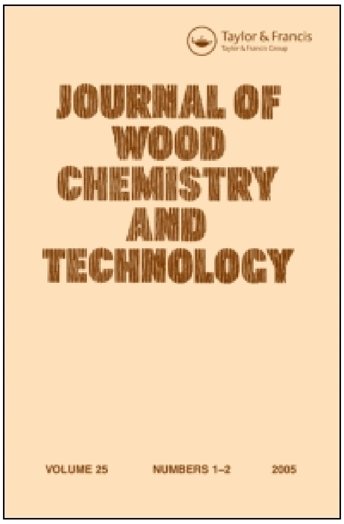

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EFFECT OF THE LOOSENING OF WOOD TEXTURE ON THE MERCERIZATION OF CELLULOSE IN WOOD

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ABSTRACT

When wood was treated with 23% aqueous sodium hydroxide followed by washing with water and drying, no lattice conversion of cellulose was observed under the experimental conditions employed. On the other hand, wood subjected to a pretreatment that results in the loosening of its morphological texture, upon mercerization, showed a varying degree of lattice conversion. The explosion process and the TFA (trifluoroacetic acid) treatment were used to achieve the loosening of wood texture. The lattice conversion of cellulose was studied by X-ray diffractograms. The extent of lattice conversion was found to depend on the conditions of the pretreatment used to achieve the loosening of wood texture. The extent of lattice conversion increased with an increase in the explosion temperature and the time at temperature, within the range of these experiments. Increased duration of TFA pretreatment, at a particular temperature, resulted in a higher degree of lattice conversion. These observed facts have been ascribed to the extent of loosening of the morphological texture of wood, which allows comparatively free swelling of cellulose in alkali.

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INTRODUCTION

In the past, several reports (1-4) have been published on the lattice conversion of cellulose by mercerization. In this case, mercerization implies treatment with aqueous sodium hydroxide having adequate concentrations followed by washing with water and drying. On the other hand, probably due to the lack of commercial application, mercerization of cellulose present in wood is seldom reported. Revol and Goring (5) have studied the mercerization of cellulose in wood and shown the formation of soda-cellulose indicating that the penetration of the caustic solution occurs, though the washing of the sodium hydroxide and drying did not result in complete lattice transformation of cellulose I to cellulose II. In our previous report (6), it was also shown that almost no lattice conversion of cellulose present in wood occurred by mercerization, although the formation of soda-cellulose had been proved to be attained. It was known (6), however, that the removal of lignin from wood resulted in increasing the extent of lattice conversion of cellulose I to cellulose II, upon mercerization.

Stone and Scallan (7) have shown that during delignification in pulping, swelling of the fiber wall increases markedly. The fiber saturation point for wood is around 0.4 ml/g, while that for pulp is about three times higher. This fact indicates, very clearly, that removal of lignin results in increasing the extent of swelling of cellulose in wood.

There are various ways of breaking the intermolecular bonding of lignin and interpolymer bonds among the main components of wood, resulting in loosening of wood texture, other than delignification.

In this sense, steaming and explosion process as well as trifluoroacetic acid (TFA) treatment were used as pretreatments for mercerization of wood, in the present study. In fact, in the present research, we have used mercerization and X-ray diffraction studies of the steamed and exploded as well as TFA treated wood samples as a method to follow, qualitatively, the extent of loosening of wood texture in relation with the pretreatment conditions.

EXPERIMENTAL

The wood species used in this work was White birch (Betula platyphylla var. japonica).

Explosion Treatment : Explosion of wood was carried out as described in an earlier communication (8). The apparatus is equipped with a boiler which can be set to a desired temperature. Wood meal of 40 to 80 mesh was placed in the pressure kettle. Steam from boiler was passed in the kettle and the desired temperature was attained almost instantaneously. After different time intervals, the pressure was released suddenly which resulted in the 'explosion' of the wood meal. The wood meal was subjected to steaming at three different temperatures 210, 190 and 170 °C for four different durations at each temperature — 15, 10, 5 and 2 min prior to the explosion process. After the explosion, samples were collected without removing any fraction and freeze-dried.

TFA (Trifluoroacetic acid) Pretreatment : To the unexploded oven-dried wood meal (20-80 mesh), trifluoroacetic acid was added (4.6 ml TFA/g wood) and kept shaking for a desired period ranging from 20 to 300 min at 25 °C. After the desired duration, the samples were washed with deionized water till the wash water was neutral in pH., filtered and dried in a vacuum oven.

Acetylation by the PCA Catalyst Method : The exploded-freeze-dried sample was further dried in a vacuum oven at 40 °C for 24 h. The completely dried wood meal (3 g) was pretreated with a mixture of acetic acid (5.28 ml) and acetic anhydride (0.84 ml) at room temperature overnight. The acylating mixture containing acetic anhydride (17.82 ml), acetic acid (9.6 ml) and catalyst PCA (perchloric acid, 0.038 ml) was added and allowed to stand at room temperature for 1 h followed by shaking at 35 °C for 3 h. The reaction was ceased by adding a solution of 0.0309 g potassium carbonate in 3 ml acetic acid and shaking at 35 °C was continued for further 30 min. The esterified wood meal was recovered and dried.

Acetylation by the TFAA Catalyst Method : Trifluoroacetic anhydride (16.2 ml) and acetic acid (6.85 ml) were mixed together and stirred at 50 °C for 30 min. This mixture was added to the oven-dried wood sample (3 g) and kept shaking at 50 °C for 2 h. The acetylated wood meal was recovered and dried.

Mercerization : The oven-dried samples, either exploded or TFA pretreated or exploded-esterified were mercerized by 23 % aqueous sodium hydroxide at room temperature for 24 h including vacuum impregnation for 1 h . After mercerization for 24 h, they were washed with deionized water till the wash water was neutral in pH, filtered and dried in a vacuum oven at 40 °C for 48 h.

X-ray Diffraction : X-ray diffractograms were obtained with disks of 2.0 cm in diameter, pressed from various wood meal samples at a pressure of 3.0 ton/cm^2. The diffraction patterns were measured from 40° to 3° values of 2 θ using Ni-filtered Cu-K radiation at 35 KV and 20 mA. The equipment used was Rigaku Denki Geiger Flex 2011B wide-angle X-ray diffractometer. The operating conditions of X-ray diffractometry were the same as described in a previous report (9).

RESULTS AND DISCUSSION

Wood in its native form contains cellulose with the cellulose I crystalline modification as a main constituent. The mercerization of wood with 23 % aqueous sodium hydroxide for 24 h followed by the washing of sodium hydroxide and drying does not result in the transformation of cellulose I to cellulose II crystalline modification as can be seen from Fig. 1. Diffractogram 1 is for the wood in native form and 2 for the same after mercerization. It is clear that no lattice transformation has taken place. This can be explained as follows. Wood is composed of three main high molecular weight constituents. Hemicellulose and lignin are deposited in between the adjacent cellulose fibrils giving it an interrupted lamellar structure. Intramolecular as well as intermolecular interactions are present within and among these wood components so that none of the physical or physicochemical characters of an individual wood component is displayed independent of the other components. Even chemical bonds exist between wood

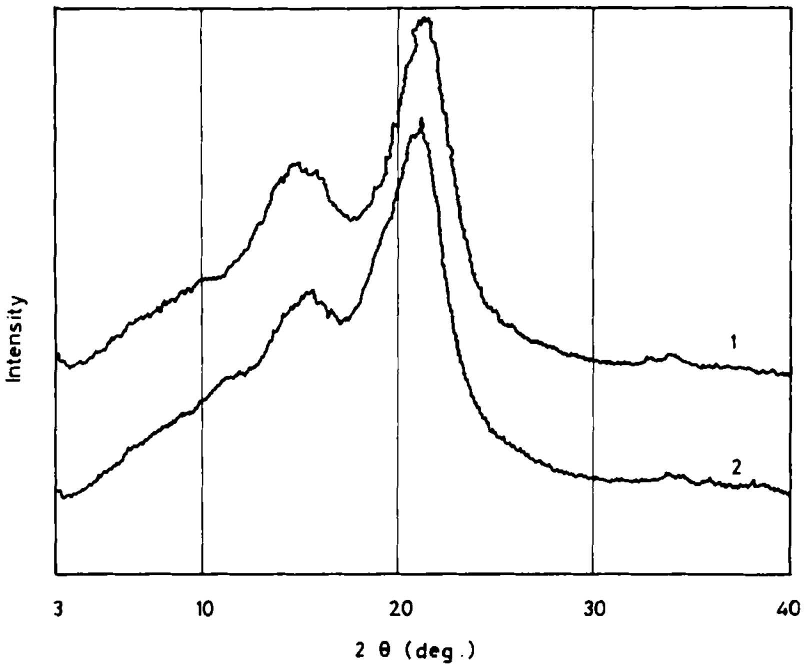

Fig. 1 Effect of the mercerization on the lattice conversion of cellulose present in wood.
1. Wood in native form. 2. Same after mercerization and recrystallization.

components as are found in lignin-carbohydrate complexes. These facts give an overall very tough and compact morphological texture to wood which restricts either the penetration of the caustic solution or the subsequent swelling of cellulose within wood in alkali and hence no lattice conversion is observed.

From the present investigation we cannot distinguish whether constraint of the presence of lignin is due to limitation of the degree of penetration of the caustic solution into the cellulose structure or to the constraint on swelling of the cellulose. But as mentioned earlier, Revol and Goring (5) and also we (6) have demonstrated the formation of soda-cellulose making it clear that the presence of lignin or the tough and compact morphological texture of wood does not limit the penetration of caustic solution into the cellulose structure. This means that the constraint of lignin is due to constraint on swelling of the cellulose. Jeffries and Warwicker (4) have shown that the swelling of cellulose is an important factor for the lattice transformation. When the fiber is allowed to swell freely in alkali, high conversion is obtained. If the swelling is restricted, the degree of mercerization is lower. Hence, it is quite reasonable to believe that the lattice transformation of cellulose within wood did not take place due to the restriction on free swelling of cellulose.

Figures 2 and 3 reveal the X-ray diffractograms of the exploded-mercerized samples. X-ray diffractograms shown in Fig. 2 are for the samples which were subjected to steaming at different temperatures—210, 190 and 170 ^{o}C but for the same duration—10 min, prior to the explosion process. After the explosion treatment they were mercerized with 23 % aqueous sodium hydroxide for 24 h. Diffractograms of the samples subjected to steaming at the same temperature—190 ^{o}C but for different durations—15, 10, 5, 2 min followed by explosion and mercerization with 23 % aqueous sodium hydroxide for 24 h are shown in Fig. 3. A rough estimate of the ratio of cellulose-I to cellulose-II, in other words, the relative extent of lattice conversion can be obtained from such a series of diffractograms by considering the intensities at the diffraction angle at which the transition between the two lattice modifications is more distinctly indicated (10). The diffraction angle of $2\,\theta = 16.2^{o}$ seems to be most suited for this purpose (6, 10).

Thus, the relative ratio of lattice conversion from cellulose I to cellulose II within wood were obtained according to the method of Ellefsen et al. (10). However, it may be noted that the values obtained for the lattice conversion ratio (LCR) in this work are not absolute but relative and, hence, in this paper, the LCR is referred to as RLCR (relative lattice conversion ratio). In fact, in this case, wood subjected to steaming at 210 ^{o}C for 15 min followed by explosion and mercerization was used as cellulose II

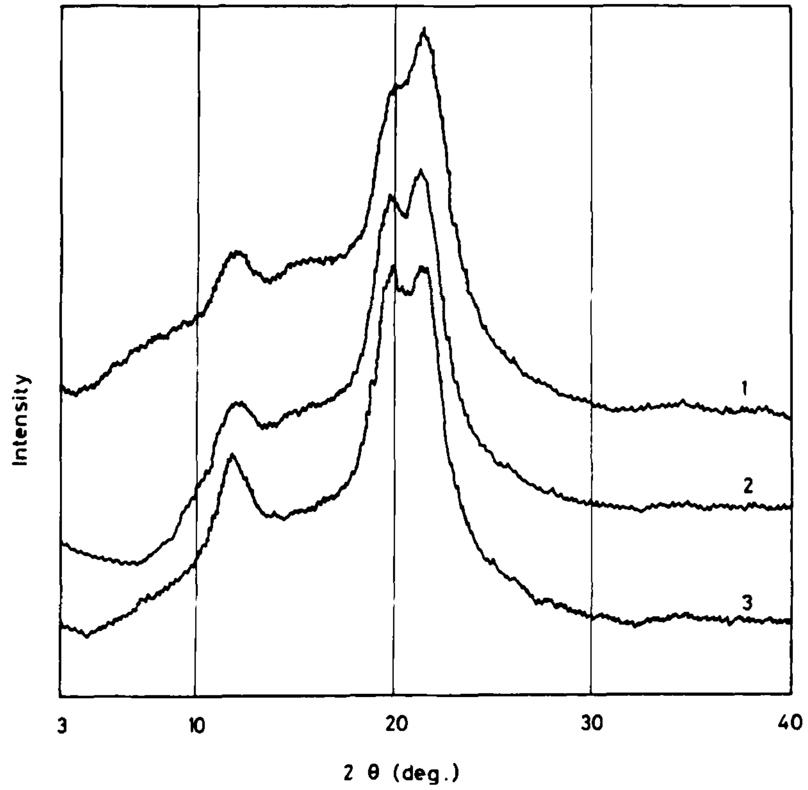

Fig. 2 Effect of the explosion temperature on the lattice conversion of cellulose present in exploded—mercerized wood. Explosion temperature 1. 170°C, 2. 190°C, 3. 210°C. Explosion duration in all the cases was 10 min.

standard and that mercerized without any pretreatment as cellulose I. The results are plotted in Fig. 4, showing that the mercerization of sample subjected to steaming at 210 °C even for short time (2-5 min), as well as at 190°C for more than 10 min prior to the explosion process, results in almost complete lattice conversion. From Figs. 2-4, we can say that as the explosion temperature and the pre-explosion steaming duration of the explosion treatment increase, the extent of the lattice conversion also increases.

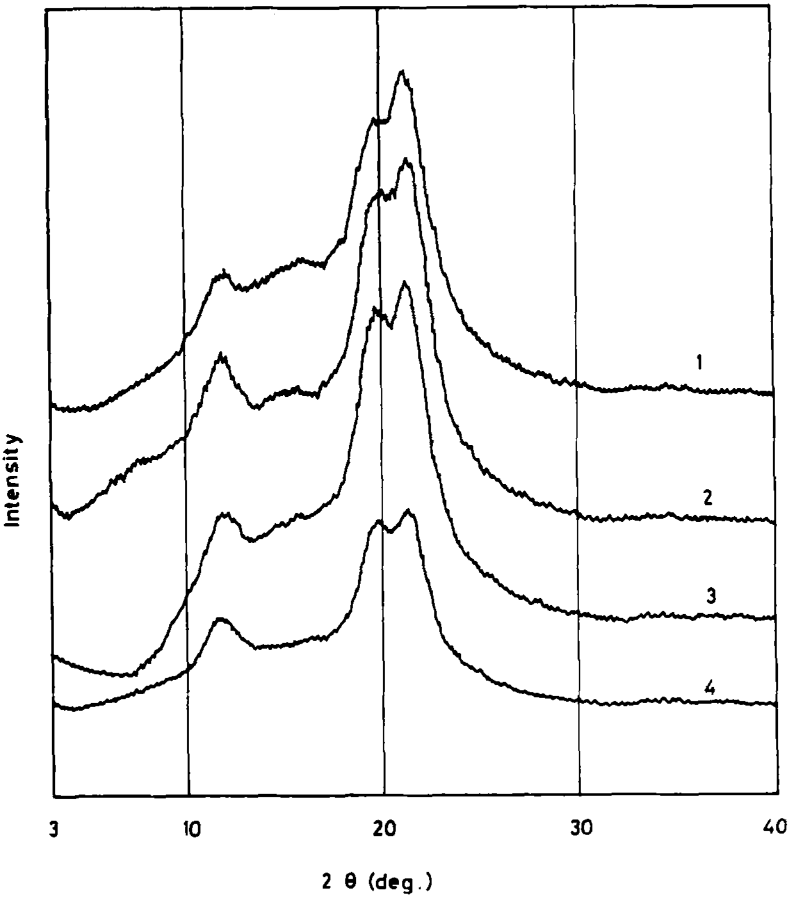

Fig. 3 Effect of the explosion duration on the lattice conversion of cellulose present in exploded—mercerized wood.
Explosion duration 1. 2 min., 2. 5 min., 3. 10 min., 4. 15 min.
Explosion temperature in all the cases was 190^{o}C.

These results obtained should be considered in relation to the results of autohydrolysis of wood reported by Lora and Wayman (11). They used autohydrolysis conditions ranging from 175 ^{o}C for 10-120 min to 215 ^{o}C for 0-8 min, which cover wider conditions compared with our present experiments. After autohydrolysis, significant quantities of lignin became soluble in subsequent aqueous dioxane,

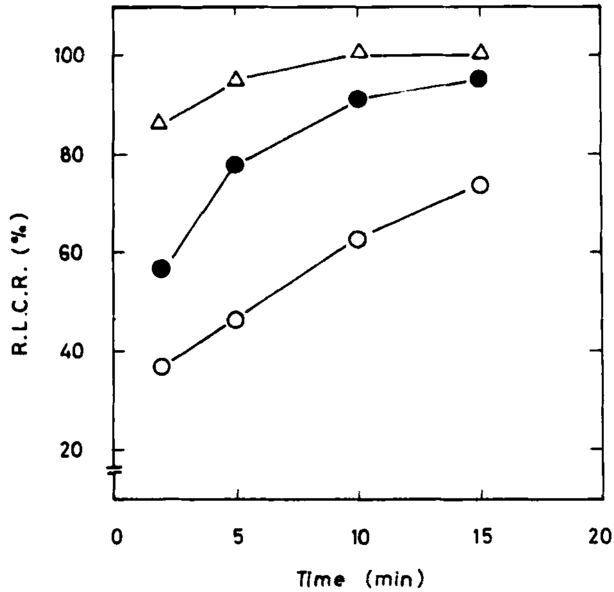

Fig. 4 Relation between the explosion conditions of wood and the relative lattice conversion of cellulose.
Explosion temperature ○ 170°C, ● 190°C, △ 210°C.

which shows degradation of lignin by the action of steaming. There was an optimum time at each autohydrolysis temperature for maximum lignin solubility. They are 80 min at 175 °C, 60 min at 185 °C, 25 min at 195 °C, 16 min at 205 °C, and 4 min at 215 °C (11). These results were interpreted to mean that two consecutive reactions were taking place (11). In the faster first reaction, lignin becomes soluble in the solvent, primarily because of the breaking of lignin-carbohydrate bonds, in addition to the depolymerization of lignin. In the slower second reaction, the soluble lignins, in the presence of the organic acid formed during the autohydrolysis, undergo condensation and repolymerization, becoming insoluble.

From the comparision of the present explosion conditions with those of the autohydrolysis conditions and the results mentioned above, it can be said that the pre-explosion steaming conditions employed in the present work, involve mainly, the first fast reaction, the breaking of lignin-carbohydrate bonds as well as the depolymerization of lignin, thus resulting in the loosening of wood texture. This must explain the facts derived from Figs. 2-4, that the extent of lattice conversion increases directly with the increase in the pre-explosion steaming temperature and duration.

The results of Fig. 2 can also be explained by Lora and Wayman's finding (11) that the maximum amount of soluble lignin as well as the amount of soluble lignin after certain autohydrolysis time at each temperature increased as the temperature increased. The maximum lignin contents extracted by 9 : 1 dioxane-water were reported to be 64.6, 78.7, 88.2, 91.0 and 91.6 % for autohydrolysis conditions of 175 ^{o}C-80 min, 185 ^{o}C-60 min, 195 ^{o}C-25 min, 205 ^{o}C -16 min and 215 ^{o}C-4 min, respectively (11). From the above arguments it is quite understandable that as the pre-explosion steaming proceeds for longer time or at higher temperature within the limit of the experimental conditions of this investigation, the extent of loosening of wood texture will be higher. And, the higher the extent of loosening of wood texture, the higher will be the degree of swelling of cellulose in alkali resulting in the greater extent of lattice conversion of cellulose within wood.

The diffractogram (curve 1) shown in the upper region of Fig. 5 is for a sample subjected to steaming at 170 ^{o}C for 2 min followed by explosion and mercerization under the same conditions as mentioned earlier. It reveals a partial lattice conversion, which means a mixture of cellulose-I and cellulose-II. The acetylation of the same sample by PCA (perchloric acid) catalyst method, followed by saponification and mercerization causes only little change and the diffractogram (Fig. 5, curve 2), shows slightly higher degree of lattice conversion than the preceding curve (Fig. 5 curve 1). However, if the same sample (pre-explosion steaming at 170 ^{o}C for 2 min) is acetylated by TFAA (trifluoroacetic anhydride) catalyst method and then saponified and mercerized under the same conditions, it shows a total lattice conversion to cellulose-II, as seen in the lower region of Fig. 5 (curve 3).

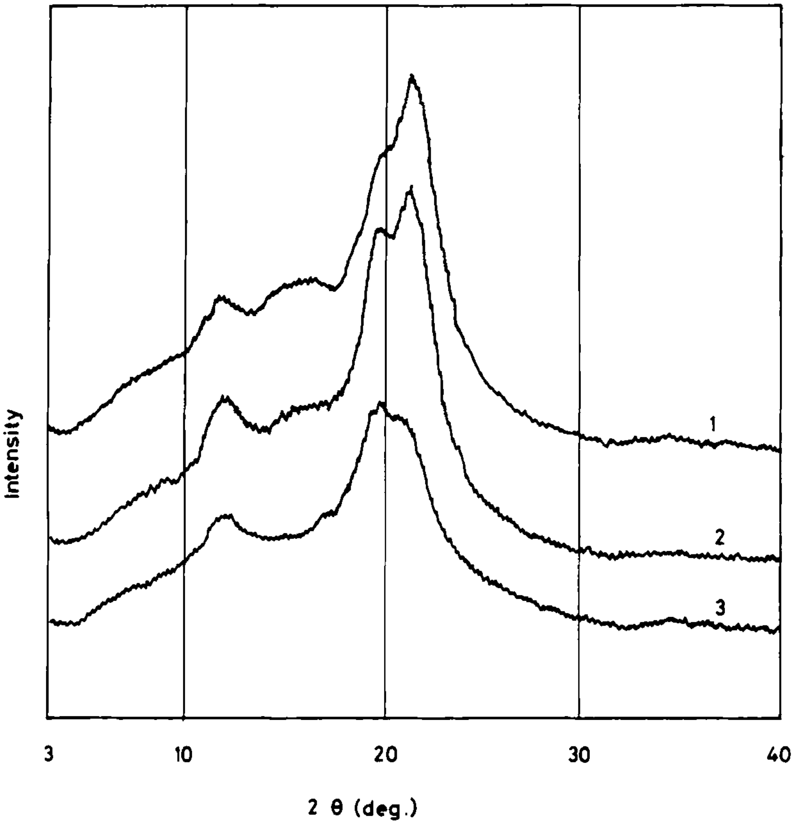

Fig. 5 Effect of the acylating system on the lattice conversion of cellulose present in wood.
1. Exploded (170°C/2 min)—mercerized wood., 2. Exploded (170°C/2 min)—acetylated by PCA catalysist method—mercerized, 3. Exploded (170°C/2 min)—acetylated by TFAA catalyst method—mercerized.

This means that the change from a partial lattice conversion exhibited by exploded-mercerized sample to a total lattice conversion observed for exploded-acetylated-mercerized sample is due to the acetylation by TFAA catalyst method. Furthermore, our previous results (6) have made it clear that the mere acetylation by a milder method like the one using DMF/ pyridine/acid choride

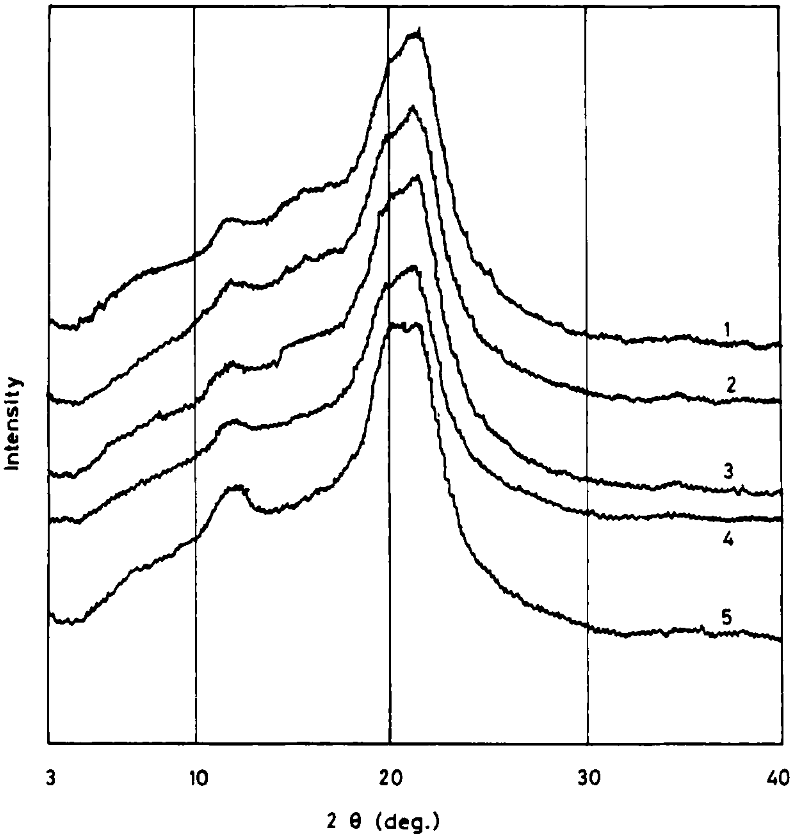

Fig. 6 Effect of the TFA pretreatment duration on the lattice conversion of cellulose present in wood.
Pretreatment duration 1. 20 min, 2. 40 min., 3. 60 min., 4. 120 min., 5. 300 min.
Pretreatment temperature in all the cases was 25°C.

reaction system has no effect on the lattice conversion of cellulose. Then, the change from a partial lattice conversion (mixture of cellulose-I and cellulose-II) to a total lattice conversion to cellulose-II observed in curve 3 of Fig. 5 is, most likely, due to the effect of trifluoroacetic acid which is formed during the acetylation by TFAA catalyst method. Trifluoroacetic acid is known to cleave O-benzyl groups. Marsh and Goodman (12) have reported on the selective fission of the benzyl-aryl ether bond among ether linkages by the action of trifluoroacetic acid at room temperature. Hence, it might be possible that the O-benzyl aryl groups present in lignin, that is, the two kinds of α-O-4 bonds (as in cyclic and in open ethers), are cleaved by trifluoroacetic acid which results in loosening of the wood texture. This prompted us to follow, qualitatively, the extent of loosening of wood texture by TFA pretreatment.

Wood meal pretreated with TFA at 25 ^{o}C for different durations was mercerized by 23% aqueous sodium hydroxide for 24 h. X-ray diffractograms obtained are shown in Fig. 6. Similar to the pre-explosion steaming intervals, duration of TFA pretreatment is directly related to the extent of lattice conversion of cellulose. Though the explosion process and TFA pretreatment proceed by different mechanisms, both result in the loosening of the morphological texture of wood.

CONCLUSION

The extent of conversion of cellulose-I to cellulose -II, in exploded wood, by mercerization with alkali has been ascribed to the extent of loosening of wood texture. In fact, the extent of lattice conversion of cellulose in wood, after mercerization of exploded samples, can be used as a qualitative measure for the loosening of wood texture by the explosion process. The examined explosion temperature (170-210 ^{o}C) and the pre-explosion steaming duration (2-15 min) were found directly related to the degree of lattice conversion of cellulose present in wood. Trifluoroacetic acid treatment had a similar effect, though perhaps by a different mechanism.

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