研究速報

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The Behavior of Water in Bamboo (Pulsed NMR Method)

竹の中の水の挙動 (NMR法)

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1. Introduction

Bamboo is a natural polymeric material, which is composed of cellulosic crystalline part and ligneous amorphous part mainly. The other constituents are hemicellulose and water. The morphological structure is so complex that a complete understanding of the structure is not known so far. The tensile strength of the bamboo containing water is decreased and the impact strength increased when the water content of the bamboo increased.[1] Therefore the water in bamboo behaves as a plasticizer. In order to get a more information of the water behavior, a pulse NMR method is used for this investigation.

2. Experimental

2-1 Preparation of samples

Middle part between joints of a bamboo (Matsu, Dendrocalamus) was cut into strips (0.5×5.5×5 cm) after removing the cuticle. The bamboo strips were immersed in water then. The water content of the bamboo was varied with different drying time of the water immersed bamboo strips in air.

2-2 T_1, T_2 measurement

"Brukers minispec PC 20" which is designed for pulse NMR method was used. The bamboo strips were put in a test tube and put in the sample holder of the instrument. The spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) was determined with 180°—90° and 90° pulse respectively. Since the method is established, the detail of the calculation will be omitted.[2] The preliminary experiment indicated the existence of two water fractions of different mobility. It will be shown later that one is free water and the other bound water. The T_1s and T_2s will be noted as T_{1f}, T_{1b}, T_{2f} and T_{2b} respectively. The suffix "f" indicates free water and "b" indicates bound water. Fourier transformation was made then for more clear understanding.

Since "minispec 20" is designed for reading liquid/solid (L/S) ratio directly after an indicated procedure, the water content of bamboo strips was determined from the displayed L/S ratio.[3]

3. Results and Discussions

The free induction decay (FID) of bamboo containing water after 90° pulse was shown in Fig. 1. The plot of the logarithm of signal versus time was shown in Fig. 2. It was composed of two straight lines. This indicated the existence of two water fractions of different mobility. Since the line (B) located below the extension line of line (A), the decay is not additional. For a more clear understanding of the decay, a Fourier transformation was made then, i. e. a spectra of signal height versus frequncy. Fig. 3 is one of these spectra. It is obvious that the chemical shift indicated the existence of two water fractions of different mobility. Fig. 4 is another example. Considering the shape of the signal is assumed as a Lorentz type if the magnetic field is homogeneous, two Lorentz curves composing the spectra are assumed. It is also shown that the full width at half maximum intensity ($v_{\frac{1}{2}}$) and T_2 have the relation of equation (1)

$$v_{\frac{1}{2}}=\frac{1}{\pi T_2} \qquad (1)$$

Therefore approximate T_2 value as well as the ratio of the two water species could be determined after separating the spectra into two. The ratio is determined by the area of the spectra. The long T_2

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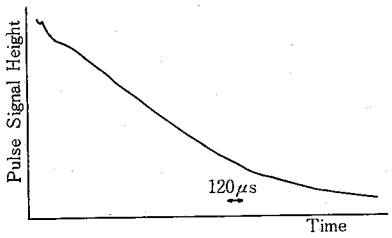

Fig. 1 Free Induction Decay (FID) of Bamboo (water content, 34%)

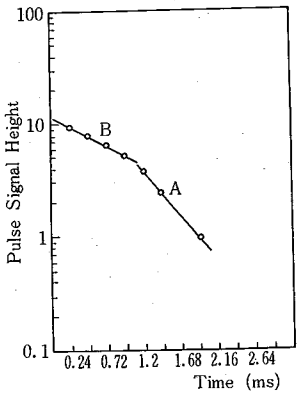

Fig. 2 Free Induction Decay of Bamboo (water content, 34%)

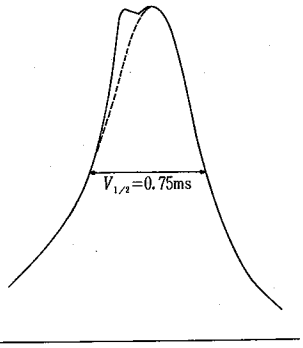

Fig. 3 NMR Spectra of Bamboo (water content, 15.4%)

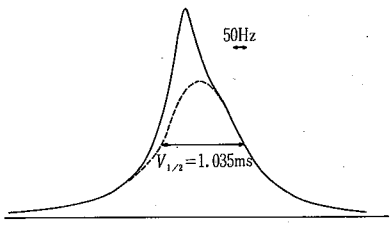

Fig. 4 NMR Spectra of Bamboo (water content, 34%)

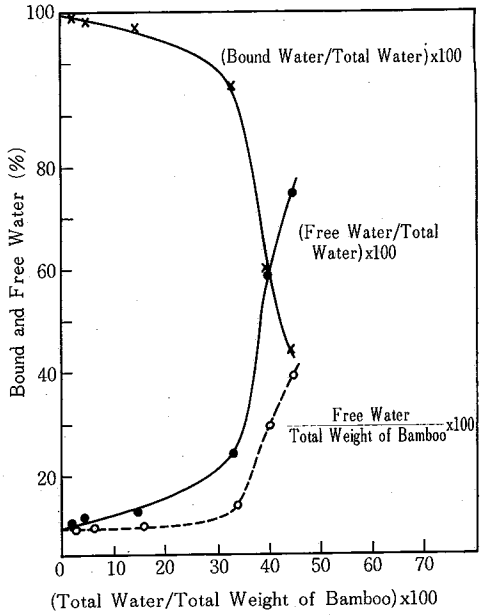

Fig. 5 Bound or Free Water vs. Water Content of Bamboo

values are almost three times over short T_2 values. The former is due to free water and the later, bound water.

The free water content or bound water content versus total water in bamboo were plotted (Fig. 5). It was found that most of the free water was bound when the water content was less than 30% and the free water increased gradually at first, and increased drastically when the water content was more than 30%.

For measurements of T_1, "minispec 20" is designed for memorizing the relative signal height at different time after 180°—90° pulse, then a modification is made to make plot on a straight one and T_1 is calculated. This procedure is printted and T_1 is shown in the displaying board.

In Fig. 6, both the original relative signal height versus time (●) and the modified relative signal height versus time (○) are plotted. The ln $\frac{M_0-M}{2M_0}$ values are also shown in Fig. 6 (where M_0 is relative signal height at infinitive time and M is that at reference time). It is obvious that the original one was composed of two lines, which indicated two T_1 values corresponding to two water fractions. But it is difficult for determining the long T_1 values accu-

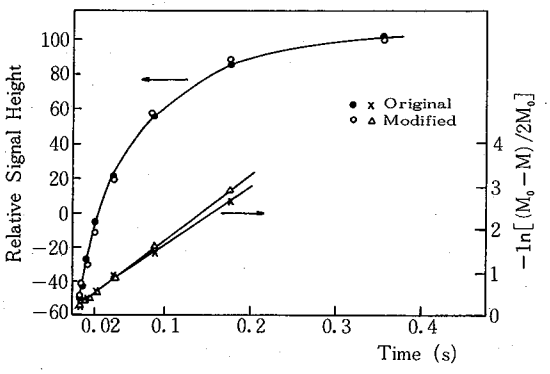

Fig. 6　180°-90° Signal Height of Bamboo (water content, 34%)

rately. Therefore, the modified one was a single straight line i. e. the "minispec PC 20" displays an average value of two T_1.

The relation of T_1-water content and T_2-water content is shown in Fig. 7. Both T_2 increased with the increase of the water content. Considering the variation of bound water and free water with the total water content as shown in Fig. 5, the contribution of bound water will be greater below 30% water content and that of free water will be greater above 30% water content. Therefore, that T_1 below 30% water content will parallel to T_{2b} and T_1 above 30% water content will parallel to T_{2f} is reasonable.

Since free water content increased gradually even at water content less than 30%, and the parallelism of T_1 and T_{2b} i. e. T_1/T_{2b}=constant=150, a same relaxation mechanism and a relative rapid exchange are suggested for bound water and free water.[4]

Using following four equations, the correlation time (τ_c) of bound water can be determined.[5),6)]

$$T_1^{-1}=\left(\frac{6}{5}\right)r^2u^2R^{-6}\tau_c \times[(1+W_0^2\tau_c^2)^{-1}+4(1+4W_0^2\tau_c^2)^{-1}] \quad (2)$$

$$T_2^{-1}=\left(\frac{9}{5}\right)r^2u^2R^{-6}\tau_c \times\left[1+\left(\frac{5}{3}\right)(1+W_0^2\tau_c^2)^{-1}+\left(\frac{2}{3}\right)(1+4W_0^2\tau_c^2)^{-1}\right] \quad (3)$$

$$T_1^{-1}=PT_{1b}^{-1}+(1-P)T_{1f}^{-1} \quad (4)$$

$$T_2^{-1}=PT_{2b}^{-1}+(1-P)T_{2f}^{-1} \quad (5)$$

r : Gyromagnetic ratio of proton

u : Magnetic moment of proton

R : Distance between proton

τ_c : Correlation time　$\tau_f=3\times10^{-12}$ sec.

W : 2×20 MHz

$r^2u^2R^{-6}=8.7\times10^9$ s^{-2} for water

T_{1f} : T_1 of free water

T_{2f} : T_2 of free water

T_{1b} : T_1 of bond water

T_{2b} : T_2 of bond water

P : Bond water/total water

Fig. 8 is the relation of $1/p$ (abscissa) and T_1 obtained from eq. (4) divided by 150 as well as T_2 obtained from eq. (5). It is seen from Fig. 8, T_2 and $T_1/150$ will coincide when the $\tau_c=10^{-7}$ sec. Comparing with τ_c of the free water (3×10^{-12} sec) and of living body (10^{-6} -10^{-12} sec), the water in bamboo is rather strongly bound.

4. Conclusions

1. Pulse NMR method is used for determining the T_1 and T_2 values of water in bamboo for a broad range.
2. There is two water fractions of different mobility in bamboo. Most of water is bound when total water content is less than 30% and free water increased drastically when water content is more than 30%.
3. Correlation time of bound water in bamboo is about 10^{-7} sec and the water is rather strongly bound compared with those of other living bodies.

5. Acknowledgement

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