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Effect of intermittent heat treatment on crystallinity in wood cellulose

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Abstract The effect of intermittent heat treatment on cellulose crystallites in wood was studied to evaluate quantitatively the changes of crystallinity induced by intermittent and continuous heating. The changes in crystallinity were found to be strongly affected by the intermittent heat treatment. The increased crystallinity, the width of the crystals, and the piezoelectric properties were the same for the first intermittent heating as for continuous heating. Further intermittent heating for the same time duration and temperature had no effect on the above properties, probably due to the stopping of the thermal reaction during the interval. Our results suggested that intermittent heat treatment has certain critical cooling temperatures that stop the thermal reaction and are closely related to the duration of the interval. Samples once exposed to a certain duration of heat treatment and then cooled need more time, about twice that of the first duration of intermittent heating compared with continuous heating, to reach maximum crystallinity in wood cellulose.

Key words Wood cellulose · Intermittent heat treatment · Crystallinity · Piezoelectricity

Introduction

Our previous study[1] revealed that certain durations of continuous heat treatment on wood under dried and moist conditions increased the crystallinity in wood cellulose. Although some researchers have reported a change in the crystallinity of cellulose after continuous heat treatment,[2–4] no reports have dealt with the effects of intermittent heat treatment. Therefore, our knowledge of the crystalline and piezoelectric behavior of wood cellulose under intermittent heat treatment is poor. It is assumed that if the thermal reaction during continuous heat treatment of wood stops before the end of the experiment, crystallization in wood cellulose might be different for continuous and intermittent heating, even for the same period of heat treatment. Therefore, the objective of this study is to determine the effects of continuous and intermittent heat treatment on wood with the aim of explaining the variations in crystallization in wood cellulose for these two heating methods.

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Materials and methods

Specimens and conditions of heat treatment

Buna (*Fagus crenata*) was used for the experiment. About 40–80 mesh wood powder was prepared and compressed into a 2 cm diameter pallet at 2×10^6 Kgf/m^2 for 2 min by the pressure gauge to prepare a sample. Each sample contained 0.5 g of wood powder. The samples were dried in an oven at 105°C for 1.5 h and then cooled in a desiccator with absorbent silica gel. The heating temperature was controlled at 200°C from 10 min to 8 h of heating in an oven. The piezoelectric constant d'_{25} was measured from thin rectangular plates of about 1.00 mm thickness cut at 45° to the fiber direction. A gold electrode was evaporated onto both surfaces of the edge grain of a thin specimen. The samples were dried in a vacuum for 2 h and were kept in absolutely dry conditions with phosphorus pentoxide for several days.

Measurements

Degree of crystallinity

The X-ray diffraction patterns of untreated and heat-treated samples were recorded by a Rigaku RAD-1A diffractometer. The degree of crystallinity[5,6] was determined from the ratio of the integral intensity of crystalline

portions to the total intensity of the sample over a range of $2\theta = 5°$ to 40°.

Width of crystal

The width of the crystal[7] obtained from (200) diffraction was determined by the following formula:

Width of crystal (t) = $K \times \lambda/B \cos\theta$ (Å)

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

Piezoelectric constant

The piezoelectric constant was measured at a frequency of 10 Hz by a Rheolosolid (Toyo Seiki Co.) at 20°C. Dried nitrogen gas was poured into the measuring chamber to avoid water absorption during the measurement.

Results and discussion

Degree of crystallinity and width of crystal

In the case of continuous heat treatment, maximum crystallization and increased crystal width occurred after 1 h at 200°C. Therefore, the intermittent heat treatments undertaken consisted of 6 times for 10 min, 4 times for 15 min, 3 times for 20 min, 2 times for 30 min, and single times for 45 and 15 min. 1-minute interval was allowed between successive heat treatments, and the sample was kept in a desiccator during that interval for cooling. Although all the specimens were subjected to the same 1-hour heat treatment, none of the results of intermittent heat treatments reached the maximum crystallinity (Fig. 1) or maximum crystal width (Fig. 2) obtained by continuous heating. The relative crystallinity and width of the crystal in the case of intermittent heat treatments of 6 times for 10 min, 3 times for 20 min, and 2 times for 30 min were almost the same as those in the case of 10, 20, and 30 min of continuous heat treatment, respectively (Fig. 1). There is evidence that heat treatment caused the increase in crystallinity owing to crystallization in a quasicrystalline region in wood cellulose.[8] Almost the same results were observed with the first intermittent heat treatment and the continuous heating process, but no change in crystallinity or width of crystals were observed beginning with the second and further intermittent heat treatments.

At the time of the first heat treatment, some heat energy is consumed during crystallization in the quasicrystalline region. It is then necessary to produce more heat energy than that of the first heat treatment for further crystallization in the rest of the quasicrystalline region. In the case of intermittent heat treatment, the same heat energy is produced each time (the same temperature and duration), which may have no positive effects on crystallizing the rest of the quasicrystalline region. During the heat treatment,

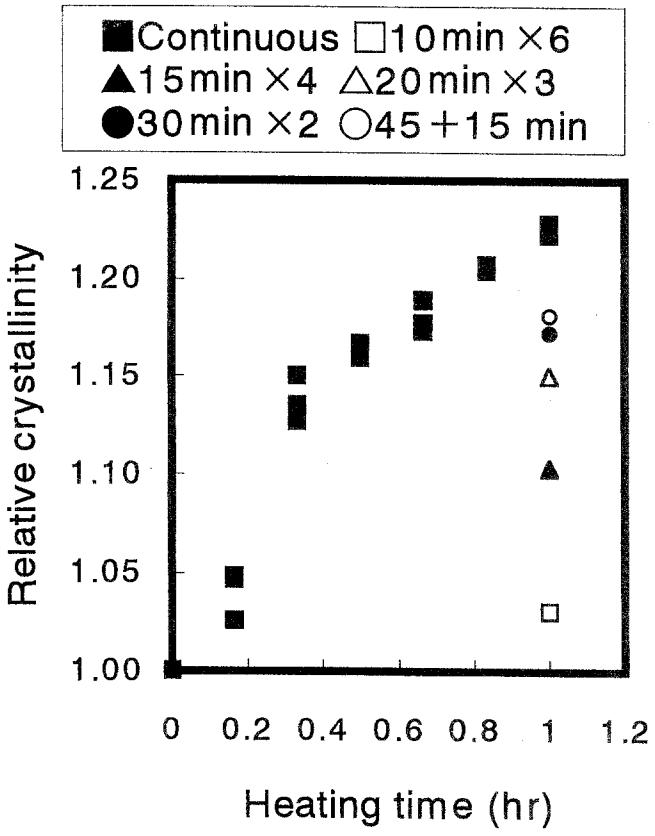

Fig. 1. Changes in crystallinity induced by continuous and intermittent heat treatment at 200°C

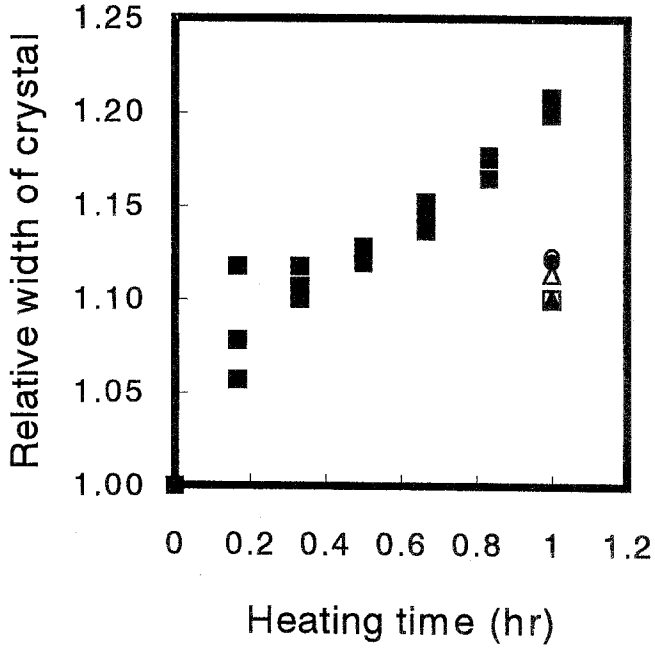

Fig. 2. Changes in crystal width induced by continuous and intermittent heat treatment at 200°C. Symbols are same as in Fig. 1

the wood component moves easily because of the heat energy, and inner stresses should be decreased, which results in crystallization in the quasicrystalline region, but intermittent heating using the same temperature and

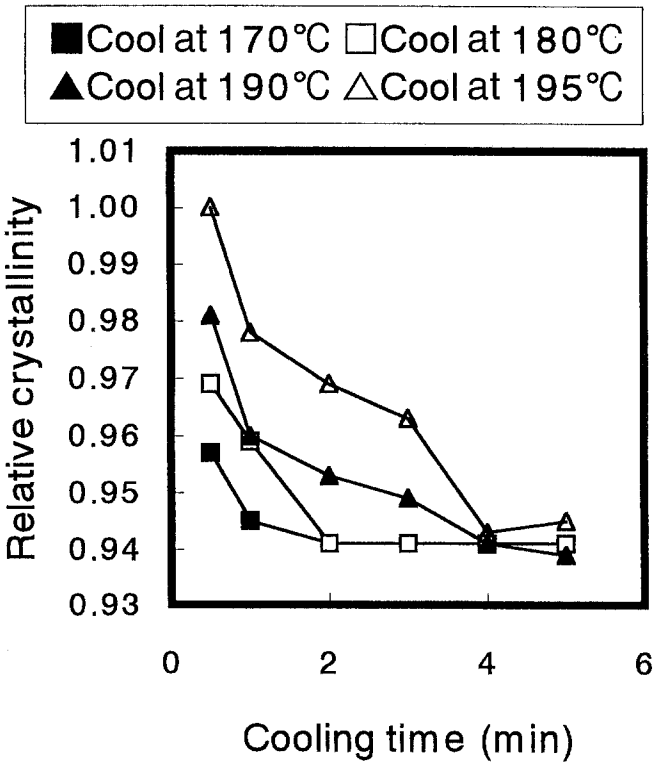

Fig. 3. Relative changes in crystallinity treated at 200°C and cooling at various temperatures with various time intervals

duration did not further change the inner stresses that favor crystallization in the quasicrystalline region, resulting in no increase in crystallinity. Based on these results, it can be seen that intermittent heat treatment has a major effect on the crystallization process. This effect might be due to the interval's contribution to stopping the thermal reaction from progressing during the heat treatment.

These results indicated the need of further experimentation.

Therefore, another experiment was done with the heat treatment 3 times for 20 min. In this case samples were kept in another drying oven (instead of a desiccator) at 170°C, 180°C, 190°C, and 195°C from 30-s to 5-min intervals. The degree of crystallinity achieved for this experiment is shown in Fig. 3. A gradual increase in crystallinity was observed at 30-s interval, reaching the same maximum crystallinity as seen with continuous heating when the cooling temperature was 195°C. Increasing crystallinity was found in the case of 1-, 2-, and 3-min intervals depending on the cooling temperature. On the other hand, an insignificant change in crystallinity was observed with the 4- and 5-min intervals irrespective of the cooling temperature. An increased time interval and decreased cooling temperature might enhance the possibility of stopping the thermal reaction, resulting in the prevention of an increase in crystallinity and vice versa. Our results suggest that intermittent heat treatment has a certain critical cooling temperature at which the thermal reaction is stopped, and that it is closely related to the duration of the interval.

The relative crystallinity $f(t)$ was calculated from $(Y - Y_{\text{lowest}})/(Y_{\text{highest}} - Y_{\text{lowest}})$, where Y_{highest} is the crystallinity after 1 h of continuous heating, Y is the individual crystallinity of each sample, and Y_{lowest} is the lowest crystallinity under intermittent heat treatment. From these data the rate of decreasing crystallinity, such as the relaxation time of crystallization (τ), was determined by the following equation

$$f(t) = e^{-t/\tau}$$

where t is the duration of the cooling interval. The values of τ were 2.5 min when samples were cooled at 195°C, 1.1 min at 190°C, 0.74 min at 180°C, and 0.39 min at 170°C. Therefore, the decreased cooling temperature resulted in decreased τ.

For long-term heat treatment, the experimental design was changed to clarify the behavior of both crystallization and decrystallization. Samples were kept in the desiccator for 1-min intervals after 10, 20, and 30 min of heat treatment; then continuous heating was carried out for 30 min to 8 h. In this report, interval 1, interval 2, and interval 3 were the 10-, 20-, and 30-min heat treatments before continuous heating, respectively. The increase and decrease in crystallinity were somewhat less after intermittent heat treatment than after continuous heating (Figs. 4a, 5a, 6a). The maximum crystallization occurred about 20 min later with intermittent heat treatment than with continuous treatment for interval 1 (Fig. 4a), whereas it happened about 40 min later in the case of interval 2 (Fig. 5a) and about 1 h later for interval 3 (Fig. 6a). Crystallization with intermittent heat treatment can be quantitatively explained based on these results. The width of crystals showed results similar to those for the crystallinity for interval 1 (Fig. 4b), interval 2 (Fig. 5b), and interval 3 (Fig. 6b). When an interval is allowed between two successive heat treatments, the wood might have a tendency to remain at the state prevailing at that time and require more heat energy than continuous heat treatment to activate and ready the wood component for the next reaction. Therefore, more time is required for intermittent heat treatment than continuous heating to reach maximum crystallinity. Our results revealed that a duration about twice as long as that of the first intermittent heat treatment is needed to reach maximum crystallinity.

Piezoelectric constant

It was revealed that the relative value of the piezoelectric constant d'_{25} reached its maximum after 1 h of continuous heating at 200°C (Fig. 7), which coincides with the results of the crystallinity experiment. Intermittent heat treatments were performed three times for 20 min each and twice for 30 min each. The piezoelectric constant was measured after each heat treatment to clarify the piezoelectric behavior after intermittent heating. After the first intermittent heat treatment the piezoelectric constant increased to the same level as was seen with continuous heating, but there was no increase in the piezoelectric constant after further intermit-

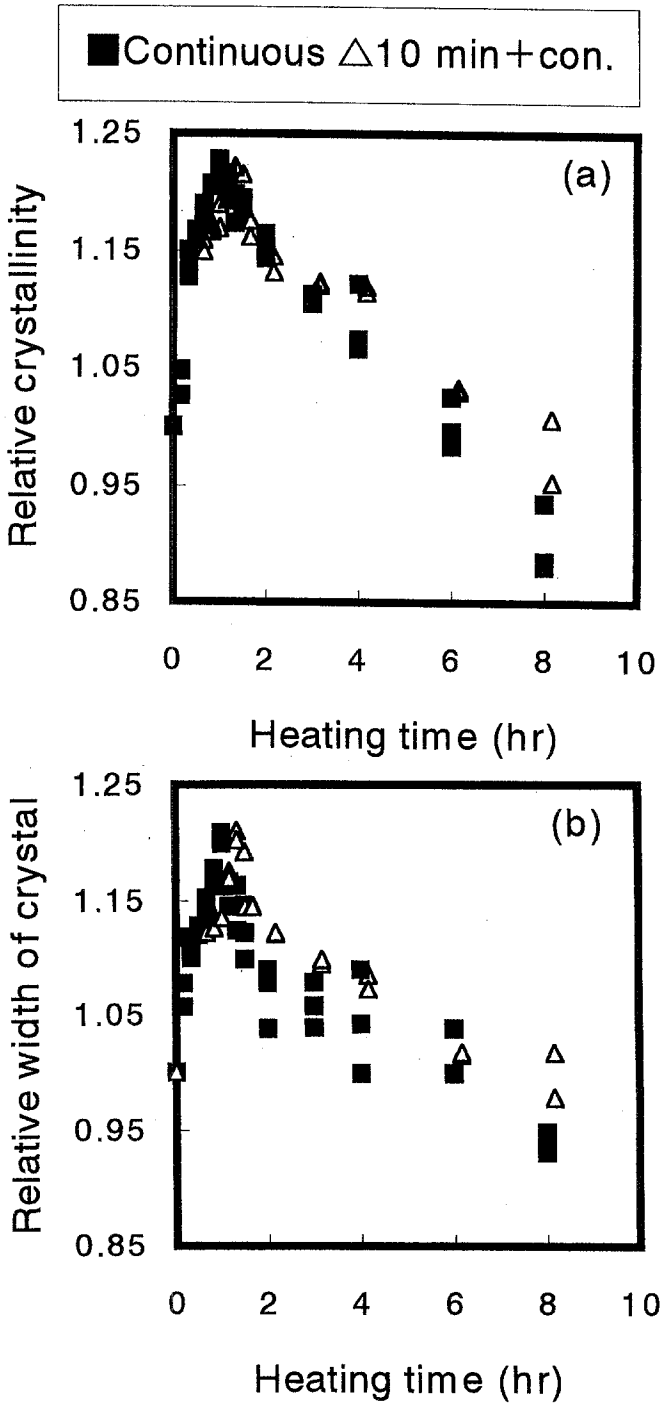

Fig. 4. Changes in crystallinity (**a**) and width of crystal (**b**) induced by continuous and intermittent heat treatment at 200°C (10min heating before continuous heat treatment)

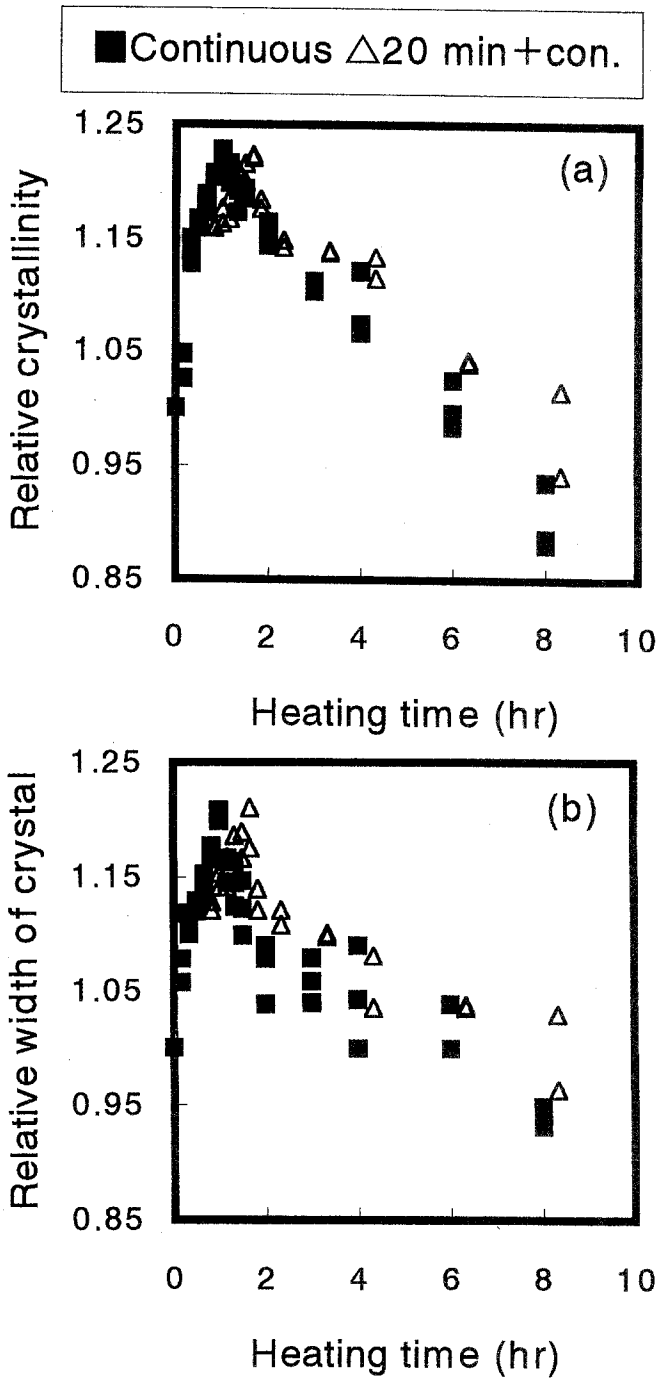

Fig. 5. Changes in crystallinity (**a**) and width of crystal (**b**) induced by continuous and intermittent heat treatment at 200°C (20min heating before continuous heat treatment)

tent heat treatment (Fig. 7). Hirai et al. stated that the piezoelectric constant greatly depends on the degree of crystallinity.[9] In the case of intermittent heat treatment, the piezoelectric constant did not change owing to the unchanged state of crystallinity by further heating. The results regarding the degree of crystallinity after intermittent heat treatment are strongly supported by the results of the piezoelectric constant tests.

Conclusions

The following conclusions can be drawn from this investigation. (1) The increase in crystallinity, the width of the crystals, and piezoelectricity occurred only after the first heat treatment with intermittent heating. Further heating for the same time and at the same temperature has no positive

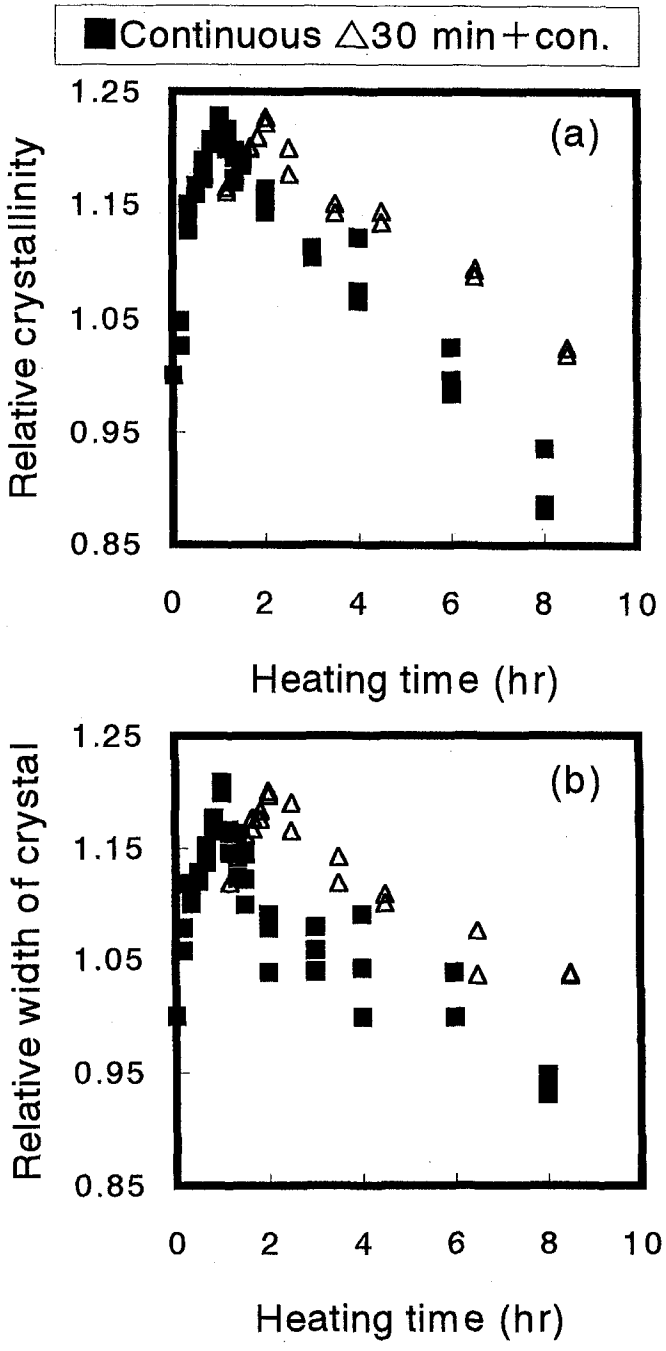

Fig. 6. Changes in crystallinity (**a**) and width of crystal (**b**) induced by continuous and intermittent heat treatment at 200°C (30 min heating before continuous heat treatment)

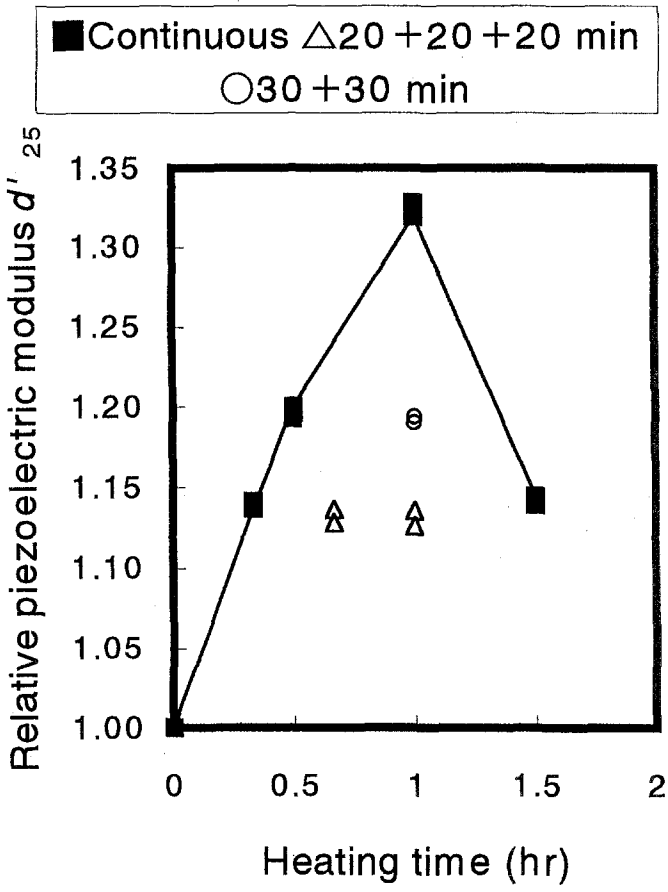

Fig. 7. Changes of piezoelectric modulus d'_{25} induced by continuous and intermittent heat treatment at 200°C

effects on those properties, which might be due to the stopping of the thermal reaction during the time of interval. Our results indicate that intermittent heat treatment has a certain critical cooling temperature that stops the thermal reaction, and it is closely related to the duration of the interval. (2) The possibility of stopping the thermal reaction is enhanced by an increase in the duration of the interval and a decrease in the cooling temperature, which prevents the increase in crystallinity and vice versa. (3) Longer heating after the first intermittent heat treatment can change the crystallinity in wood cellulose, but more time is needed to reach maximum crystallinity, about twice the duration of the first intermittent heating.

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