-rank lectures and will join together in a fruitful and pleasant scientific atmosphere.

The Seminar will be held on February 3rd, 2006 in the Rector’s Office in Bielsko-Biała (Willa Sixta). A seminar program and a list of invited lectures will be available soon on www.itimp.ath.bielsko.pl.