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ORIGINAL ARTICLE

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Behavior of piezoelectric, dielectric, and elastic constants of wood during about 40 repeated measurements between 100°C and 220°C

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Abstract This study investigated the behavior of piezoelectric, dielectric, and elastic constants and the crystallinity in wood cellulose by repeated measurements ($n = 42$) between 100°C and 220°C. There was an insignificant change in the piezoelectric constant during repeated measurements in this temperature range. On the other hand, thermal decomposition of the amorphous region contributed to the decreasing trend of dielectric and elastic constants, although only a small increase in the elastic constant was found at the time of the initial measurements. The increase in the repeated measurements in this temperature range resulted in an increase in the piezoelectric loss modulus constant d_{25}'', which is closely related to energy loss. The d_{25}'' peak shifted to a higher temperature with increasing measurements, which might be due not to the increase in rigidity of the wood specimen but to the increase in total peak area, which was observed during the later measurements. At the same time, variations of piezoelectric loss modulus d_{25}'' and e_{25}'' at advanced stages of the measurements suggested damage and structural changes in the wood.

Key words Wood cellulose · Repeated measurement · Piezoelectric constant · Dielectric constant · Elastic constant

Introduction

Piezoelectric effects are displayed by materials that contain a distinctive crystalline structure. This crystalline structure, in turn, imparts a distinctive combination of electrical and mechanical properties to the material. In wood, too, the crystalline areas in cellulose are widely believed to be the fundamental source of its piezoelectric nature. Some reports revealed that the piezoelectricity in wood is due to the crystalline state of the wood cellulose.[1–4] On the other hand, there is some evidence that continuous heat treatment of wood contributes to crystallization in wood cellulose, resulting in an increase in crystallinity.[5,6] Therefore, it is assumed that repeated measurements of piezoelectricity in wood from low to high temperature may cause a gradual increase in crystallinity as well as piezoelectricity. This type of experimentation, however, required a decrease in temperature each time to restart the measurement. At present, our knowledge about the piezoelectric, dielectric, and elastic behavior of wood during repeated measurements at high temperatures is poor. The objective of this study was to clarify the effect of repeated measurements on the piezoelectric, dielectric, and elastic constants of wood between 100°C and 220°C.

Materials and methods

Specimens

Spruce (*Picea sitchensis*) and buna (*Fagus crenata*) were used in the experiment. Rectangular pieces were cut from wood at 45° angles with respect to the fiber direction for measurement of piezoelectric, dielectric, and elastic constants. Each sample was about 2.4 × 1.0 × 0.15 cm. Gold was evaporated onto both surfaces of the edge grain of a thin specimen by an ion sputtering device, and then silver electrodes were attached to the opposite edge of the sample. The electrode area of the sample was 1.12 cm^2. On the other hand, about 40–80 mesh of wood powder was compressed into a 2 cm diameter pallet at 2 × 10^6 Kgf/m^2 for 2 min by a pressure gauge to prepare a sample for measuring the crystallinity and the width of crystals in wood cellulose by X-ray diffraction. Each sample contained 0.5 g of wood powder.

Conditions of heat treatment and measurements

The specimens for measuring piezoelectric, dielectric, and elastic constants were dried in a vacuum for 2 h and were

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kept in an absolutely dried condition with phosphorus pentoxide for several days. The piezoelectric, dielectric, and elastic constants were measured at a frequency of 10 Hz by a Rheolographsolid (Toyo Seiki) over a temperature range between 100°C and 220°C. In this experiment, the piezoelectric strain modulus $d^* = d' + id''$, stress modulus $e^* = e' + ie''$, dielectric modulus $\varepsilon^* = \varepsilon' - i\varepsilon''$, and elastic modulus $E^* = E' + iE''$ were measured. The experiment was repeated 42 times with the same sample, and the temperature was decreased naturally from 220°C to 100°C after each measurement to restart the experiment, which took about 1 h. The samples made from wood powder were also enclosed in the measuring chamber to investigate the change of crystallinity in wood cellulose. The rate of temperature increase was about 2°C/min, and dried nitrogen gas was poured into the measuring chamber to avoid water absorption during the measurement. One sample for X-ray measurement was collected from the measuring chamber after the end of each heating cycle and kept in a desiccator with silica gel. The X-ray diffraction pattern was recorded from the heat-treated wood samples. The degree of crystallinity was determined by the integral method,[7,8] and the width of the crystal was calculated according to Hamed et al.[9]

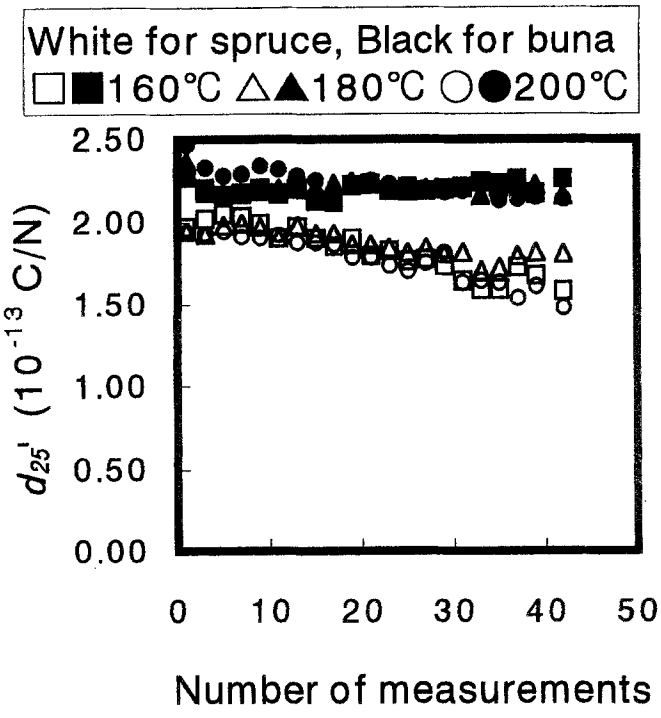

Fig. 1. Changes in the piezoelectric constant d_{25}' during repeated measurements between 100° and 220°C

Results and discussion

Piezoelectric, dielectric, and elastic constants and crystallinity

The data were recorded from three temperatures, and an insignificant change in the piezoelectric constant d_{25}' was observed for all three temperatures in the case of buna and with a decreasing trend for spruce (Fig. 1). The piezoelectric constant is believed to be highly dependent on the crystalline state of the wood cellulose. The increased crystallinity in wood cellulose contributes to the increase in piezoelectricity and vice versa.[10] The results suggested that the crystallinity in wood cellulose did not change significantly during the repeated measurements on wood in this temperature range, resulting in an almost unchanged piezoelectric constant throughout the measurements, although spruce did show a slightly decreasing trend.

A small increase in the elastic constant E' was observed during the initial stages of the measurements for buna and spruce (Fig. 2). Thereafter, an insignificant change was observed at the intermediate stages of the measurements for both spruce and buna. At the advanced stages of measurements a drastic fall in the elastic constant was found for spruce and a gradual decrease for buna. The elastic behavior of wood depends on the state of the crystalline and amorphous regions.[4] Although the results of the piezoelectric constant indicate an insignificant change in the crystalline state during the repeated measurements, thermal decomposition of the amorphous region in wood must be taken into consideration in this temperature region. Therefore, the decrease in the elastic constant E' might be due to thermal decomposition of the amorphous region.

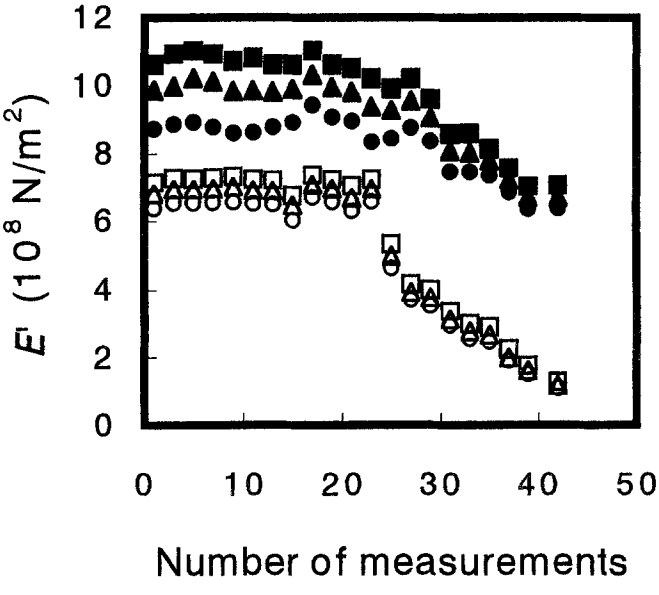

Fig. 2. Changes in the elastic constant E' during repeated measurements between 100° and 220°C. Symbols are the same as in Fig. 1

Generally, the amorphous region is created by the disordered fibers of cellulose, hemicellulose, and lignin molecules and may retain lower bonding energy, which contributes to the more rapid thermal degradation of this region than other regions. There is evidence that hemicellulose degrades thermally about four times as fast as wood, α-cellulose degrades at about the same rate as wood, and lignin degrades at about half the rate of wood.[11] Almost all of the hemicellulose may consist of an amorphous region.

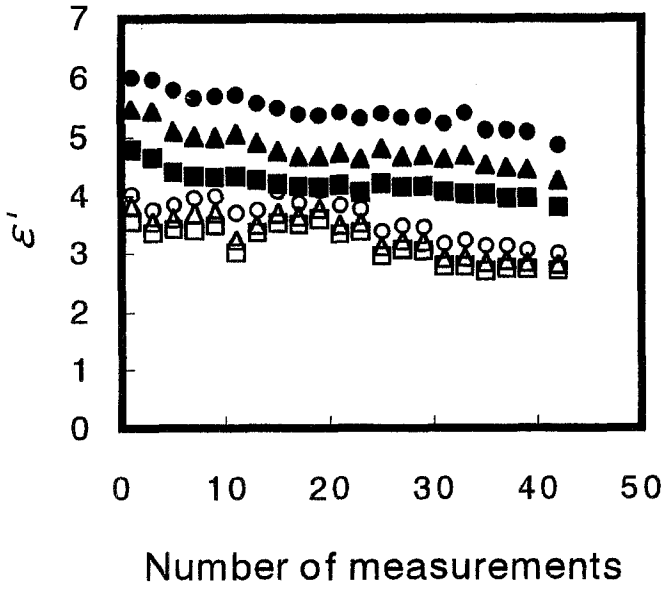

Fig. 3. Changes in the dielectric constant ε' during repeated measurements between 100° and 220°C. Symbols are the same as in Fig. 1

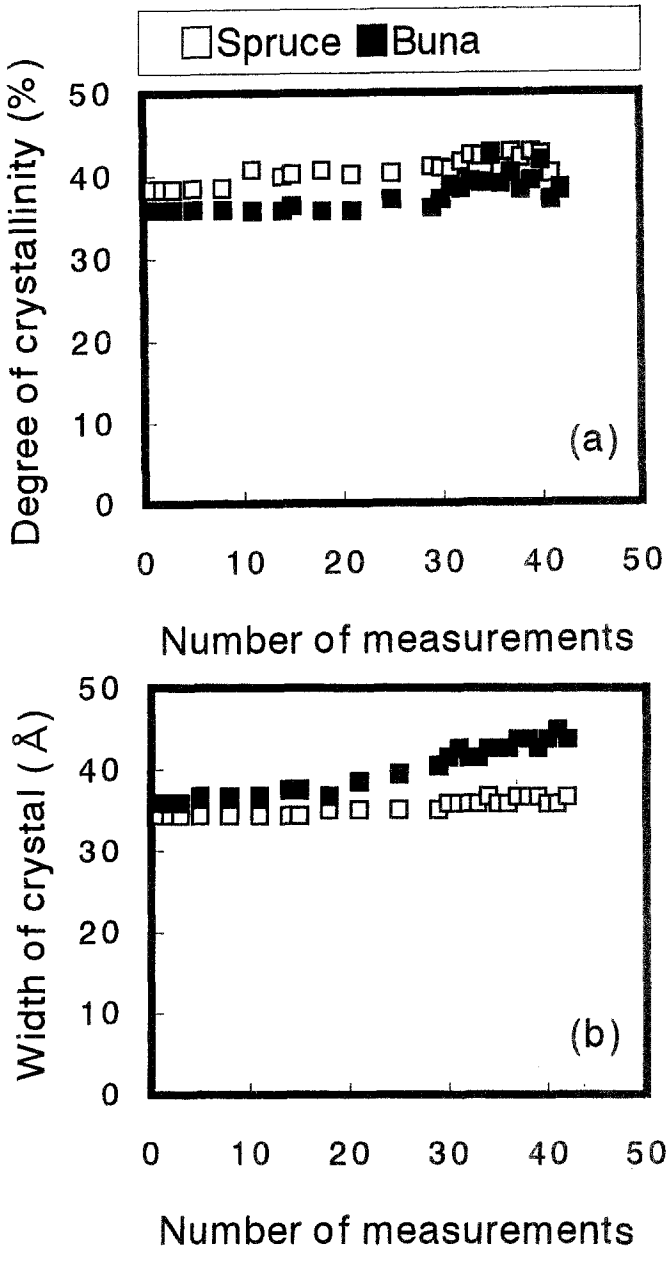

Fig. 4. Effect of repeated measurements on the degree of crystallinity (**a**) and the width of the crystals (**b**) between 100° and 220°C

Therefore, the faster degradation of hemicellulose decreases the large amorphous region and finally decreases the elastic constant.

The decreasing trend for the dielectric constant ε' was observed from the beginning of the repeated measurements, though the decrease was small (Fig. 3). The trend toward a decreasing dielectric constant can be explained as the result of the decreased amorphous region in wood due to thermal decomposition, because dielectric behavior is mostly influenced by the state of the amorphous region.

An insignificant change in crystallinity was observed until about the 30th measurement in the wood samples enclosed in the measuring chamber (Fig. 4a) for the piezoelectric, dielectric, and elastic constant measurements. After about 30 measurements, a small increase of crystallinity was observed in the case of buna, but it was insignificant in the case of spruce. At the same time, however, it was found that the weight of the sample decreased by about 5% (data not included in this article). The increased crystallinity at the later stages of the measurements might be due to the decrease in amorphous region in wood after heat treatment because wood samples were treated by more than 200°C for about 7 h. Therefore, the change in absolute crystallinity seems insignificant, with only a slightly increasing trend throughout the experiment. In the case of heat treatment of wood, the partly degraded wood components become mobile and the inner stresses are low, which favors crystallization in quasicrystalline regions. The mobility of wood components might be affected by the repeated measurements during the time of decreased temperatures needed to restart the experiment, resulting in insignificant or only a slight increase in crystallinity. Thus the results for the piezoelectric constant and crystallinity in wood cellulose were in agreement. On the other hand, the width of the crystals showed a small increasing trend at the later stages of the measurements in the case of buna (Fig. 4b) and a small increase in crystallinity for buna, which is also observed in Fig. 4a.

Loss tangent tan δ of elastic, piezoelectric, and dielectric constants

The elastic loss tangent (tan δ_E) of spruce increased significantly at the advanced stages of the measurements (Fig. 5), and the values of E' drastically decreased. Therefore, the increase in tan δ_E was due to the greater decrease of E' than of E''. On the other hand, the increase in tan δ_E in buna was comparatively less than that of spruce, but it tended to increase at the end of measurements (Fig. 5). Although the

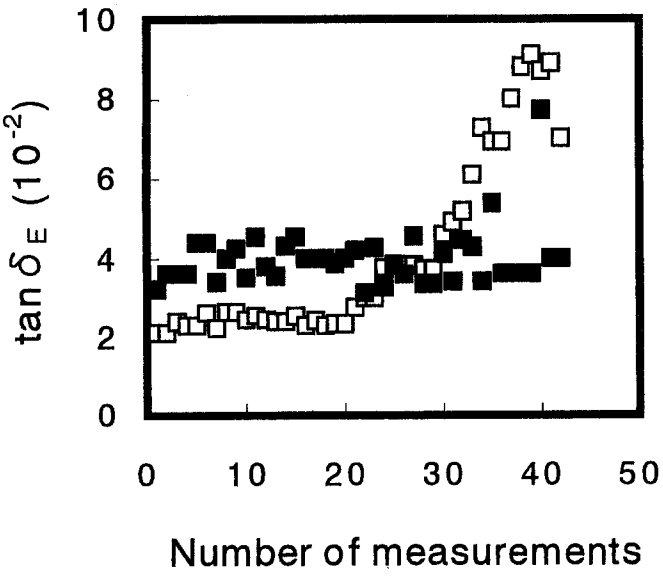

Fig. 5. Changes in tan δ_E at the peak of tan δ_d during repeated measurements between 100° and 220°C. Symbols are the same as in Fig. 4

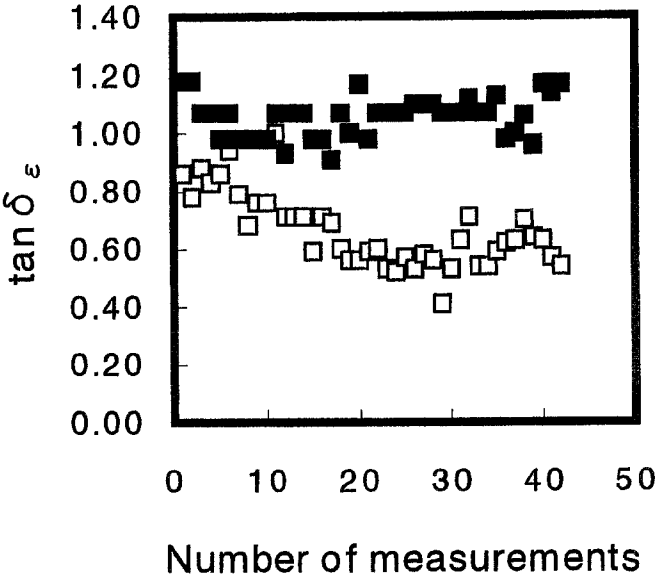

Fig. 7. Changes in tan δ_ε at the peak of tan δ_d during repeated measurement between 100° and 220°C. Symbols are the same as in Fig. 4

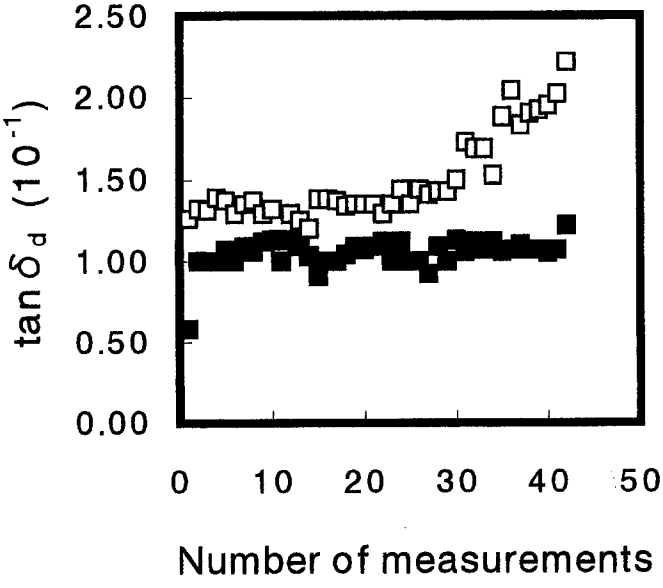

Fig. 6. Changes in tan δ_d at the peak temperature (about 180°–190°C) during repeated measurements between 100° and 220°C. Symbols are the same as in Fig. 4

E' values for buna gradually decreased, the change might not vary significantly from the values of E''.

The piezoelectric loss tangent (tan δ_d) increased gradually in spruce, and an insignificant change occurred in buna (Fig. 6). The insignificant change of d_{25}' was observed for buna, and there was a decreasing trend for spruce. Therefore, the value of tan δ_d for spruce should increase even at a constant value for d_{25}'', although the value for d_{25}'' was found to increase gradually for both spruce and buna. In buna, however, the change in d_{25}' was insignificant, which affects the tan δ_d increase for buna, resulting in less change in tan δ_d for buna than for spruce.

The decrease in the dielectric loss tangent (tan δ_ε) was greater for spruce than for buna with increasing measurements (Fig. 7). Figure 3 shows the decreasing trend of ε', but the ε'' values decreased rapidly at higher temperatures. Therefore, the results of tan δ_ε agree with the results of ε' and ε''. This result indicates decreased conductivity in wood during repeated measurements in this temperature range.

Peak shift and width of d_{25}''

The peak of d_{25}'' gradually shifted to a higher temperature for both spruce and buna with the increasing number of measurements (Fig. 8a); and the width of the peak also increased gradually (Fig. 8b). The width of the peak increased about 43% for both wood species. The increased peak width reflects the increased range of temperature of the energy loss and the wood structure loosening. When the measurements increased, the peak temperature of d_{25}'' advanced to a higher temperature, which was not observed at the beginning of the measurements. Therefore, the peak area of d_{25}'' was enhanced significantly at the later stages compared with the early stages of measurements, which is closely related to energy loss. The shift of the peak to a higher temperature might be due not to the increased rigidity of the wood specimen but to increased energy loss at the higher temperature and the increased total peak area of d_{25}''.

Variations of absorption in piezoelectric modulus

It was found that the variations of d_{25}' and d_{25}'' in piezoelectric modulus d^* were insignificant at the early stages of the measurements (Fig. 9a for spruce, Fig. 10a for buna), whereas they varied significantly at the advanced stages (Fig. 9b for spruce, Fig. 10b for buna). This type of variation

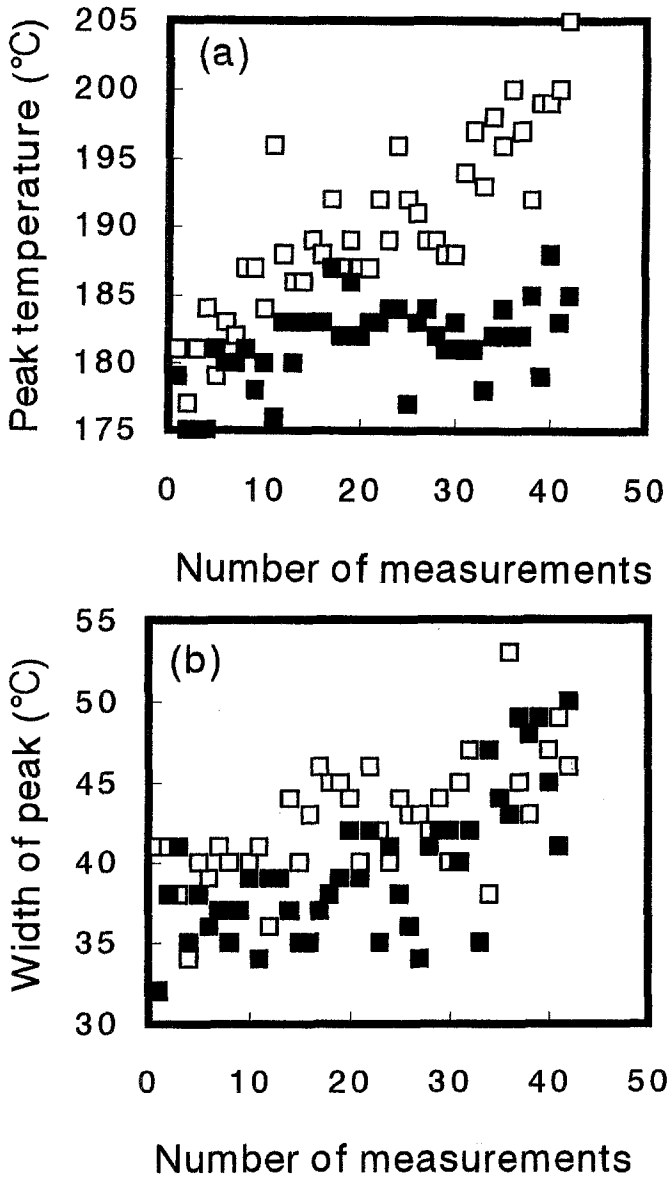

Fig. 8. Peak shift (**a**) and width of peak (**b**) of d_{25}'' during repeated measurements between 100° and 220°C. Symbols are the same as in Fig. 4

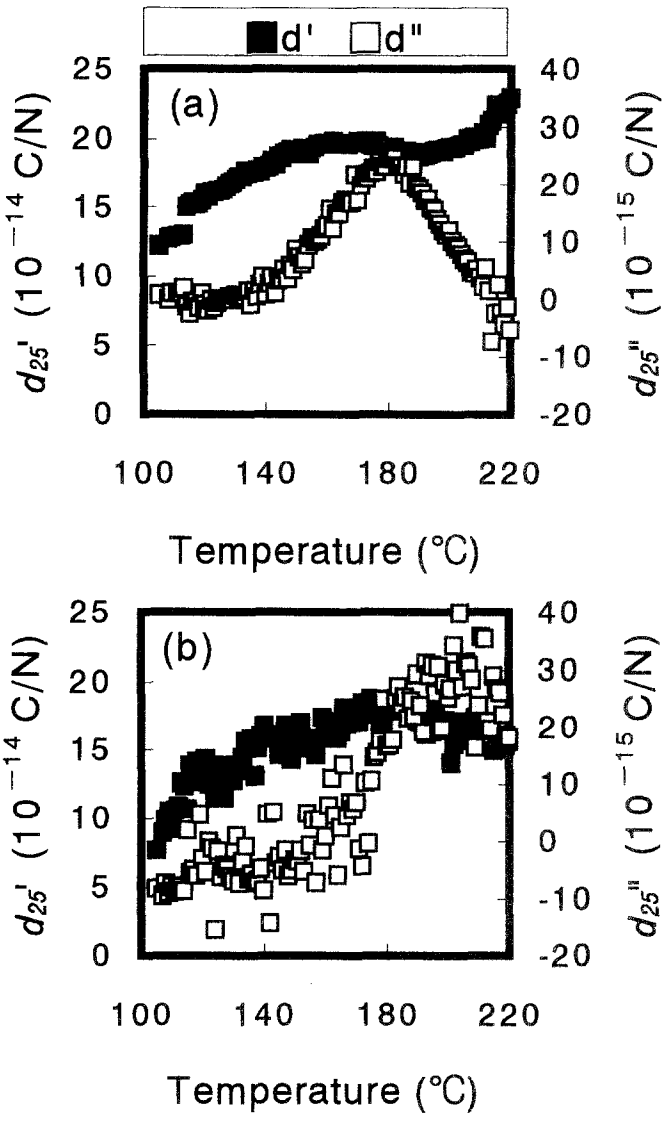

Fig. 9. Variations in the dispersion of spruce in the case of d_{25}' and d_{25}''. **a** First measurement. **b** Fortieth measurement

might be due to damage and structural changes in the wood.

The variations in the piezoelectric absorption d_{25}'' and e_{25}'', which indicate the piezoelectric strain and stress constants, respectively, are addressed now. In the case of d_{25}'', normalized data $g(x_k)$ were calculated from the experimental data $f(x_k)$ by Y/Y_{max}, where, Y and Y_{max} are the individual and maximum values of absorption, respectively. The approximated equation $G(x)$ was obtained as follows:

$$G(x) = a \cdot \exp\left[-b(x-c)^2\right]$$

where a, b, and c are the parameters; and x is the temperature. The differences d_k between normalized data and data obtained from the approximated equation were determined by

$$d_k = G(x_k) - g(x_k)$$

Finally, the standard deviation σ was obtained from the following equation.

$$\sigma = \sqrt{\frac{\sum_{k=1}^{N} d_k^2}{N-1}}$$

where N represents the number of data. In the case of e_{25}'', the standard deviation was determined by the same procedure as for d_{25}''.

The standard deviations d_{25}'' and e_{25}'' proceeded with little variation up to about 25–30 measurements and then increased significantly with the increased measurements in spruce, whereas an increasing trend was seen for buna (Fig. 11). The increase in the standard deviation was higher in spruce than buna. Our results indicate that various kinds of

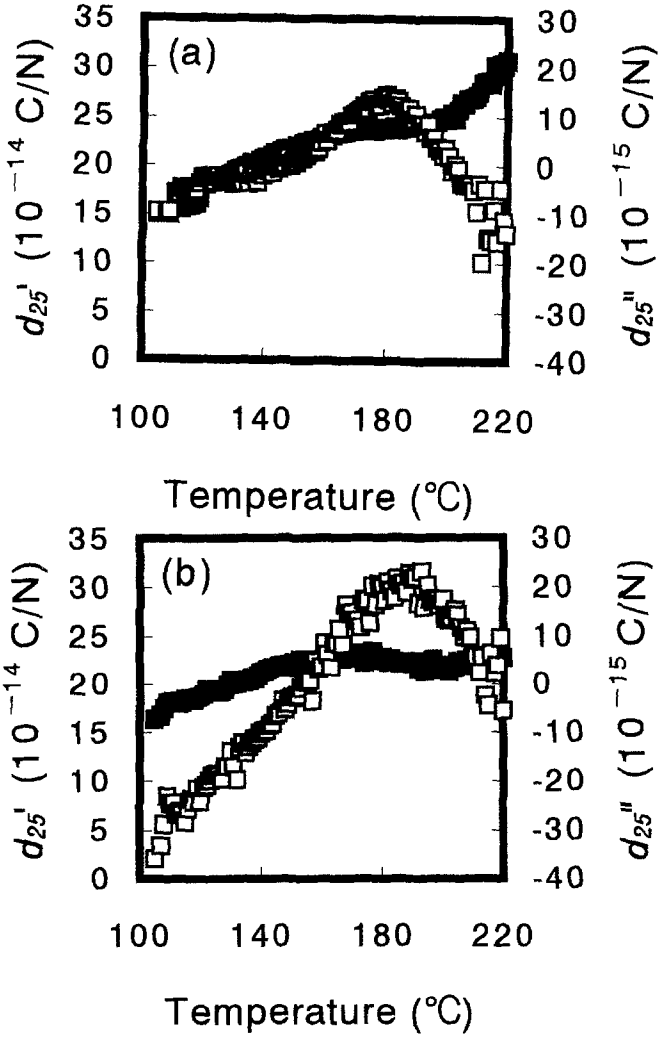

Fig. 10. Variations of dispersion of buna in the case of d_{25}' and d_{25}''. **a** First measurement. **b** Fortieth measurement. Symbols are the same as in Fig. 9

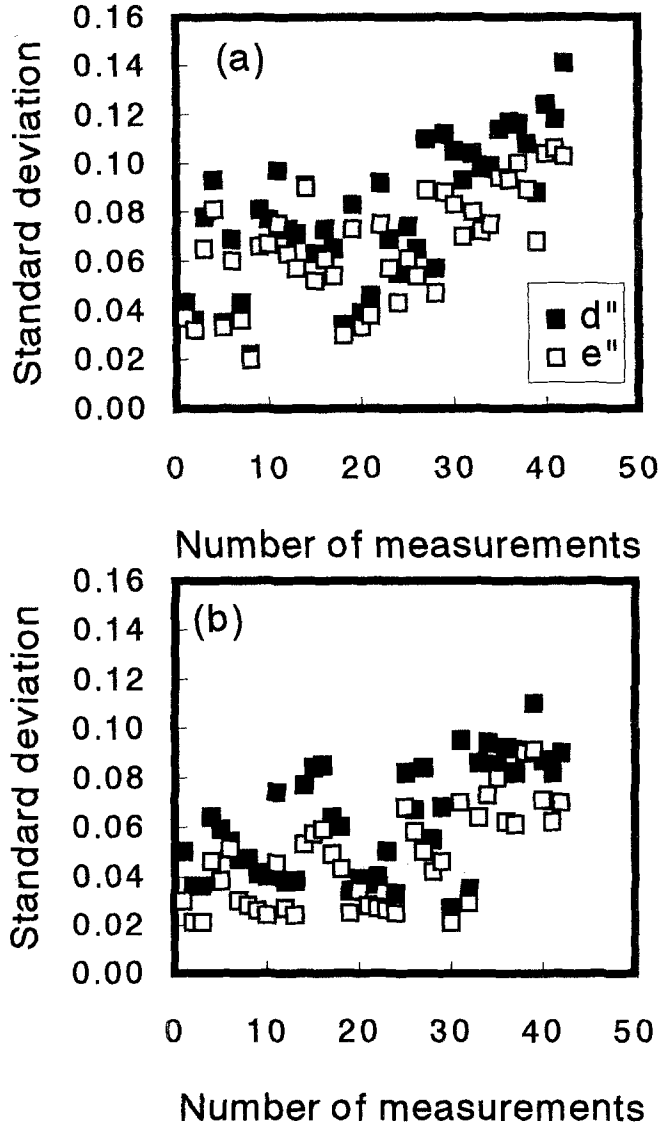

Fig. 11. Standard deviation of d_{25}'' and e_{25}'' of spruce (**a**) and buna (**b**) during repeated measurements between 100° and 220°C

damage (e.g., fractures in the wood fibers) occurred at the advanced stages of measurements, and structural changes might also develop.

Conclusions

This research investigated the effect of repeated measurements (n = 42) on the piezoelectric, dielectric, and elastic constants of wood between 100°C and 220°C. Based on the results, the following conclusions can be drawn.

1. There was an insignificant change in the piezoelectric constant, a decreasing trend for the dielectric constant from the beginning of the measurements, and little increase in the elastic constant at the initial stage followed by a decrease. The changes were probably due to an almost unchanged crystalline state and thermal decomposition in the amorphous region.

2. The repeated measurements in this temperature region did not significantly change the crystallinity in wood cellulose because the mobility of the wood components might be affected at the time the temperature is decreased and the inner stresses rise, conditions that do not favor crystallization in quasicrystalline regions.

3. The total peak area of d_{25}'' increased at the later stages of repeated measurements, which is closely related to energy loss. At the same time there may be structural changes in wood.

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