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ORIGINAL ARTICLE

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Influence of heating history on dynamic viscoelastic properties and dimensions of dry wood

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Abstract To obtain new information about the mechanical and physical properties of dry wood in unstable states, the influence of heating history on viscoelastic properties and dimensional changes of dry wood in the radial, tangential, and longitudinal directions was studied between 100° and 200°C. Unstable states of dry wood still existed after heating at 105°C for 30 min and were modified by activated molecular motion in the first heating process to temperatures above 105°C. This phenomenon is thought to be caused by the unstable states reappearing after wetting and drying again. Dry wood components did not completely approach the stable state in the temperature range tested, because they did not entirely surpass the glass transition temperatures in most of the temperature range. In constant temperature processes at 135° and 165°C, E' increased and E'' decreased with time regardless of the direction. This indicated that the unstable states of dry wood components were gradually modified with time at constant temperatures. On the other hand, anisotropy of dimensional change existed and dimension increased in the longitudinal direction, was unchanged in the radial direction, and decreased in the tangential direction with time at constant temperatures.

Key words Dry wood · Unstable state · Dynamic viscoelastic property · Dimensional change · Heating

Introduction

The wood of trees grows in water-swollen conditions, and when used is usually in an air-dried condition. Thus, it is dried before use. Various reports have been concerned with the physical properties of air-dried and heat-treated wood. The hygroscopicity of wood is reduced by heat treatment.[1] The dynamic elastic modulus (E') and relative crystallinity have maximum values at a specific combination of treatment temperature and period.[1,2] The crystallization of cellulose and the deterioration of hemicellulose by heat treatment have been considered to cause these results. Obataya et al.[3] showed that the reduction of hygroscopicity by heat treatment is modified by steam treatment at 95°C or boiling for 1 h; however, the effects of heat treatment on the microstructures of wood have not yet been clarified in detail.

On the other hand, a new concept for the physical properties of wood was recently reported. Wood subjected to changes in temperature and/or swelling state shows a lower elastic modulus and greater fluidity judging from creep or stress relaxation measurements than wood kept for a long time under constant temperature and humidity.[4–7] In addition to those reports, Nakano[8] interpreted that the increase in relaxation caused by quenching was due to the free volume temporarily created by freezing the molecular chain motion of wood components, most probably lignin, during quenching; however, the amount of free volume was not measured directly. A similar interpretation, called the free volume theory, is already well known for various amorphous polymers.[9,10]

Only a few studies of dried wood in relation to the unstable state have been reported. Ishimaru[11] studied the mechanical properties of wood dried at different rates and different temperatures. Stress relaxation at all drying temperatures decreased with an increase in the time required for drying; in other words, with a decreasing drying rate. Takahashi et al.[12] reported that creep of wood immediately after drying was greater than in stable wood that had been conditioned for a long time. Furuta et al.[13] investigated the physical property changes of dry wood due to heating and drying histories by measuring dynamic viscoelastic properties, and suggested that the microstructure of wood was largely affected by the heating and drying history. Kojiro et al.[14] showed the effects of heating from 100° to 200°C on

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the dynamic viscoelastic properties of dry wood by continuous measurement of dynamic viscoelasticity and weight loss.

To understand the mechanical properties of unstable wood, the relation between the physical and mechanical properties of wood in the unstable state has to be studied. However, until now, the viscoelastic properties of unstable wood have mainly been studied in the radial direction using water-swollen wood, and little attention has been paid to the relation between viscoelastic properties and other physical properties of unstable wood in the dried state. The combined study of these properties is effective for understanding the physical properties of unstable wood, as in the previous reports.[14,15]

Accordingly, in the present study, the viscoelastic properties and the dimensional changes of dry wood in the radial, tangential, and longitudinal directions were measured and the results of both measurements are discussed.

Materials and methods

Materials

Test samples were taken from the outer region of a log of Japanese hinoki (*Chamaecyparis obtusa* Endl.), and their sizes to measure dimensional changes were 30 mm radial (R), 3 mm tangential (T), and 0.8 mm longitudinal (L) for the radial direction; 30 mm (T), 3 mm (R), and 0.8 mm (L) for the tangential direction; and 30 mm (L), 1 mm (R), and 1 mm (T) for the longitudinal direction. For measuring the dynamic viscoelastic properties, the dimensions were 40 mm (R), 3 mm (T), and 0.8 mm (L) for the radial direction; 40 mm (T), 3 mm (R), and 0.8 mm (L) for the tangential direction; and 40 mm (L), 1 mm (R), and 1 mm (T) for the longitudinal direction. Measurements were carried out in dry air, after the sample was boiled in water for 1 h and dried in an air drier at 30°C for 1 h to give a moisture content less than 5%, and almost oven-dried at 105°C for 30 min after setting in the analyzers.

Methods

The temperature dependence of the dynamic elastic modulus (E') and loss modulus (E'') was measured by the tensile forced-oscillation method using an automatic dynamic viscoelastometer (Seiko Instruments, DMS6100). Measurements were conducted over a temperature range of about 100°C–200°C for dry wood at programmed heating rates. Frequencies of the measurement were 0.5, 1, 2, 5, and 10 Hz, the span was 20 mm, and the displacement amplitude was 5 μm. The tensile directions were radial, tangential, and longitudinal. The temperature dependence of dimensions was measured by a thermomechanical analyzer (Seiko Instruments, TMA/SS6100). The span was 20 mm and the load was 5 g, which was the minimum load for the test. Both measurements of dynamic viscoelastic property and dimension were carried out under the same temperature programs.

Results and discussion

Influence of heating history on viscoelastic properties and dimensional changes of dry wood in the radial direction for temperatures between 100° and 200°C

To examine the influence of heating history, the same sample was heated repeatedly and the viscoelastic properties and dimensions of dry wood were compared in the first and second heating and cooling processes between 100° and 200°C. Figure 1 shows the measuring program for Fig. 2, which in turn shows the influence of heating history on viscoelastic properties at 0.5 Hz and dimensional changes in the radial direction of dry wood in the first and second heating and cooling processes with a programmed heating

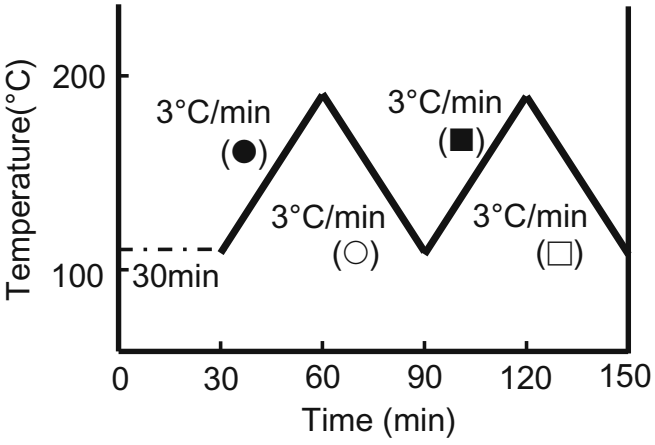

Fig. 1. Temperature program for measurements of dynamic viscoelastic properties and dimensional changes from 100° to 200°C shown in Fig. 2. *Symbols* correspond to those used in Fig. 2

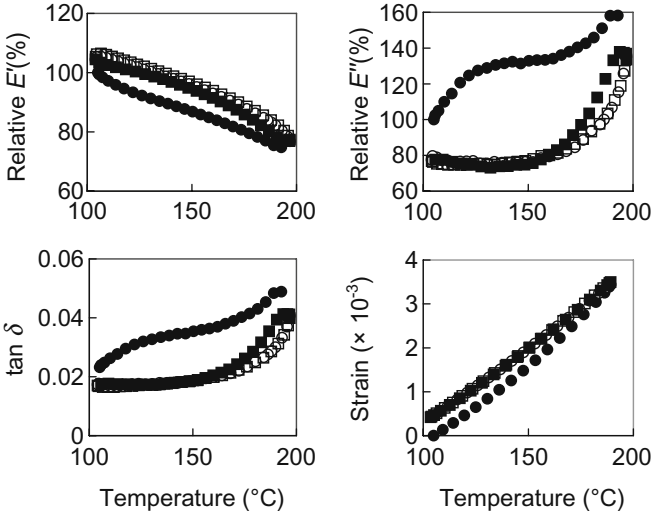

Fig. 2. Influences of heating history on viscoelastic properties at 0.5 Hz and dimensional change in the radial direction of dry wood. Relative E' and relative E'' are relative to values at 105°C in the first heating process. *Circles*, first heating and cooling processes; *squares*, second heating and cooling processes; *filled symbols*, heating processes; *open symbols*, cooling processes

and cooling rate of 3°C/min. The frequency of the measurement of viscoelastic properties shown below was only at 0.5 Hz, because the most typical tendency was recognized at 0.5 Hz and a similar tendency was obtained at other frequencies. Relative E', which is relative to E' in the first heating at 105°C, was smaller in the first heating process than in later processes. Relative E'', which is relative to E'' in the first heating at 105°C, and tan δ in the first heating process were larger than in later processes. Relative E' in the second heating process was slightly smaller than that in the second cooling process, and relative E'' and tan δ were a little larger than those in the second cooling process. Dimensional changes in the first heating process were clearly different from those in later processes. Furthermore, viscoelastic properties and dimensional changes in the later processes, except for first heating process, were almost the same if the sample was previously cooled or heated in the same manner in this temperature range. In this relation, Ishimaru[11] found that wood subjected to changes in temperature and/or swelling state showed a lower elastic modulus and greater fluidity, and interpreted that the phenomenon was caused by localized stress in the microstructures of wood cell walls, which was caused by changes in environmental conditions such as temperature and humidity. From this interpretation, the cause of the present results, that is, differences in dynamic viscoelastic properties and dimensional changes between the first heating process and later processes, was considered as follows. When wet wood is dried, localized stresses are produced in the microstructures of wood components in cell walls. These stresses weaken intermolecular and intramolecular hydrogen bonds and lower resistances to deformation. According to Goring,[16] softening temperatures of dry wood components are 134°–235°C for lignin, 165°–217°C for hemicelluloses, and 231°–253°C for cellulose. Thus, unstable states in the microstructures of dry wood still existed at 105°C in the first heating process and those strains were modified by activated molecular motion with rising temperature in the first heating process. If this is correct, the phenomenon resulting from the unstable state should reappear after wetting and drying again. The behavior of the viscoelastic properties and dimensional change in the first and second measurements after boiling and drying again, using the same sample, were therefore compared.

Figure 3 shows the measuring program for Fig. 4, which in turn shows the viscoelastic properties and dimensional changes of the same sample in the first heating and cooling processes for both the first and second measurements after boiling and drying subsequent to the first measurement. The behaviors of the viscoelastic properties and dimensional changes in the second measurement were almost the same as those in the first measurement; in other words, after boiling and drying again, a similar unstable state to that in the heating process in the first measurement reappeared. This means that the above consideration is correct. In addition, considering the measurement temperature and time used in this study, thermal degradation of wood components is thought to hardly affect the above phenomenon.[14]

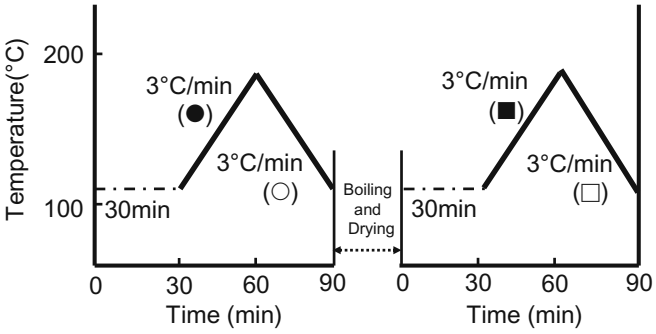

Fig. 3. Temperature program for measuring viscoelastic properties at 0.5 Hz and dimensional change in the radial direction of dry wood in the first measurement, and after boiling and drying. Results are shown in Fig. 4, *symbols* correspond to those used in Fig. 4

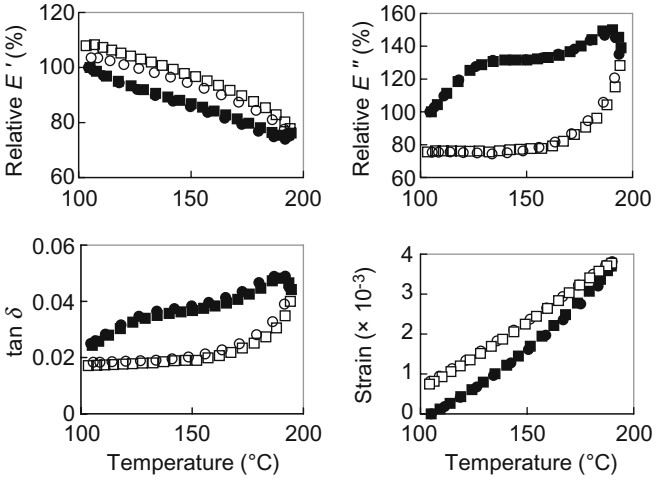

Fig. 4. Viscoelastic properties at 0.5 Hz and dimensional change in the radial direction of dry wood in the first measurement, and those in the second measurement after boiling and drying. *Circles*, first heating and cooling processes; *squares*, heating and cooling processes after boiling and drying; *filled symbols*, heating processes; *open symbols*, cooling processes

Influences of elevating temperature range on viscoelastic properties and dimensional changes of dry wood in the radial direction for temperatures between 100° and 200°C

Figure 5 presents the measuring program for Fig. 6, which in turn shows the influences of elevating temperature range on viscoelastic properties at 0.5 Hz and dimensional changes in the radial direction of dry wood in heating and cooling processes with a programmed heating and cooling rate of 3°C/min. Relative E' in each heating process was smaller than that in the corresponding cooling processes. Relative E'' and tan δ in each heating process were larger than in the corresponding cooling processes. Dimensional changes in the heating process were clearly different from those in cooling processes; moreover, the behaviors of viscoelastic properties and dimensional changes in the heating processes were almost the same as just before the cooling processes in the same temperature ranges. These results indicate that the microstructures of dry wood components were stabi-

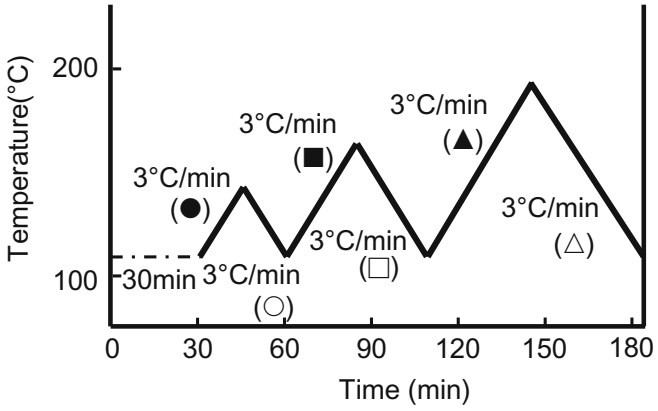

Fig. 5. Temperature program for measuring influences of heating temperature range on viscoelastic property at 0.5 Hz and dimensional change in the radial direction of dry wood. Results are shown in Fig. 6, *symbols* correspond to those used in Fig. 6

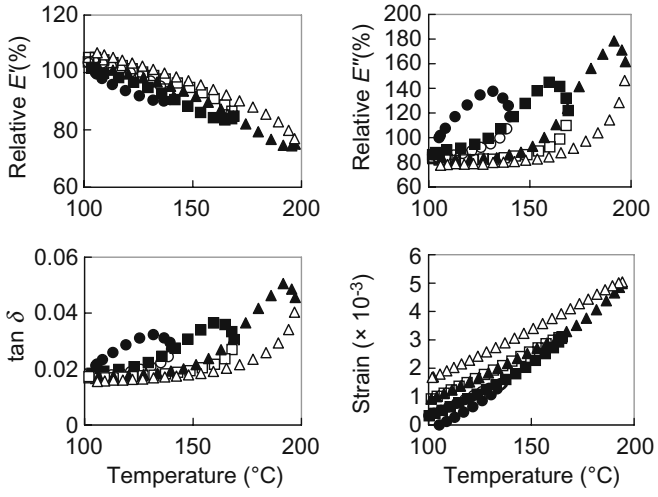

Fig. 6. Influences of heating temperature range on viscoelastic property at 0.5 Hz and dimensional change in the radial direction of dry wood. *Circles*, 100°–140°C; *squares*, 100°–170°C; *triangles*, 100°–200°C; *filled symbols*, heating processes; *open symbols*, cooling processes

lized with the rising temperature. As mentioned above, dry wood components do not entirely surpass glass transition temperatures in most of the temperature range tested; thus, they have not completely approached the stable state at these temperatures. These results are only for the radial direction, because the most typical tendency was recognized in the radial direction, although similar tendencies were observed in the tangential and longitudinal directions.

Anisotropy in the influence of heating history on viscoelastic properties and dimensional changes of dry wood

Until now, the influence of heating on viscoelastic properties and dimensional changes of dry wood has been investigated for samples in the radial direction and has been hardly reported for the tangential and longitudinal directions. However, anisotropy in the influence of heating on viscoelastic properties and dimensional changes of dry wood possibly exists. To clarify this, the following measurements were performed.

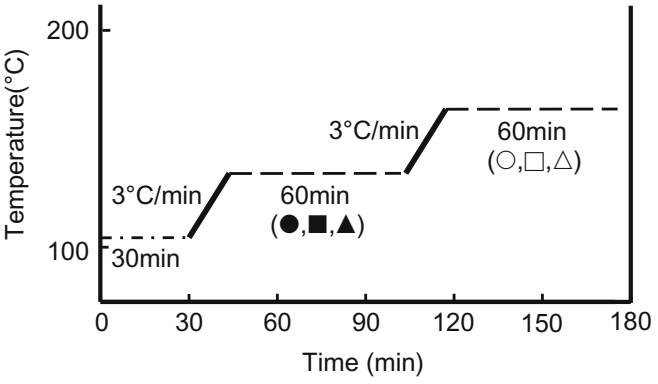

Fig. 7. Temperature program used for the results given in Figs. 8 and 9. *Symbols* correspond to those used in Figs. 8 and 9

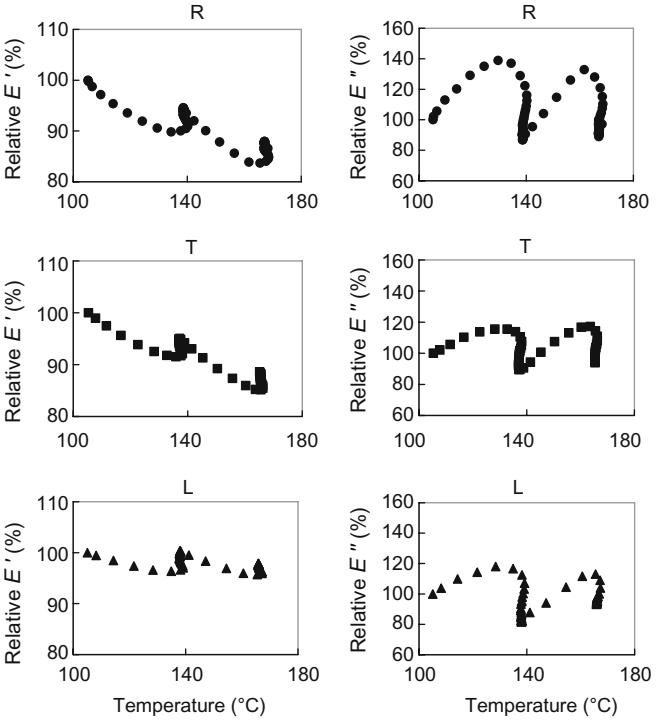

Fig. 8. Influences of heating history on viscoelastic properties at 0.5 Hz and dimensional changes of dry wood in radial, tangential, and longitudinal directions. *Filled circles*, radial direction; *filled squares*, tangential direction; *filled triangles*, longitudinal direction

Figure 7 presents the measuring program for the results shown in Figs. 8 and 9. Figure 8 shows the temperature dependence of viscoelastic properties at 0.5 Hz and dimensional changes in the radial (R), tangential (T), and longitudinal (L) directions in the first heating process with a programmed heating rate of 3°C/min from 100° to 170°C, and in the constant temperature process around 135° and 165°C. Each of relative E' and relative E'' showed quite similar behaviors in R, T, and L directions, although the decrease in relative E' in the L direction with an increase

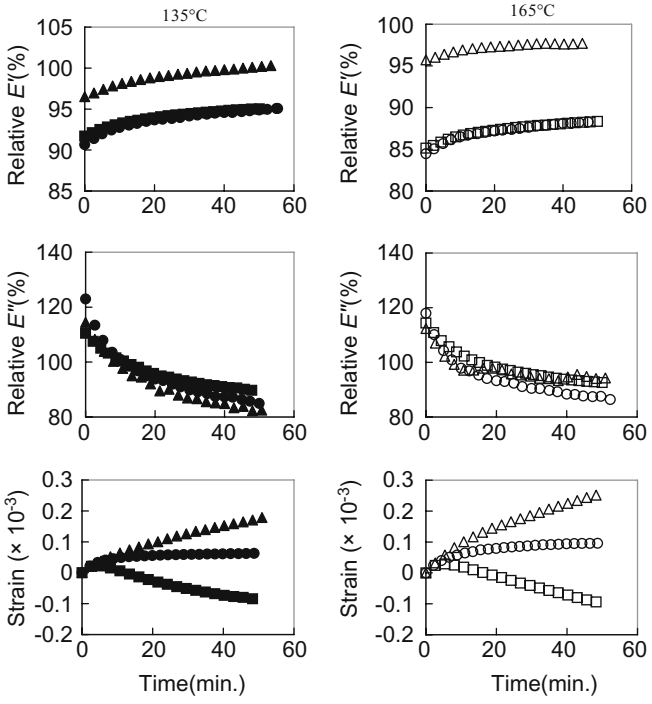

Fig. 9. Changes in dynamic viscoelastic properties at 0.5 Hz and dimensional changes in radial, tangential, and longitudinal directions of dry wood with time at 135° and 165°C. *Circles*, radial direction; *squares*, tangential direction; *triangles*, longitudinal direction; *filled symbols*, 135°C; *open symbols*, 165°C

in temperature was smaller than in the R and T directions. In the constant temperature process in Fig. 9, relative E' increased and relative E'' decreased with time at each constant temperature, regardless of direction. A similar result was obtained only in the R direction by Kojiro et al.[14] On the other hand, in the constant temperature processes at 135° and 165°C, dimensions increased in the L direction, were unchanged in the R direction, and decreased in the T direction with time. Meanwhile, dimensions in all directions increased slightly in the early stage of the process, probably because of a slight increase in temperature resulting from a time lag in the temperature program.

As is clear from the result in Fig. 9, which shows increase in relative E' and decrease in relative E'' at constant temperatures, the microstructures of dry wood stabilized with time at constant temperatures. From the standpoint of free volume theory, which is well known for the amorphous polymer, the dimension of dry wood is considered to change due to the decrease in free volume with time at constant temperature. One of the purposes of measuring dimensional change was to obtain information about free volume; however, it became clear that obtaining information about free volume from the results of dimensional change was difficult because of anisotropy of dimensional change in these processes and because wood is porous.

Sobue et al.[17] found that the lattice strain coincided approximately with the shrinkage of small wood samples in the desorption stage, and this strain disappeared by rewetting the samples. They considered that this strain resulted from compressive stress in cellulose crystals developed by shrinking the amorphous region during the desorption stage. Therefore, the result of the present study, that is, dimensional increase with time at constant temperature in the longitudinal direction, indicates that the compressive strain in the longitudinal direction developed by drying was modified by heat to some extent as well as by moisture adsorption.

Conclusions

This study examined the influence of heating history on viscoelastic properties and dimensional changes of dry wood in the radial, tangential, and longitudinal directions for temperatures between 100° and 200°C. The main conclusions of the study are:

1. Unstable states in the microstructures of dry wood still existed at 105°C in the first heating process, and these strains were modified by activated molecular motion in the first heating process; this phenomenon reappeared after wetting and drying again.
2. Dry wood components did not completely approach the stable state in the temperature range tested, because they did not entirely surpass the glass transition temperatures in most of the temperature range.
3. In constant temperature processes at 135° and 165°C, relative E' increased and relative E'' of dry wood decreased with time regardless of direction. On the other hand, anisotropy of dimensional change existed and dimensions increased in the L direction, were unchanged in the R direction, and decreased in the T direction with time at constant temperatures. This result indicates that the compressive strain in the longitudinal direction developed by drying was modified by heat to some extent as well as by moisture adsorption.

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