

Changes in Dielectric Properties and the Mechanism of Water Adsorption of wood by Heat Treatment

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INTRODUCTION

In the heat treatment under nitrogen gas, wood degrades between 60°C and 200°C, decomposes between 160°C and 450°C, carbonizes between 600°C and 1800°C, and graphitizes between 1600°C and 3000°C¹⁾. Chemical changes mainly occur up to the early stage of carbonization, but after that physical changes become dominant¹⁾. In the field of wood physics, the heat treatment of wood has been investigated to improve the dimensional instability of wood due to moisture changes, to enhance the acoustical properties of wood, and to fix permanently the large compressive deformation of wood. These treatments are restricted within 200°C. Recently, however, as the requirement of high-grade utilization for the treated wood raises, much attention has been paid to the changes in the structure and properties of wood by the treatment in much higher temperature range. The electrical properties of the treated wood drastically change depending on the treatment temperatures. It is known that the treated wood is an insulator below 300°C, a semiconductor between 300°C and 800°C, and a conductor above 800°C¹⁾. On the other hand, it is known that functional groups of wood constituents almost disappear²⁾ by heat treatment up to 400°C and nanometer-scale micropores are produced in wood through the formation of graphite^{18, 19} above 450°C. Therefore, it is considered that the mechanism of water adsorption on wood depending on treatment temperature. In this paper, the changes of dielectric properties in the wide range of temperature (-150~20°C) and frequency (20~1MHz) for wood treated at temperatures up to 800°C are investigated. Moreover, the dielectric relaxation due to motions of water molecules adsorbed on wood treated at various temperatures was examined to clarify the state of the adsorbed water.

RESULTS

A relaxation was detected in the dry specimens treated below 300°C and between 500°C and 600°C, respectively. The Cole-Cole's circular arc law was well applicable to these relaxations. The former relaxation has been ascribed to the motions of methylol groups in the non-crystalline region of the cell wall. This relaxation decreased in magnitude with increasing treatment temperature and disappeared above 400°C (Fig.1). The latter relaxation had a large magnitude depending on measuring temperature (Fig.2). The distribution of relaxation times was very narrow. The values of conductivity remarkably began to increase above 500°C. This result suggested the formation of two-phase system including portions with large conductivity in an insulator. Therefore, the relaxation may be ascribed to that due to the interfacial polarization. Dielectric measurements were impossible for the specimens treated above 650°C because of their extremely high conductivities.

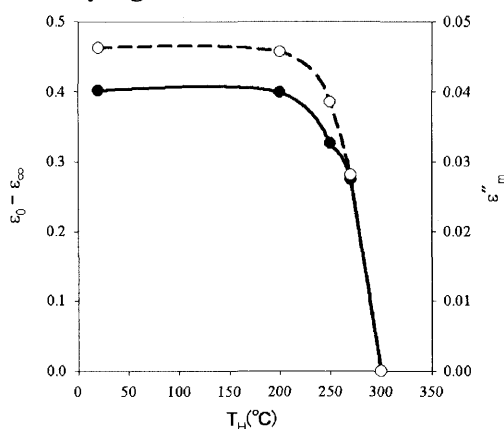


Figure 1 Relationship between relaxation magnitude ($\epsilon_0 - \epsilon_\infty$) due to the motions of methylol groups and treated temperature (T_H) for wood.

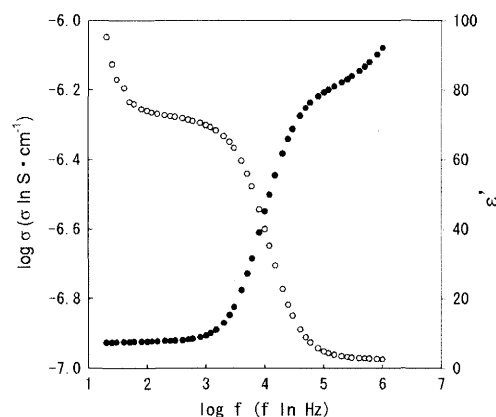


Figure 2 Relationship between logarithmic conductivity ($\log \sigma$) or dielectric constant (ϵ') and logarithmic frequency ($\log f$) at -30 °C for wood treated at 600 °C.

Three relaxations were observed in the specimens conditioned at high levels of relative humidity. The relaxation in the highest frequency range was ascribed to the motions of adsorbed water molecules. The relaxation in the middle frequency range remained unchanged by the alcohol–benzene extraction of specimens. Its location was independent of measuring directions, but moved to higher frequency range with increasing moisture content. The relaxation in the lowest frequency range was remarkably affected by extractives involved in the specimens. However, it was not detected in the specimens impregnated with methyl methacrylate (MMA)(Fig.3). This result suggested that it was due to the electrode polarization. The Cole-Cole's circular arc law was well applied to two relaxations recognized in the specimens impregnated with MMA. The relaxation magnitude in the middle frequency range was extremely large and the distribution of relaxation times was very narrow. These characteristics suggested the relaxation of the Maxwell-Wagner's type which resulted from the interfacial polarization in the heterogeneous structure including portions of adsorbed waters with large electric conductivity in an insulator of the cell walls.

The dielectric relaxation due to motions of water molecules adsorbed on wood treated at various temperatures up to 550°C was investigated from observed relationships (Fig.4) between activation enthalpy (ΔH) and entropy (ΔS) in the relaxation. The relationships assumed two straight lines with different slopes depending on treatment temperature. Given the same ΔS , the ΔH for water molecules adsorbed on wood treated at temperatures below 400°C were larger than those treated above 450°C. It was considered that the former water molecules were adsorbed mainly on hydroxyl groups by strong hydrogen bonds to form ice-like structures. On the other hand, since hydroxyl groups of wood constituents were not detected in heat treatments above 400°C, it was considered that water molecules are condensed in nanometer-scale micropores formed during the carbonization of wood at higher temperatures. The relationship between ΔH and ΔS for the motion of water adsorbed on wood treated above 450°C was similar to the value extrapolated from the value of bulk water under 0°C. This result suggested that water molecules adsorbed on charcoals were in the supercooled state.

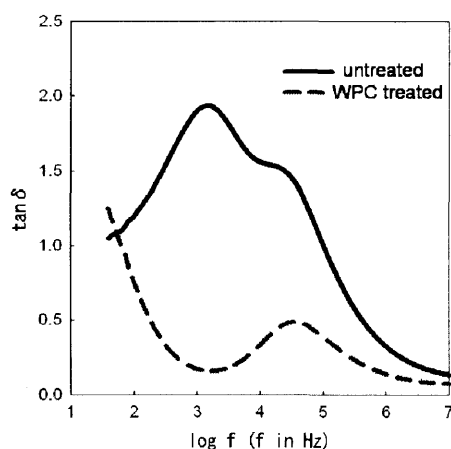


Figure 3 The logarithm of dielectric constant ($\log \epsilon'$), and the loss tangent ($\tan \delta$) against the logarithm of frequency ($\log f$) at 20°C in the longitudinal directions for the extracted and methyl methacrylate impregnated hinoki wood specimens conditioned at 97% RH.

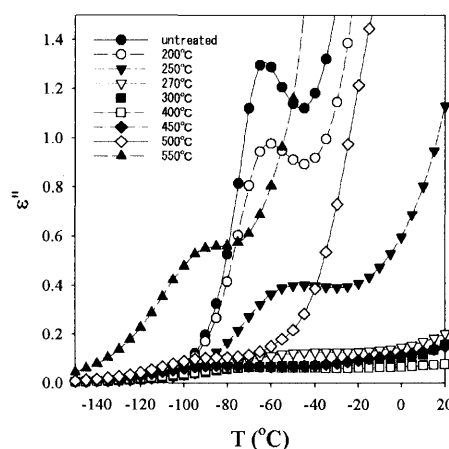


Figure 4 Relationships between dielectric loss (ϵ'') and temperature T at 1MHz for wood treated at the indicated temperatures and conditioned at 97%RH.

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