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Relaxation Properties of Carboxymethylated Wood plus Metallic Salts in Aqueous Solution

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Summary

Stress relaxation of carboxymethylated wood (CMW) containing various metal ions was measured under two conditions. One measurement was carried out in water and the other in water initially and later in 0.5% acetic acid; water was replaced with 0.5% acetic acid 10 minutes after the measurements in water. The metal ions were Na^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Al^{3+}, and $Fe(III)^{3+}$. On the basis of the results, the interaction between CMW molecular and metal ions is discussed.

In water, relaxation rigidity (Gr) of CMW containing Na^+, Mg^{2+}, Ca^{2+}, and Zn^{2+} is smaller than that of CMW, and that of CMW-Na is the highest among them. Gr of CMW containing Al^{3+} and Fe^{3+} (CMW-Al and CMW-Fe(III)) is higher than the others. These results lead to the conclusion that the interaction between main-chains of CMW containing divalent metal ions decreases in water because of dissociation of metal ions, while that of CMW-Na increases by the screening effect of Na^+. As for CMW-Al and CMW-Fe(III), since they dissociate little, Gr does not decrease in comparison with the other CMW containing metal ions. When water was replaced with 5% acetic acid solution 10 minutes after the measurement in water, Gr of CMW-Al and CMW-Fe(III) decreased rapidly. The facts suggest that the crosslinking between CMW molecules and their metal ions remains when in water.

Introduction

We reported that metal ion binds to the side-chain carboxyl group of molecular chain of half-esterified or etherified wood, and that the mobility of modified wood components, in particular, of cellulose main-chains, changes remarkably by the introduction of metal ions (Nakano 1990, 1991). Furthermore, it was clarified that divalent and trivalent metal ions form crosslinks between the main-chains, while monovalent metal ions do not. Factor related to the mobility are the charge (valency), the radius, and the amount of metal ion. The relationship among them is represented by a simple equation (Nakano 1991).

If the bonding between metal ion and the side-chain carboxyl group of molecular chain of carboxymethylated wood is ionic, crosslinking can be broken in water or acid solution because of dissociation of containing metal ions. The interaction between main-chains is then influenced by both nature of metal ion and the degree of ionization. In this work, in order to clarify the effects caused by dissociation of metal ion in water, stress relaxation property of carboxymethylated wood (CMW) containing various metal ions is examined in water; the measurement is also made by replacing the water with acetic acid 10 minutes after the measurement in water. Crosslinking in CMW by metal ion is broken in acetic acid. In the experiment, Japanese linden (*Tilia japonica* Smik.) was used as specimens. The interaction between CMW and metal ion is discussed.

Experimental

Wood specimens were prepared from Japanese linden (*Tilia japonica* Smik.) with rectangular dimensions of 0.8(T) × 0.1(L) × 7(R) cm; T, L, and R are tangential direction, longitudinal, and radial directions of cutting, respectively. After carboxymethylation, metal ions were introduced into CMW by impregnation of metal salt solutions. The metal salts were sodium acetate, calcium acetate, zinc acetate, aluminium acetate, and iron(III) acetate. The procedure was the same as in the previous reports (Nakano 1990).

Two kinds of torsional stress relaxation experiments were made using the same apparatus (Nakano *et al.* 1986). One measurement was carried out for sample soaked in water and the other by replacing water with 0.5% acetic acid 10 minutes after the measurement in water. The measurement temperature was 30°C. The specimens were impregnated with water and then allowed to soak overnight at room temperature, before the measurement was started.

CMW containing metal ion is hereafter referred to, for example, as CMW-Na for a CMW containing Na^+.

Results and Discussion

Figure 1 shows stress relaxation curves of CMW containing various metal ions in water at 30°C. The amount of metal ion introduced into CMW was about 1 mmol/g. In the time range of 10 to 10^4 sec, relaxation rigidities Gr of CMW-Na, CMW-Mg, CMW-Ca, and CMW-Zn are smaller than that of CMW. CMW-Na has the highest rigidity among them, and rigidites of