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Research into the Mercerization Process of BeechWood Using the Waxs Method

Abstract
The objective of this study was to establish the relationship between the condition of mercerization of beechwood (concentration of NaOH solution and time of treatment) and the degree of conversion cellulose I → cellulose II using the wide angle X-ray scattering (WAXS) method. The present study is the continuation of recently performed investigations into the determination of the efficiency of the mercerization process of various lignocellulosic fillers, such as flax and hemp fibres as well as pinewood. Our investigations indicated a significant influence of the type of natural materials and the technological parameters of the mercerization process. The studies of the supermolecular structure of beechwood showed that the conditions of mercerization had the greatest effect on the transformation of cellulose I into cellulose II. The polymorphic transformation depends on the concentration of sodium hydroxide solution as well as the time of chemical treatment. The increase in alkali concentration in the range 10% up to 25% caused an increase in the content of cellulose II. With increasing time of mercerization (from 15 to 90 minutes), the amount of cellulose II increases. The alkali treatment also caused a significant fall in the content of crystallinity of the wood. However, the shape dependence of the degree of crystallinity vs. time mercerization is similar for each concentration of sodium hydroxide solution.

Key words: *wood, cellulose, mercerization, WAXS method.*

Introduction

Wood is one of the most abundant, low-cost materials among the natural fibres; therefore, it has attracted much research interest. Attempts have been made with varied success to use wood fibre as a reinforcement for thermoplastic polymers [1-3]. The low compatibility between the hydrophilic wood fibre and the hydrophobic polymer matrix is one of the major reasons for the limited use of wood fibre as a reinforcement. To improve the interfacial bonding, various surface treatments have been attempted, like stretching, calendering, thermotreatment and chemical modification [4-6].

At present, there is a tendency to use mercerization for the surface modification of cellulose fibre. Mercerization changes both the crystalline and amorphous regions in cellulose. Mercerization depends on the type and concentration of the alkalic solution, its temperature, the time of treatment, the tension of the materials, as well as the additives [7]. It is reported that alkalization, both slack and with tension, increases the strength uniformity along the fibre length.

Mercerization treatment is also believed to improve the fibre surface adhesive characteristics by removing natural impurities such as pectin, waxy substances and natural oils [8]. Several authors suggest that wood alone does not react significatinfly with etherifying/esterifying reagents since the hydroxyl groups in wood are not readily accessible. Hence, the raw material must be pretreated with NaOH [9].

When native cellulose (cellulose I) is mercerized with sodium hydroxide, the transformation of its crystal structure from cellulose I to cellulose II takes place. The geometry of both celluloses is monoclinic, with 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). The polymorphic transformation cellulose I → cellulose II is realized by intermediate products like alkalicellulose and hydratocellulose. This conversion has been studied with various methods and materials [10, 11].

Regarding the mercerization of wood cellulose, Revol and Goring [12] suggested that lignin in wood cell walls may prevent the intermingling process during alkali swelling. On the other hand, Murase et al. [13] suggested that lignin does not prevent the alkali swelling and the crystallization of cellulose II. Shiraishi et al. [14] reported that the partial delignification of wood preceding mercerization caused a partial lattice conversion to cellulose II, and the ratio of the lattice conversion was increased with the degree of delignification. Based upon the experimental results, it is strongly believed that lignin in wood plays a role in the transformation of the cellulose crystal structure during mercerization. Different lignin contents of wood cell walls should therefore affect the degree of mercerization of wood cellulose [15].

Until now, however, the transformation mechanism has not been completely understood. The mercerization of the wood has been studied less than that of non-woody cellulose samples.

The objective of this study was to establish the relationship between the condition of mercerization (concentration of NaOH solution and time of treatment) and the degree of conversion cellulose I → cellulose II by the WAXS method. Optimal conditions of mercerization ensure the improvement of the tensile properties and absorption characteristics, which are important in the composing process.

Experimental

Materials

The experimental material comprised the two most commonly used Polish timber species, pinewood (*Pinus sylvestris L.*) as a softwood species and beechwood (*Fagus silvatica*) as a hardwood species. The size of the wood sawdust ranged from 0.5 to 1.0 mm.

Chemical treatment

The wood was dried at 70 °C for 24 h in a vacuum oven and then was immersed in NaOH with different concentrations of solution – 10%, 15%, 17.5%, 20% and 25%. The samples were mercerized by 15, 30, 45, 60 and 90 minutes for each concentration. After alkali treatment, the wood fibres were washed with distilled water to neutralize the excess sodium hydroxide (a final pH of 7 was

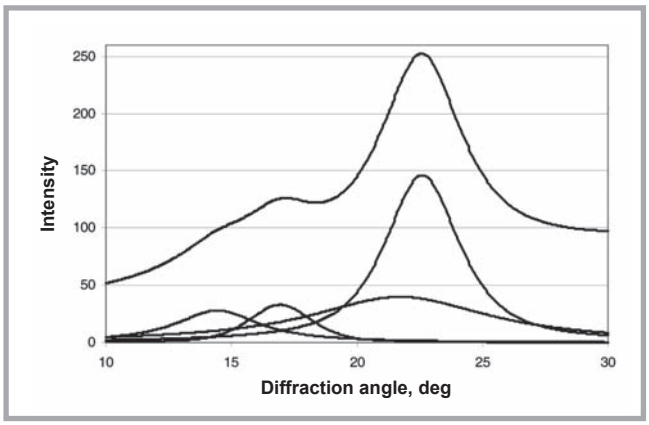

Figure 1. X-ray diffraction pattern of crude beechwood.

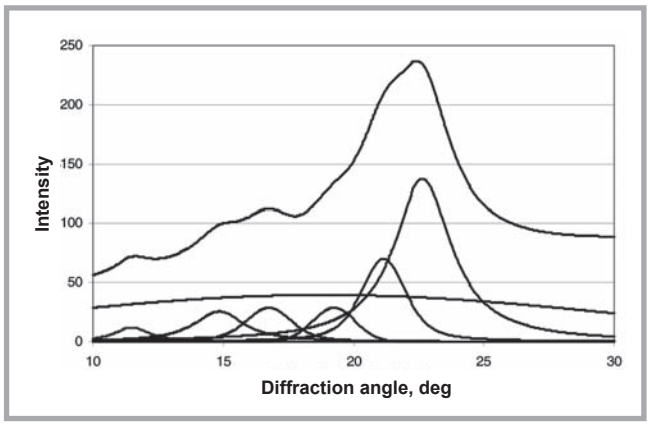

Figure 2. X-ray diffraction pattern of beechwood mercerized by 17.5% alkali solution and 60 minutes.

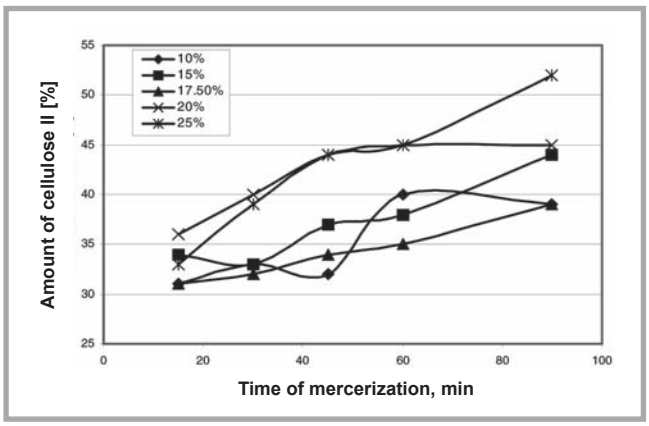

Figure 3. The amount of cellulose II vs. the time of mercerization.

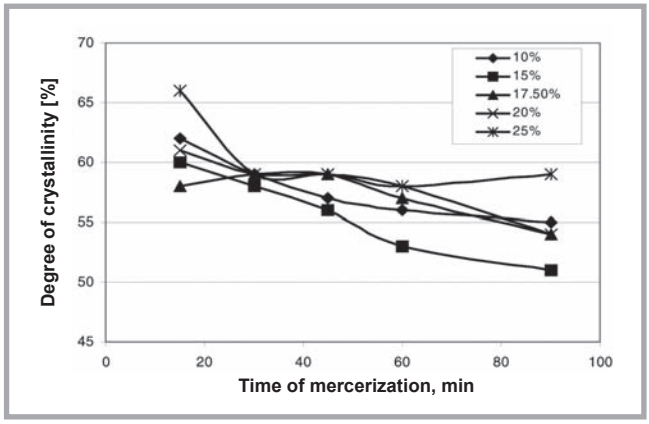

Figure 4. The degree of crystallinity of beechwood vs. the time of mercerization.

maintained) and then were dried for 48 h at room temperature until a constant weight was achieved.

Structural investigations

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

Results and discusion

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

On the diffractograms of the wood after mercerization, three additional peaks from cellulose II were registered. In ***Figure 2***, the X-ray diffraction of beechwood after mercerization in 17.5% NaOH for 60 minutes is shown as an example. X-ray diffraction peaks with various intensities were noticed, which indicated that the conversion degree of cellulose I into cellulose II was differentiated and depended on the conditions of chemical treatment.

The amount of cellulose II as a function of time mercerization for various concentrations of NaOH solution is shown in ***Figure 3***.

Figure 3 shows a significant influence of the concentration of the NaOH solution as well as the time of the reaction on the supermolecular structure of beechwood. With increasing time of mercerization (from 15 to 90 minutes), the amount of cellulose II increases. However, in the case of the alkali process by 10% and 20% NaOH solution the increase of cellulose II took place for up to 60 minutes and subsequently the amount of this polymorph's structure remained almost the same. The greatest efficiency of polymorphic transition of cellulose was noted in the highest concentrations of NaOH solution (20% and 25%), where above 40% of cellulose I was transferred into cellulose II after only 45 minutes. When the beechwood was mercerized with 10%-17.5% sodium hydroxide solution, the content of cellulose II did not show important differences.

A similar observation was reported earlier in our work [18], where mercerization of flax fibres in the range from 10% up to 16% concentration of NaOH caused an increase in the amount of cellulose II in 15 minutes of the alkali process. Unexpectedly, above this time, the content of cellulose II remained on the same level. It's very interesting that beechwood is less susceptible to the crystal conversion of

cellulose I into cellulose II in comparison with natural fibres like flax. In the case of flax fibres, the amount of cellulose II reaches a maximal value in the range of 60-76%; however, the beechwood has a value of 39-52%.

Moreover, earlier investigations indicated that the degradation of cellulose is present when native cellulose was modified by an alkali solution above 20% concentration [18]. Unexpectedly, in the case of mercerization of beechwood by 25% of NaOH solution, the amount of cellulose II was increased. This situation suggests that the presence of different components in the wood may be responsible for the partial blocking of the degradation process of cellulose. In agreement with Murase et al. [13], the lignin hardly prevents the alkali swelling of cellulose in wood.

The analysis of the degree of crystallinity indicated that the mercerization process caused a decrease in the total contents' crystalline phase (***Figure 4***). The degree of crystallinity of crude beechwood was 65%.

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

On the basis of the obtained data, the authors can say that the ability to transform cellulose I to cellulose II in wood depends not only on the conditions of the mercerization process but also the composition of the wood has to be taken into consideration. This is a subject of the authors' futher investigations, where different species of wood (hardwood and softwood) will be analysed.

Conclusions

The studies of the supermolecular structure of beechwood showed that the conditions of mercerization had the greatest effect on the transformation of cellulose I into cellulose II. The polymorphic transformation depends on the concentration of sodium hydroxide solution as well as the time of chemical treatment. The increase in the alkali concentration in the range of 10% up to 25% caused an increase in the content of cellulose II. By increasing the time of mercerization (from 15 to 90 minutes), the amount of cellulose II increased. The greatest effectiveness of the structural phase transition was reached during the application of the NaOH solution (with concentrations of 20% and 25%), where above 40% of cellulose I was transferred into cellulose II after 45 minutes.

The alkali treatment also caused a significant fall in the content of crystallinity of the wood. However, the shape dependence of the degree of crystallinity vs. the time of mercerization is similar for each concentration of sodium hydroxide solution.

Acknowledgements

This research was supported by the University Grant of Poznan University of Technology 32-171/08-DS.

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Received 23.05.2008 Reviewed 4.12.2008