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ORIGINAL ARTICLE

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Study of crystalline behavior of heat-treated wood cellulose during treatments in water

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Abstract The crystalline behavior of heat-treated wood cellulose treated at 85% relative humidity (RH), in water, or boiled in water after heat treatment was investigated. The normal increased crystallinity was significantly depressed for samples that were oven-dried and then treated in 85% RH or in water. In the case of boiling-water treatment, a more pronounced increased in crystallinity was initially observed, which then decreased gradually. The crystallinity decreased more than untreated wood for samples that were heat treated for long periods and was slightly higher than the decreased crystallinity from the beginning of the above two treatments. On the other hand, no significant change in crystallinity was observed for samples of increased crystallinity or decreased crystallinity that were treated under high-moisture conditions, for all three treatments. The results show that the crystalline state of wood cellulose heat treated under oven dry or high-moisture conditions behave differently if treated in water after heat treatment. Results suggested that the mechanism of crystallization might be different for samples that are subjected to heat treatment under oven-dry and high-moisture conditions.

Key words Wood cellulose · Heat treatment · Watering and boiling treatment · Crystallinity

Introduction

The increase in the degree of crystallinity of wood cellulose caused by heat treatment under highly moist conditions is almost twice that obtained by oven-dry heating.[1] Although the increase in the crystallinity of wood cellulose by heat treatment under oven-dry conditions has been reported by other researchers,[2–5] no report has been found that examines the further changes of already increased crystallinity in wood cellulose after heat treatment. The effect of water on increased crystallinity after heat treatment was examined in this study. It can be assumed that the increased crystallinity of heat-treated wood cellulose under oven-dry and highly moist conditions may behave differently if the heat-treated wood samples are treated in water. The different behavior of the crystalline state of wood cellulose may increase our knowledge regarding wood drying by heat treatment, because the crystalline state significantly influences other properties such as the elasticity, absorptive capacity, and other industrially valuable physical properties of the fiber.[6] Therefore, the objective of this study was to determine the crystalline behavior such as the degree of crystallinity and the width of crystal of heat-treated wood cellulose treated with fresh water and boiled in water after heat treatment.

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Materials and methods

Spruce (*Picea sitchensis* Carr.) and buna (*Fagus crenata* Bl.) were used for the experiments. Wood powder of about 40–80 mesh was prepared from the respective wood species. For heat treatment under the oven-dry condition, wood powder was compressed at 200 Kgf/cm^2 into a 2-cm diameter pellet for 2 min. Each sample contained 0.5 g of wood powder. The samples were dried at 105°C for 2 h in the drying oven and then the degree of crystallinity and width of crystal of untreated wood cellulose were measured. The heat treatment was carried out at 220°C in the drying oven with durations ranging from 10 min to 4 h. For heat treatment under the highly moist condition, 1 g of oven-dried wood powder was mixed with 3 ml of water. After mixing the wood powder with water, the sample was enclosed in a microreactor. The heat treatment was carried out in a silicon oil bath using the same temperature and timing schedule as for the oven-dry condition. The heat-treated wood powder was collected from the microreactor and dried in air for 1 week. The sample was prepared in the same manner

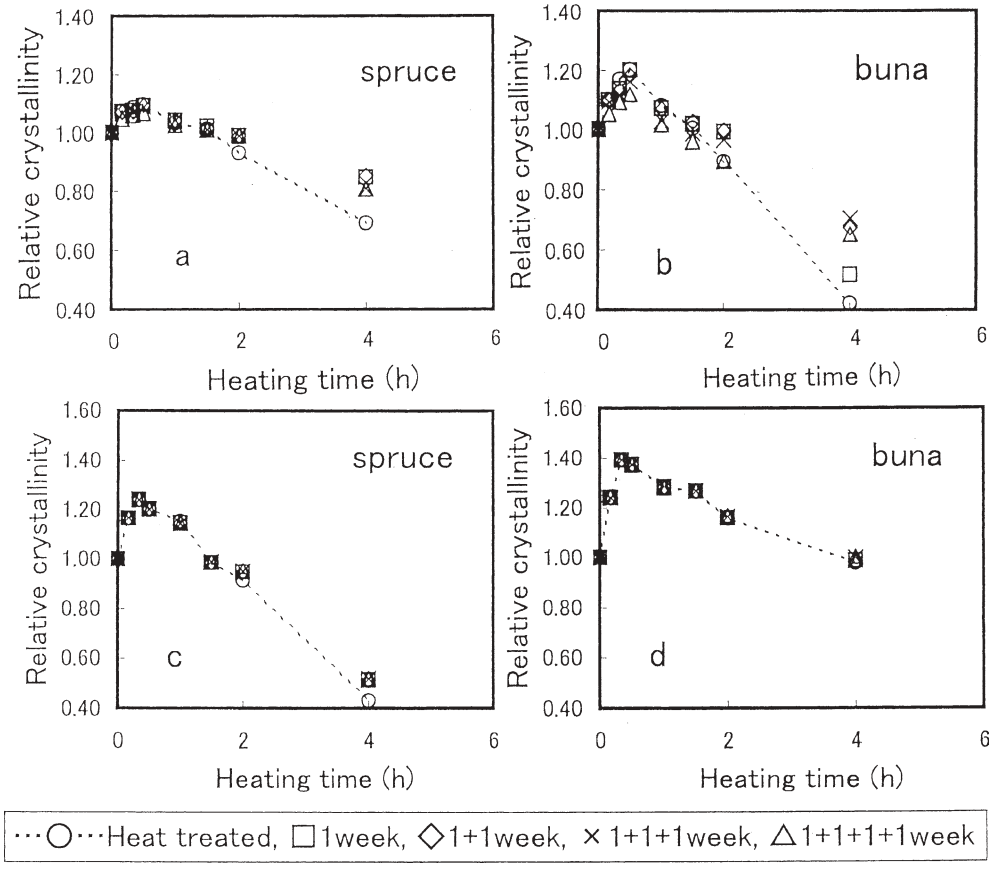

Fig. 1a–d. Changes in crystallinity of oven-dry (**a**, **b**) and high-moisture (**c**, **d**) heat-treated (220°C) wood after treatment at 85% relative humidity

and then dried at 105°C for 2 h. The degree of crystallinity[7] was determined from the ratio of the integral intensity of crystalline portions to the total intensity of the sample over the range of 2θ of 5° to 40°.

$$\mathrm{Dr} = \left[Ic/(Ic + I\mathrm{am})\right] \times 100(\%) \quad (1)$$

where Dr is degree of crystallinity, and *I*c and *I*am are the intensities of crystalline and amorphous portions, respectively.

The width of crystal[8] was determined from the following formula:

$$t = K \times \lambda/(B\cos\theta)(\text{Å}) \quad (2)$$

where t is the width of crystal, K is the Scherrer constant (0.9), λ is the wavelength of the X-ray, B is the half-bandwidth in radians, and θ is the Bragg angle.

After the measurement of crystallinity and width of crystal, individual sets of heat-treated wood samples were treated in (KCl) 85% relative humidity, in water (3 ml), or in boiling water for durations of 1 week, 1 day, and 1 h, respectively. In this way, these treatments were performed four times for the same duration. The samples were then dried in a desiccator with silica gel for 1 week after each treatment and the X-ray diffraction pattern was recorded each time. The crystallinity and width of crystal were measured as previously described.

Results and discussion

Crystalline behavior of heat-treated wood after treatment at 85% relative humidity and in water

Decreases of crystallinity were observed for samples that were heat treated under oven-dry conditions for short durations and then treated at 85% relative humidity (RH) as shown in Fig. 1a,b. Figure 2a,b showed similar results after treatment in water. However, Fig. 1c,d and Fig. 2c,d show almost unchanged crystallinity for the same treatments using samples heated under high-moisture conditions. In the case of long heat treatments, the crystallinity decreased more than untreated wood. It is revealed from Figs. 1 and 2 that the decreased crystallinity of samples heated for long periods increased after treated at 85% RH, and in water, regardless of whether oven-dry or highly moist heating was used. The increase of decreased crystallinity was greater for the oven-dry heat-treated samples than the high-moisture heat-treated samples, although it never reached the same crystallinity of untreated wood. In the case of oven-dry heated samples treated at 85% RH and in water, the absorbed water might react with the increased crystalline portions and gradually become quasi-crystalline again. This may have caused decrystallization of wood cellulose and, finally, a decrease in the crystallinity, because heat treatment was performed under absolutely dry conditions and

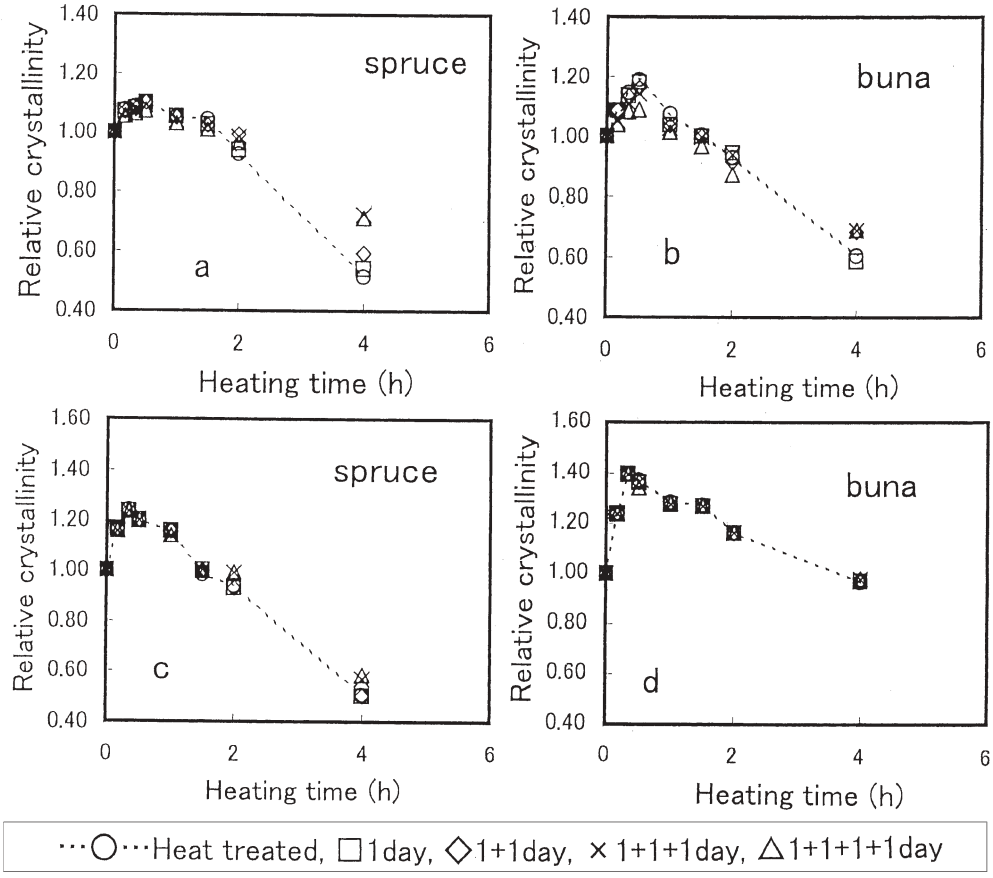

Fig. 2a–d. Changes in crystallinity of oven-dry (**a**, **b**) and high-moisture (**c**, **d**) heat-treated (220°C) wood after treatment in water

then only water without any heat was used in the treatment. In the case of high-moisture heat treatment, water was used at the time of heat treatment and then samples were prepared for the next experiment. Therefore, further use of water might not react with the increased crystalline portion, resulting in almost unchanged crystallinity.

On the other hand, the mechanism of crystallization might be different for the oven-dry and high-moisture heat treatments. In the case of high-moisture heat treatment, water is converted to steam and produces pressure inside the microreactor and the inner stress in wood becomes less than in the oven-dry condition. There is evidence that activated steam degrades lignin. Acetic acid is formed from the acetyl group of hemicellulose, and levulinic and formic acids form after degradation of the hemicellulose, resulting in partially degraded wood components becoming mobile and subsequent loosening of the inner stress in the crystalline region of cellulose.[9] However, it is assumed that the oven-dry heat treatment does not strongly affect the inner stress in wood. Under such different internal conditions in the wood, the mechanism of crystallization might differ between the above two heating conditions. Therefore, different crystalline behavior could be observed using oven-dry and high-moisture heat-treated wood samples.

Our previous study revealed that the activation energy of crystallization for the oven-dry heat treatment is more than twice that for high-moisture heating.[1] This result suggested that induced crystallization occurred and caused high stress–strain conditions inside the crystalline regions during oven-dry heating, which can be considered as an unstable crystalline state in heat-treated wood cellulose. However, lower activation energy for crystallization during high-moisture heating may indicate lower stress–strain conditions in the crystalline region. Under such circumstances, the increased crystallinity of oven-dry heat-treated wood might be easily reduced by treatment in water. It appears too difficult to reduce the increased crystallinity of high-moisture heat-treated wood using water only.

There is evidence that wood can be decrystallized by using a mixture of diethyl amine, sulfur dioxide, and dimethyl sulfoxide (DMSO), and that decrystallized wood is easily recrystallized by immersing it in water.[10] On the other hand, wood always has a tendency to retain its original structure. The structural and physical changes in wood might occur with heat treatment because inner stress in the wood might increase after the heat treatment, resulting in an increase of internal strain in the wood. The use of water may relax strain in the wood and thereby aid in the return to the original structural formation. This may pertain to recrystallization by the rearrangement and reorientation of the fiber of samples that were heat treated for a long time in which crystallinity decreased more than untreated wood. Therefore, increases in crystallinity may be possible for the samples in which crystallinity decreased more than

untreated wood after a long duration of heating before the treatment. The width of crystal showed similar behavior to crystallinity for the treatments in 85% RH shown in Fig. 4a,b and for the treatment in water shown in Fig. 5a,b using oven-dry heat-treated samples. This may be due to the same reasons described earlier. On the other hand, the crystal width of the high-moisture samples that were heat treated for a long time did not decrease in the same way as the crystallinity. The crystal width in treated samples is always higher than in untreated wood, even after 4h of high-moisture heat treatments which are shown in Figs. 4c,d and 5c,d. The change of crystal width was insignificant in the treatment at 85% RH, but it decreased after treatment in water, which was not found in the case of crystallinity. Presently, the reason for the different behavior between crystallinity and crystal width is not clear and further work is now in progress to determine the reasons for the difference.

Crystalline behavior of heat-treated wood after boiling in water

A significant increase in crystallinity was observed after the first boil in water, after which it gradually decreased from the second treatment for the samples of oven-dry heating, as shown in Fig. 3a,b, and was almost unchanged in the case of high-moisture heat-treated samples, as shown in Fig. 3c,d. The samples that were heat treated for long periods and showed decreased crystallinity more so than untreated wood showed a small increasing trend of crystallinity. Water and heat are both used for the heat treatment in boiling water. It was found earlier that the increase in crystallinity in the case of high-moisture heating is about twice that of oven-dry heating.[1] Therefore, further increases in crystallinity after boiling in water using samples that were oven dried may occur due to the more pronounced increase of crystallinity during high-moisture heating. Maximum crystallization occurred under high-moisture heat treatment and there was no capacity for further crystallization after boiling in water. Therefore, no significant change of crystallinity was found after boiling in water using samples that were heat treated under high-moisture conditions. Figure 6a,b shows the crystal width after boiling in water using oven-dry heat-treated wood. The result appears to be similar to that for crystallinity and may be due to the same reasons described earlier. In the case of samples that were heat treated at high moisture, the crystal width decreased after boiling in water to a similar degree to that after treatment in water, as shown in Fig. 6c,d.

Conclusions

The following conclusions are drawn from the above experimental results:

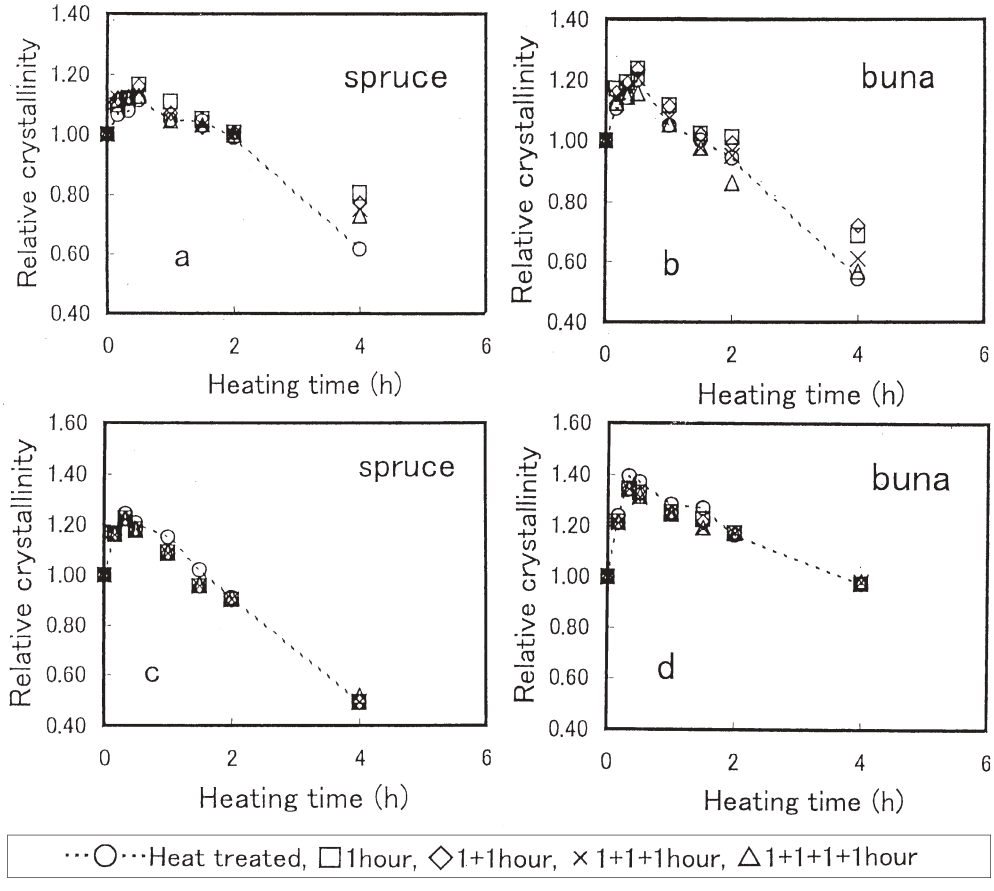

Fig. 3a–d. Changes in crystallinity of oven-dry (**a**, **b**) and high-moisture (**c**, **d**) heat-treated (220°C) wood after boiling in water

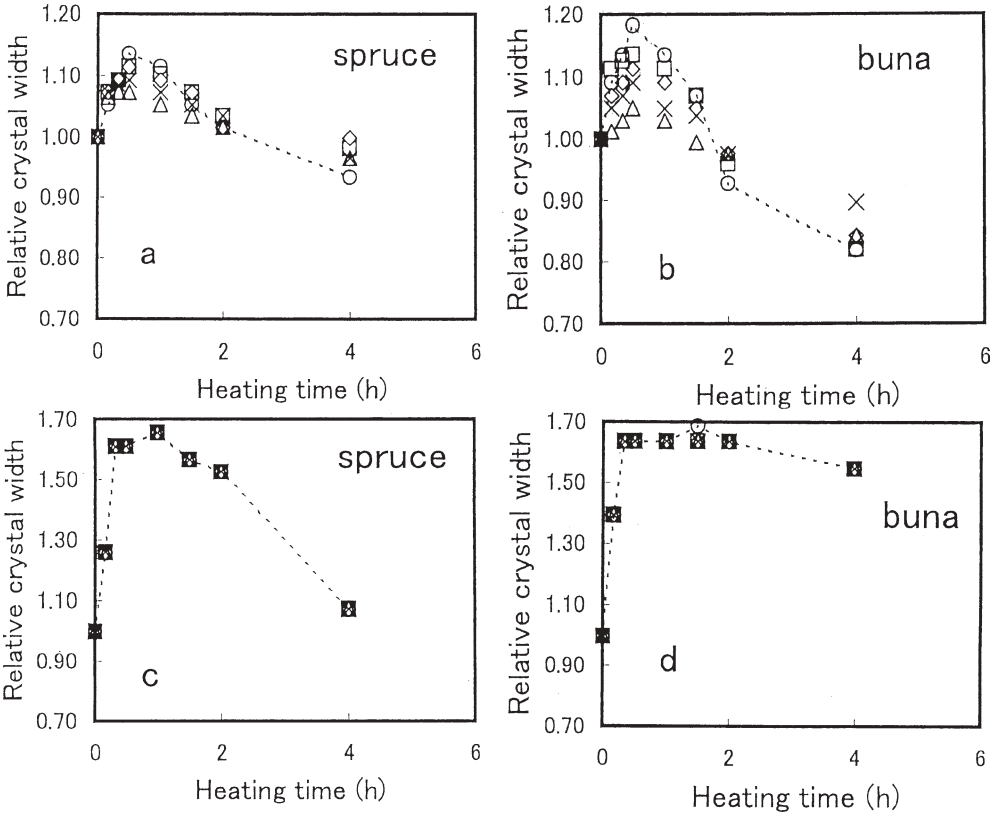

Fig. 4a–d. Changes in crystal width of oven-dry (**a**, **b**) and high-moisture (**c**, **d**) heat-treated (220°C) wood after treatment at 85% relative humidity. Symbols are the same as in Fig. 1

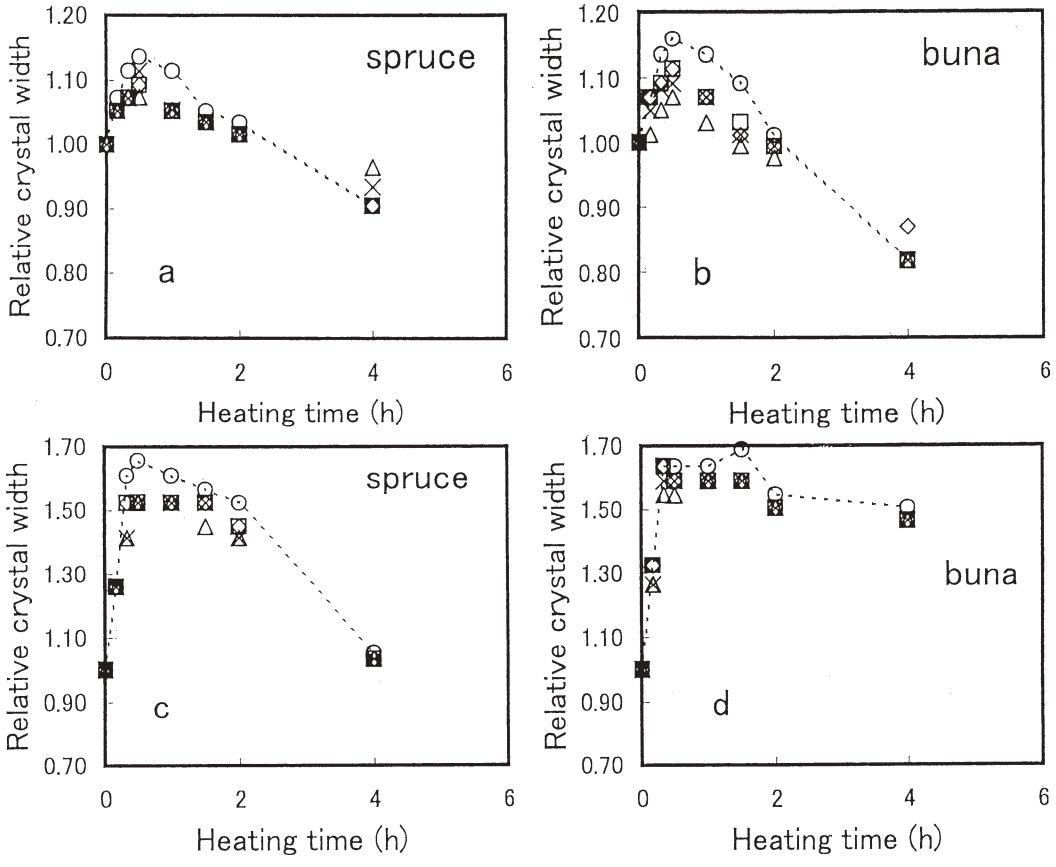

Fig. 5a–d. Changes in crystal width of oven-dry (**a**, **b**) and high-moisture (**c**, **d**) heat-treated (220°C) wood after treatment in water. Symbols are the same as in Fig. 2

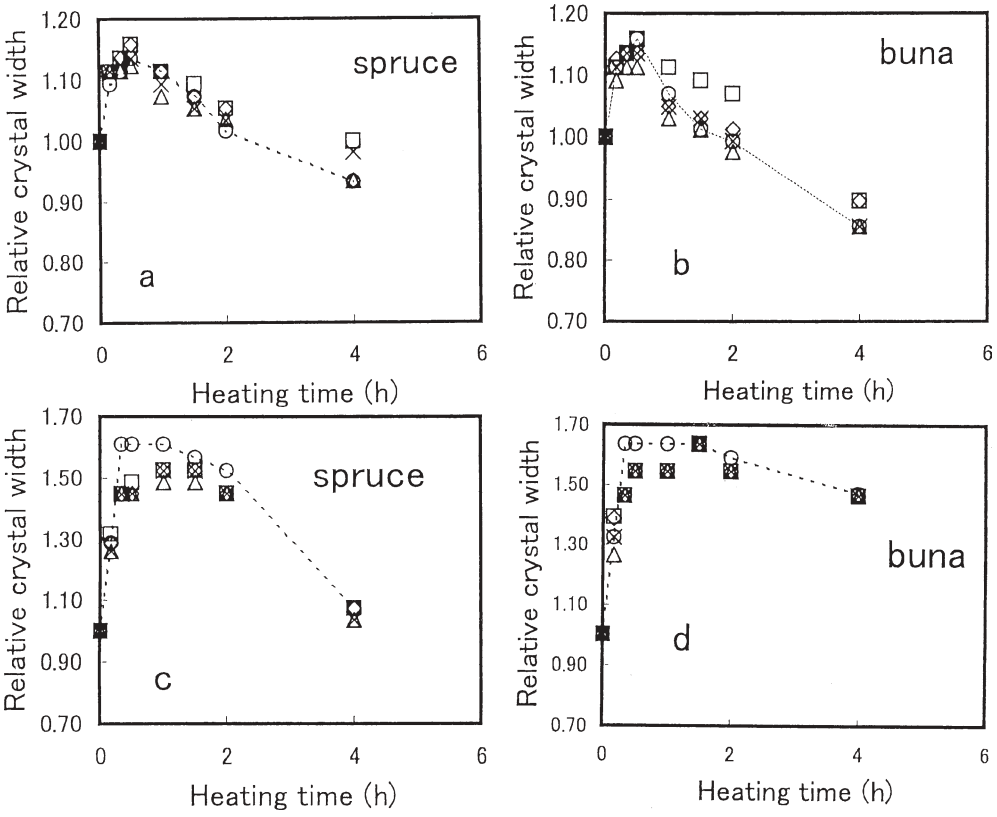

Fig. 6a–d. Changes in crystal width of oven-dry (**a**, **b**) and high-moisture (**c**, **d**) heat-treated (220°C) wood after boiling in water. Symbols are the same as in Fig. 3

1. The crystalline states of wood cellulose samples that are heat treated under oven-dry and high-moisture conditions behave differently after subsequent treatment with water.
2. We found a decreasing trend of increased crystalline portion and an increasing trend of decreased crystalline portion using water on heat-treated wood. This result indicates that the wood prefers to retain its original structural formation.
3. The results suggested that the mechanism of crystallization in wood cellulose might be different for samples that are heat treated under oven-dry and high-moisture conditions.

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