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RAPID COMMUNICATION

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Improved water permeability of sugi heartwood by pretreatment with supercritical carbon dioxide

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Introduction

Treating wood with aqueous solutions, such as preservatives, fire retardants, and dimensional stabilization agents, generally requires uniform distribution of the agents within the wood. Penetration and diffusion of such solutions into wood, however, are often obstructed in part by extractives and polyphenolic substances, especially in the heartwood.[1] These substances adhering to or accumulating in pit and porous structures of wood may block the pathways for liquid transport. This study investigated the effect of supercritical carbon dioxide (CO_2) (critical point; 31°C/7.4 MPa) pretreatment on the water permeability of sugi heartwood. Supercritical CO_2 diffuses and penetrates like gas but has solvating properties that approach those of liquid. It has low surface tension, easily seeps into micro pores and voids, and extracts nonpolar and weakly polar substances effectively. Thus, its uses for washing precision machines and semiconductors as well as dry cleaning have been investigated.[2] Ohira[3] reported that supercritical CO_2 extraction was effective in extracting some useful chemical components in wood. Takeshita et al.[4] studied the effects of supercritical CO_2 in removing heavy metals from chromated copper arsenate (CCA)-treated wood. Acda et al.[5] and Muin et al.[6] used supercritical CO_2 as a carrier solvent for preservative treatment of wood-based composites.

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In this study, we aimed to improve the water permeability of wood by pretreating the wood with supercritical CO_2 that would remove substances that inhibit the permeation. We examined the effects of some treatment conditions on the water permeability of sugi heartwood,[7,8] and observed bordered pits before and after supercritical CO_2 treatment under a scanning electron microscope (SEM).

Materials and methods

Specimens [100 mm (L) × 15 mm (R) × 15 mm (T)] were prepared from sugi (*Cryptomeria japonica* D. Don) heartwood. Twenty specimens in total were cut from mutually adjacent parts of one tree: four along the longitudinal direction and five along the radial direction. Five groups were created for five treatment conditions, each consisting of four replicates randomly selected from each of the four tree heights.

After being oven-dried and weighed, four replicates of each sample group were sealed in a batch container (inner diameter: 80 mm, height: 180 mm) at a time. The inner part of the container was evacuated using a vacuum pump, and was then filled with CO_2 (over 99.9% purity) (Nikko Sanso, Tokyo). First, CO_2 was directly transferred from a gas cylinder to the batch container. Cooled and liquefied CO_2 was then injected into the container using a pump to raise the pressure up to 12.0 MPa. The temperature was controlled using an electric heater installed outside the batch container. The pressure and temperature were raised to the target values for 30 min. Experiments were also conducted using ethanol (over 99.5% purity) (Wako, Osaka) as an entrainer (cosolvent) to extract polar substances, which are difficult to dissolve in supercritical CO_2. Ethanol (25 ml) was injected into the batch container using a pump after the temperature and pressure reached the predetermined values (mole fraction: 2.8% at 40°C, 6.3% at 80°C). Batch extraction was performed by stirring with a magnetic stirrer (approximately 200 rpm) for 7 h at 12.0 MPa. Treatment conditions of specimens were as follows: 40°C with ethanol;

40°C no ethanol; 80°C with ethanol; 80°C no ethanol; untreated. After the treatment, the pressure was released for 15 min.

After the supercritical CO_2 treatment, the oven-dried weight of the specimens was measured to calculate the extraction rate. The specimens were then conditioned at 20°C and 70% ± 2% relative humidity for 3 weeks. Then, the permeation was evaluated with the following methods. The radial and tangential sections of the specimens were coated with one-component RTV rubber (Shin-Etsu Chemical, Tokyo). The bottoms of the specimens were soaked to a depth of about 5 mm in a 1:90 diluted solution of the commercial preservative product copper azole containing copper(II) oxide, cyproconazole, 2-aminoethanol, and 2,2′-iminodiethanol as main components. The specimens were fixed on a wire basket so that the longitudinal direction of wood was vertical in the solution. Weight of the specimens was measured at 1, 3, 6, and 24 h, and the increase in weight was used as an index to evaluate permeation. Mean weight gain (%) and standard deviation of four replicates for each treatment condition were calculated.

Bulk specimens for SEM observation were excised from the core of the specimens. The bulks were split in half to expose radial surfaces, which were sputter-coated with gold in a Jeol Ion Sputter JFC-1100 (Jeol, Tokyo). Morphological observations were performed with a Jeol 5600LV SEM at an accelerating voltage of 5 kV.

Results and discussion

Extraction conditions and mean extraction rates are summarized in Table 1. The mean extraction rates were less than 1% for all treatment conditions. The extraction rate was higher at 40°C than at 80°C. In general, the solubilizing power of supercritical fluid tends to increase with increasing density.[9] This suggests that the extraction rate may be higher at 40°C with a high-density supercritical CO_2. The influence of density on the solubility at a constant temperature should be examined in the future. Our results also showed that the extraction rate at 40°C increased by adding ethanol. It is supposed that increases in extraction of highly polar substances due to addition of ethanol may be effective in increasing the total extraction rate. However, further studies about the effect of adding ethanol on the extraction rate are needed.

Changes in dimensions of the specimens observed before and after the treatment were less than 0.07% along the longitudinal direction, and less than 0.32% along the radial and tangential directions in all specimens. No change in external appearance, such as buckling or deformation, was observed.

Figure 1 illustrates the results of the permeation evaluation tests. The mean weight gain due to solution uptake are shown together with the standard deviation of four replicates. For all treatment conditions, the weight gain was larger in specimens treated with supercritical CO_2 than in untreated specimens. The weight gain was especially large at an extraction temperature of 40°C. The increases in weight gain of treated specimens due to solution uptake were about seven times larger than those in untreated specimens when ethanol was added, and were four to five times larger when no ethanol was added. The results suggest that treatment with supercritical CO_2 at 40°C was more effective than other conditions used here in removing substances that adhered to and accumulated in wood. The effect of treatment time on the permeability improvement is under investigation because it is desirable, from a practical point of view, to shorten the treatment time. At both 40°C and 80°C, the addition of ethanol increases the aqueous solution uptake. This suggests that a large fraction of the substances that were supposed to act adversely against solution uptake was solubilized by ethanol to some extent.

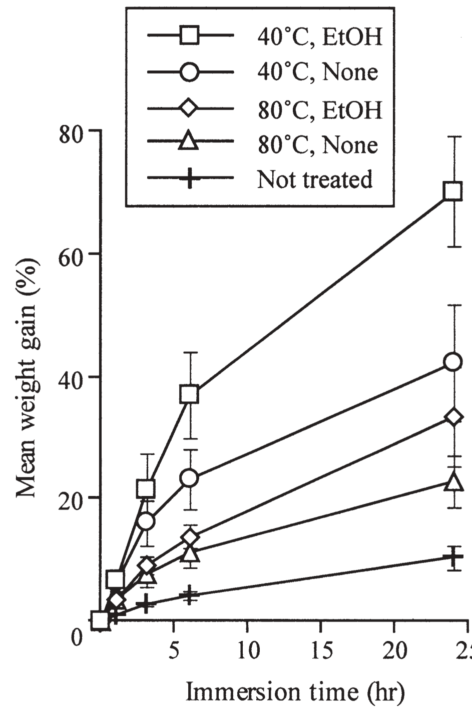

Fig. 1. Results of a permeation evaluation test using an aqueous solution of the commercial preservative product. *Bars*, standard deviation

Table 1. Mean extraction rate from sugi heartwood during supercritical CO_2 treatment

Temperature (°C)	Entrainer	*n*	Mean extraction rate (%)	Standard deviation
40	EtOH	4	0.93	0.26
40	None	4	0.75	0.26
80	EtOH	4	0.13	0.23
80	None	4	0.46	0.15

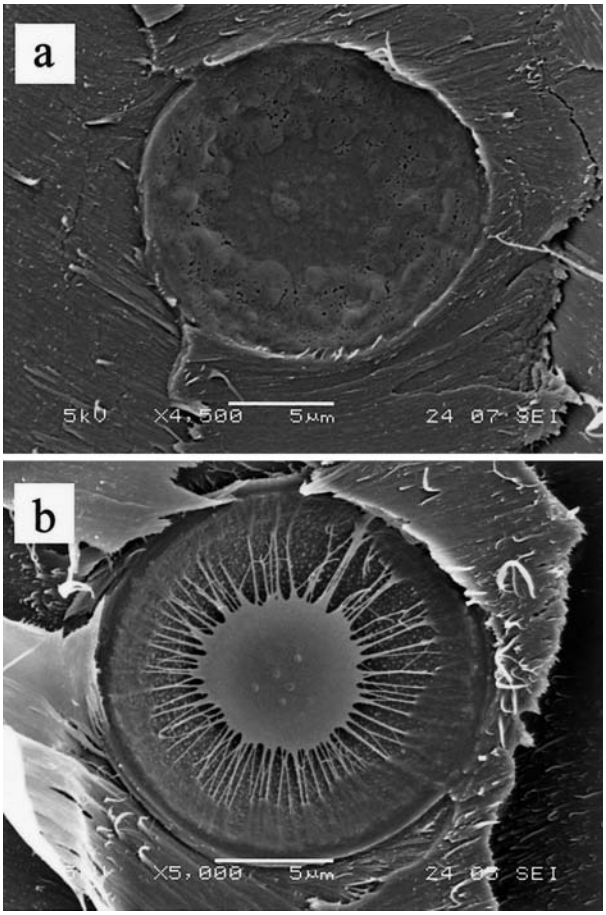

Fig. 2. Bordered pits of sugi heartwood in **a** untreated specimen, and **b** specimen after supercritical CO_2 treatment. *Bars* 5μm

Further study is needed to investigate the effects of ethanol on the extraction.

The results of the permeation evaluation tests showed that supercritical CO_2 treatment greatly improves the water permeability of sugi heartwood. To understand the mechanisms of permeation improvement, the specimens that showed the strongest permeation improvement (temperature: 40°C, with ethanol) and an untreated specimen were observed under SEM. SEM images of typical bordered pits in tracheids are shown in Fig. 2. In the untreated specimen, almost all bordered pits were completely occluded with substances that apparently made it difficult for water to pass. On the other hand, the specimens that were treated with supercritical CO_2 showed a number of bordered pits where margo was clearly visible. It is reasonable to conclude that a large fraction of the occluding substances was removed.

Matsumura et al.[10] reported that 65% to 80% of bordered pits are aspirated in sugi heartwood. According to Fujii et al.,[11] this value is 20% to 80%. From these results they indicate that there are a number of bordered pits that are incompletely aspirated. The removal of occluding substances from the bordered pits may enable water to pass again, and thus greatly improve the water permeability of wood.

The results of this study showed that supercritical CO_2 treatment improved the water permeability of sugi heartwood by up to seven times, although the extraction rate was less than 1%. The improvement of permeability may be considered to be due in part to the removal of occluding substances from bordered pits. To clarify the mechanisms of permeability improvement, supercritical CO_2 treatments under several conditions should be examined, and observation of changes in wood tissues during treatment and distribution of agents in the tissues should be investigated in detail in future work.

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