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Waxs Studies of Salix Viminalis Wood Susceptibility to Alkali Treatment

Abstract
Comminuted willow wood (Salix viminalis) was treated with sodium hydroxide solutions of 10, 15, 20 and 25% NaOH concentration, for 15, 30, 45, 60 and 90 minutes for each case of NaOH concentration. The WAXS method was used to estimate the content of cellulose II with reference to a global amount of crystalline cellulose included in the wood and gravimetric measurements were performed to estimate the mass losses caused by the alkali treatment of the wood. As a result, the changes in both the index of cellulose II content and the WPG index for the treatment period and for the NaOH concentration have been determined. In particular, it was established that: i) no cellulose I/cellulose II polymorphic transformation occurs even with 90-minute action of 10% NaOH solution, ii) the index of cellulose II content ranges from 46% with 15-minute action of 15% NaOH solution to 66% with 90-minute action of 25% NaOH solution, iii) irrespective of NaOH concentration, the WPG index approaches ca. -20% with the 15-minute treatment and then increases only to ca. -24% with the 90-minute treatment

Key words: *X-ray diffraction, cellulose, mercerization, WPG index, willow wood.*

Introduction

The sodium hydroxide solution action on a wood causes strong swelling that, in turn, leads to chemical and structural changes in the wood. One effect, among others, of the so-called mercerization process of cellulose natural resources is the polymorphic transformation of cellulose I to cellulose II [1-3].

Even though the cellulose I/cellulose II transformation was intensively investigated by employing various analytical and instrumental methods, i.e. differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and the most frequently applied X-ray diffraction methods [1, 4, 5], the conversion from cellulose I to cellulose II occurring during alkali treatment has not been completely elucidated so far.

There are a number of hypotheses that attempt to shed light on this phenomenon. Experiments conducted on ramie fibres revealed that a number of conversions of cellulose I into cellulose II occur accompanied by the formation of five different alkali-cellulose structures. When the applied alkali solutions exceed the content of 21%, then, simultaneously, the process of cellulose degradation takes place. Therefore, two different forms of the alkali cellulose II can be obtained from the same cellulose, in contrast to cellulose I obtained as a result of the treatment with sodium hydroxide at the concentration of 12-20% [1].

According to the investigations carried out by Okano and Sarko [2] as well as those by Nashimura and Sarko [3], the polymorphic transformation during mercerization begins during the formation of the alkali cellulose I as a result of the 'interlacing' of cellulose chains. However, this opinion is questioned by Hayashi and co-workers [6], who maintain that the above-mentioned transformation occurs during the rinsing of the alkali cellulose I with water. The amount of obtained cellulose II and regenerated cellulose I during the process of mercerization depends, to a considerable extent, on the conditions of the rinsing process or, to be more precise, on the temperature of the water used to rinse the alkali cellulose [7].

Employing the method of wide-angle X-ray scattering, it was demonstrated that, during the process of rinsing the alkali cellulose I with water of a high temperature, part of the alkali cellulose I returns to the form of polymorphic cellulose I. The application of higher temperatures makes it possible to recover greater quantities of cellulose I from the alkali cellulose I_I. When the temperature of the applied water is 100 °C, a mixture of cellulose I and II is obtained. More accurate investigations showed that only cellulose II is obtained from the alkali cellulose I_{II}. On the other hand, when the applied temperature is very low (0 °C), still another variant of polymorphic cellulose is obtained – cellulose IV, which, however, is very unstable and, after drying, it is transformed into cellulose II. When the alkali cellulose I_I is rinsed with water whose temperature ranges from 20 °C to 80 °C, a mixture of cellulose I, cellulose II and alkali cellulose IV is obtained, whereas from the alkali cellulose I_{II}, cellulose II and alkali cellulose IV are obtained. It was also observed that the degree of cellulose I recovery from the alkali cellulose I_I decreased together with the time of exposure to the action of alkalis [7]. It was also found that the complete transformation of the alkali cellulose I into cellulose I is not possible [8].

Besides the above-mentioned dependence of the mercerization process on the type and concentration of the alkaline solution, its temperature, time of treatment, tension of the materials and applied additives, the dependence of this complex process on lignin embedded in a wood has been partially examined as well [1, 9-11].

A number of hypotheses have been suggested concerning the impact of lignin on cellulose polymorphic transformations. Revol and Goring [12] claim that the lignin of wood during the mercerization process may inhibit the reactions of alkalis with cellulose. On the other hand, Murase and co-workers [9] maintain that lignin does not interfere with the above-mentioned reactions.

Shiraishi and co-workers [13] demonstrated that partial wood delignification, which precedes mercerization, can cause partial transformation of cellulose I to cellulose II (the quantity of cellulose II increases proportionally to the degree of delignification).

It was further found [11] that, during the mercerization of oak wood (*Quercus mongoloca*), which had earlier been subjected to the action of shiitake mushrooms (*Lentinula edodes*), cellulose I derived from the sapwood infested by the mushrooms easily underwent transformation into alkali cellulose and later into cellulose II (after rinsing the alkali cellulose with water and drying). In the case of healthy wood, the transformation of cellulose I into cellulose II takes a much longer time and its extent is much more restricted. It was also shown that wood attacked by fungi contains very little lignin. Therefore, it can be assumed that lignin prevents alkalis from affecting cellulose and its transformation into cellulose II. The degradation of crystalline cellulose caused by the action of fungi may result in its increased sensitivity to the action of alkalis and, consequently, in increased mercerization effectiveness.

Larch, pine and fir are among the tree species that are most resistant to the action of sodium hydroxide, whereas poplar, birch and lime are considered to be the least resistant to the action of NaOH [14].

In this study, an attempt was made to analyse the effect of sodium hydroxide on comminuted willow (*Salix viminalis*) wood (fractions from 0.5 to 1.0 mm). For this goal, samples consisting of willow sawdust were subjected to the action of sodium hydroxide aqueous solutions with various concentrations (from 10 to 25%) and for various time periods (from 15 to 90 minutes) and next the changes in the crystalline structure of the cellulose included in the wood were analysed by means of the WAXS method. In addition, using the gravimetric method, the weight percentage gain of the alkali treated wood (i.e. the WPG index) was also determined.

Materials and methods

Sample Preparation and Alkali Treatment Details

The willow sawdust (fraction 0.5-1.0 mm) was dried at 70 °C for 24 h. Next, the wood samples were immersed in NaOH solutions of 10, 15, 20 and 25% concentration. The sawdust was mercerized for 15, 30, 45, 60 and 90 minutes at each NaOH concentration. After the alkali treatment, the wood samples were washed with distilled water to neutralize the excess sodium hydroxide (a final pH of 7 was maintained) and then they were dried for 48 h at an ambient temperature until a constant weight was achieved.

Structural investigations

WAXS investigations of the sawdust were carried out with a Tur M-52 diffractometer. A cooper target roentgen tube operated at 30 kV and 25 mA was used as the radiation source (CuK_α λ=1.5418 Å). The WAXS measurements were performed in the 2 θ scattering angle range range from 5 to 30° with a step of 0.04/3 sec. The peak deconvolution of the WAXS patterns obtained was performed in accordance with the method of Hindeleh and Johnson [15], as improved and programmed by Rabiej [16]. On the basis of the most intense X-ray diffraction lines separating, i.e. the (101), (10-1) and (021)/(002) crystalline peaks of cellulose I and the (101), (10-1) and (002) crystalline peaks of cellulose II, the ratio of the sum of the areas under the separated peaks of cellulose II to a total area under the separated peaks of both the cellulose I and cellulose II was calculated. This ratio (named shortly as the δ_{II} index) was used as a measure of cellulose II content with reference to the global amount of crystalline cellulose included in the treated wood.

The Weight Percentage Gain of the wood samples treated (i.e. the WPG index) was determined as the difference in the oven dry weight of a given sample before modification (W_1) and after modification (W_2), according to equation (1):

$$WPG = \frac{W_2 - W_1}{W_1} \cdot 100 \qquad [\%]$$

Results and discussion

The diffraction patterns of non-treated willow wood and of the willow wood treated with 10% NaOH solution for 90 minutes are shown respectively in ***Figure 1*** and ***Figure 2***. On both diffraction curves, only the [17] (101), (10-1) and (021)/(002) characteristic diffraction peaks of cellulose I occur at 2 θ, approximately equal to 15.0°, 17.0° and 22.5°. Hence, it is clear that, for the treatment period up to 90 minutes, no mercerization of the willow wood took place under the action of 10% NaOH solution at the temperature of 20 °C.

On the contrary, on the WAXS patterns of the willow wood samples mercerized with the 15%, 20% and 25% NaOH solutions (***Figures 3-5***), additional diffraction maxima observed at 2 θ equal ca. 12.5°, 20° and 22°, besides the cellulose I diffraction peaks. This result reveals the appearance of the next cellulose allotropic form, i.e. cellulose II [17], and thereby indicates that, due to the sodium hydroxide action on the wood, the cellulose I/cellulose II polymorphic transformation had been achieved. The degree of the transformation and its dependence

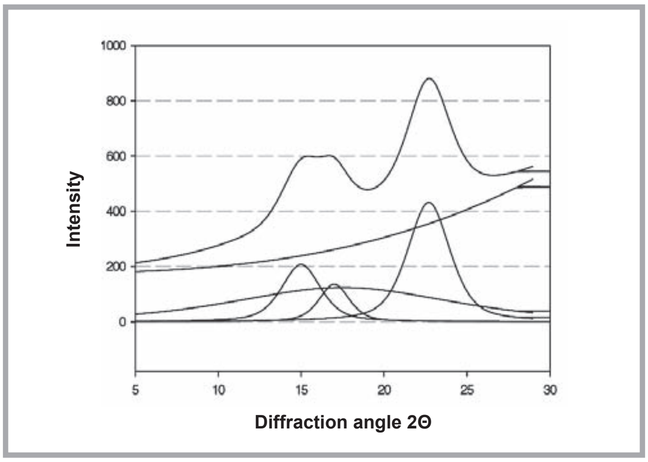

Figure 1. *X-ray diffraction pattern of untreated willow wood.*

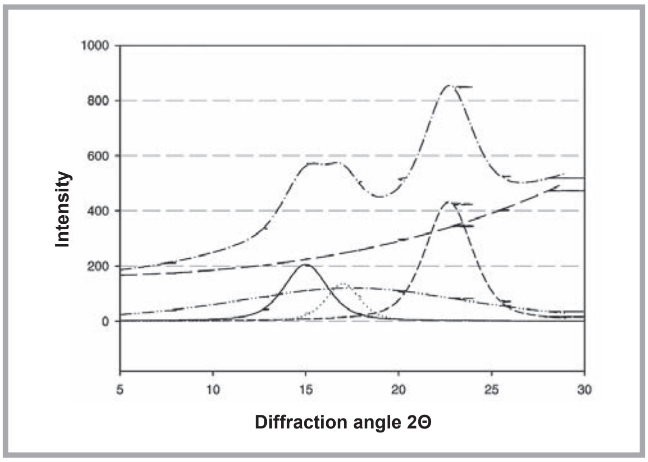

Figure 2. *X-ray diffraction pattern of willow wood treated with 10% NaOH for 90 minutes.*

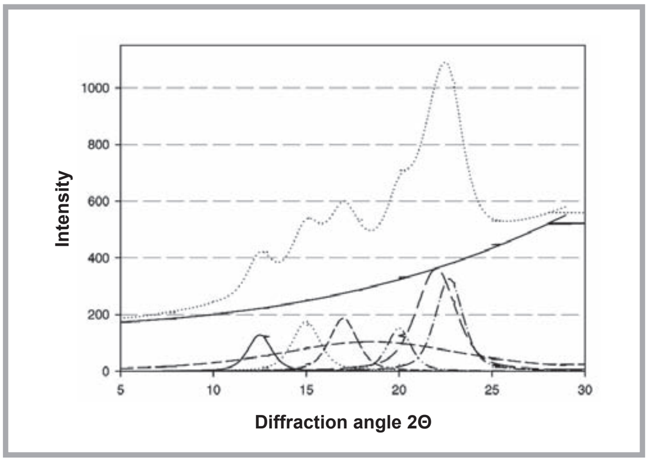

Figure 3. X-ray diffraction pattern of willow wood treated with 15% NaOH for 90 minutes.

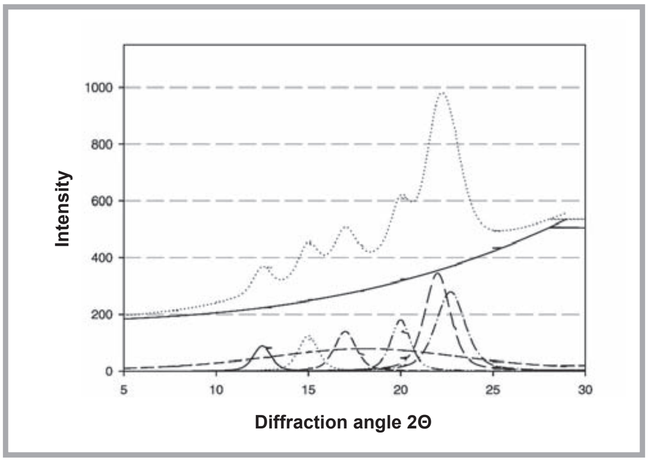

Figure 4. X-ray diffraction pattern of willow wood treated with 20% NaOH for 90 minutes.

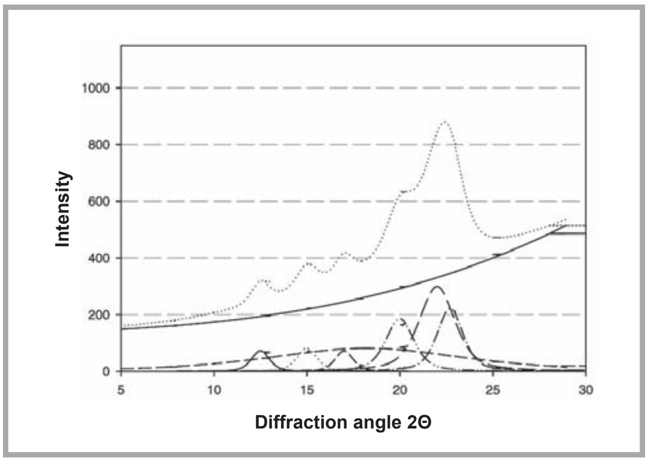

Figure 5. X-ray diffraction pattern of willow wood treated with 25% NaOH for 90 minutes.

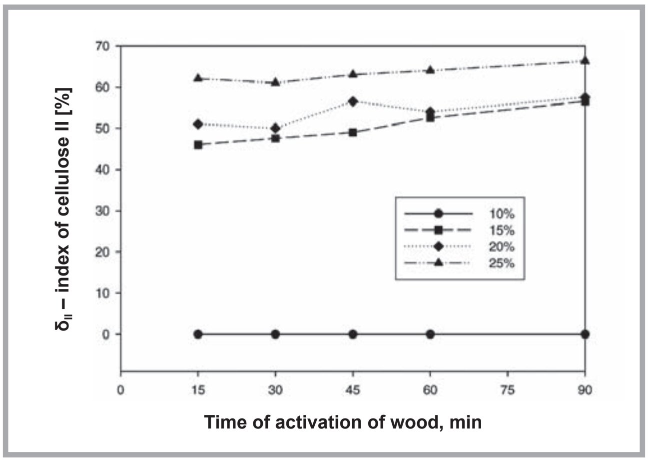

Figure 6. Index of cellulose II after treatment with sodium hydroxide.

on the treatment time and on the sodium hydroxide concentration are reflected by the changes in the δ_{II} index shown in ***Figure 6***. In general, the δ_{II} index ranges from 46% (for the minimal 15-minute treatment time with the 15% NaOH concentration) to 66% (for the maximal 90-minute treatment time with the 25% NaOH concentration). Moreover, the changes in the δ_{II} index indicate that, for each NaOH concentration, the cellulose II content increases systematically with the treatment time increase and that, in the whole range of the treatment time increase and in the whole range of the treatment time, the effectiveness of the willow wood mercerization was the highest for the samples subjected to the action of 25% NaOH solution. For comparison, in the case of the 15% NaOH concentration, the δ_{II} index increases from 46% to 56% with the increase of the treatment time from 15 to 90 minutes and in the case of the 25% concentration the δ_{II} index increases from 62% to 66% in this treatment time range.

More generally, one may conclude that mercerization of the willow wood leads to structural changes comparable with the changes determined previously for mercerized pinewood (i.e. the *Pinus silvestris* L.) [18]. As it was found, the highest degree of cellulose I/cellulose II transformation was observed in the case of 20% and 25% concentrations of sodium hydroxide solution. In both cases of NaOH action on pinewood, the δ_{II} index of cellulose II content already reached 60% after 45 minutes. When the pinewood was mercerized with 15% and 17.5% NaOH solutions, the δ_{II} index was significantly lower, i.e. after 45 minutes δ_{II} approached respectively ca. 37% and 45%. It was also found that, at a given

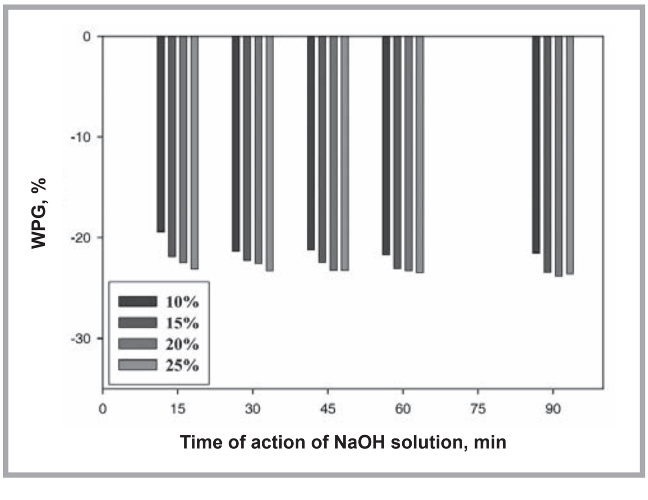

Figure 7. Values of the weight percentage gain index in dependence on time of action of NaOH solution and the concentration of the solution.

NaOH concentration, the content of cellulose II in a global amount of crystalline cellulose included in pinewood increases systematically with the increase in the mercerization period.

It is also worth emphasizing that both the pine and willow wood are less sensitive to NaOH action in comparison with natural fibres such as, for instance, flax or hemp fibres [19]. For those lignocellulosic materials, the highest increase in cellulose II content was already observed after the 7.5-minute action of sodium hydroxide. The highest efficiency of mercerization was found for the 16% NaOH solution and, in this case of NaOH action, the index of the cellulose II content reached 75% after only 10 minutes. Thus, the highest index of cellulose II content for the mercerized fibres was considerably bigger than for both pine and willow mercerized wood (65-66%). Taking into account an impact of lignin on the mercerization course [9-13], one may suppose that the relatively higher amount of lignin embedded in the woods is the main cause of the smaller degree of the cellulose I/cellulose II transformation in the mercerized woods as compared with the mercerized flax and hemp natural fibres. It is well known [10, 20] that some side processes are associated with wood mercerization, i.e. the dissolving of some of the remaining wood constituents (i.e. simple sugars, tannins, dyes, hemicelluloses, depolymerised cellulose and so on), as well as with the saponification of resin and fatty acids. These substances are removed during mercerization and consequently some mass losses of mercerized materials occur.

To estimate the quantities of substances removed from the mercerized willow wood, gravimetric measurements have been performed and, in accordance with equation (1), the weight percentage gain index (WPG) was calculated. The results obtained are presented in ***Figure 7*** (see page 99). They clearly show that the sodium hydroxide solution treatment of the willow wood leads to significant mass losses. For all the variants of the treatment conditions, the WPG index is negative, and its value ranges from -19% to -24%. It should be noticed that, even following the 15-minute NaOH treatment of the samples, the mass loss was considerable. For this treatment time, irrespective of the NaOH concentration, the WPG index equals ca. -19.5% to -21%. For the longer treatment periods, the WPG index systematically increases but finally (for the 90-minute treatment) it reaches only ca. -21.5% to -24%. In other words, irrespective of the NaOH concentration, the WPG index of willow wood increases by only 3%-4% when the treatment period increases 6 times. Finally, one may conclude that, for each NaOH concentration from 10% to 25%, the mass losses caused by willow wood mercerization weakly increase when the treatment period increases from 15 to 90 minutes.

Conclusion

In this work, the effects of sodium hydroxide solution action on willow wood (*Salix viminalis*) have been investigated for multiple treatment conditions, i.e. for willow wood treated for 15, 30, 45, 60 and 90 minutes in each case of the NaOH concentrations of 10%, 15%, 20% and 25%. On the basis of the WAXS determined δ_{II} index of cellulose II content and the gravimetrically determined WPG index of mass losses, it was established that:

- even 90-minute action of the 10% sodium hydroxide solution does not cause the transformation of cellulose I to cellulose II whereas for 15% NaOH concentration, the 15-minute treatment already causes a very distinct polymorphic transformation of the crystalline cellulose included in the wood (the δ_{II} index of cellulose II approached ca. 46% in these conditions),the effectiveness of the mercerization of willow wood is greater at 25% NaOH concentration as compared with the mercerization effectiveness with both 15% and 20% concentrations of NaOH; for instance, in the whole treatment time range, the δ_{II} index of cellulose II determined for the wood treated with 25% NaOH solution was larger by ca. 15% as compared with the index determined for the wood treated with 15% NaOH solution,an increase of 6 times in the treatment period causes only a weak increase in the mercerization effectiveness; for instance, at 25% NaOH concentration, the δ_{II} index of cellulose II content increased only from ca. 62% to 66% when the treatment period was extended from 15 to 90 minutes,irrespective of the NaOH concentration, the mass losses caused by the mercerization of the willow wood reaches ca. 20% at the minimal 15-minute alkali treatment and next weakly increase with the increase in the treatment period, i.e. finally only to ca. 24% with the maximal 90-minute alkali treatment.

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