Mechanism of water adsorption capacity change of bamboo by heating

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Abstract

The water adsorption capacity of mousouchiku bamboo (*Phyllostachys pubescens*) heated at 200°C in air for various times were examined. The samples were subsequently placed in various humidity at 20°C, to obtain relevant isotherms. These were analyzed using Hailwood and Horrobin theory, derived for hydrophilic macromolecules, and Dubinin and Radushkevich theory, previously used to describe the behavior of microporous carbons. The results show that the water adsorption capacities of the samples changed after heating for 2 to 5 hr and imply that over this time the number of hydroxyl groups decreased markedly while the number of micropores formed increased.

Keywords: **Bamboo, heating, Water, Adsorption, Hailwood - Horrobin Theory, Dubinin - Rudshkevich Theory**

Introduction

Bamboo is a resource that grows rapidly and abundantly. It is one of the more useful natural resources. Although bamboo has been used extensively for making handcrafted articles, it has not been widely exploited by industry. Today, most bamboo stands are destroyed or ignored and an effective end-use for bamboo should be sought given its contribution to the forest biomass.

Heat treatment is an effective means of processing bamboo. Numerous studies have shown that heat-dried bamboo absorbs a variety of substances (Abe et al. 1996a, 1996b, 2001a, 2001b; Fujiwara. 2003a). One recent investigation demonstrated its ability to condition the humidity of a room (Fujiwara. 2003b). However, the full adsorption capacity of bamboo is unknown and an investigation of how these changes with heating could provide information that allows the biomass of bamboo to be exploited.

Therefore, this study considers the adsorption capacity of bamboo samples heated at a fixed temperature of 200°C for different times. The results are interpreted using different theories to provide a mechanism that accounts for the change in the adsorption capacity of bamboo with heating time.

Experiments

Bamboo samples were taken from a 6-year-old mousouchiku (*Phyllostachys pubescens*) culm harvested on October 2004, in Shimane Prefecture in Japan. They consisted of 27 internodes designated as No. 1 to No. 27 from the bottom to the top of the culm. The centers of internodes No. 14 and 15 were used to provide block samples with rectangular dimensions of 20×5×5 (L×R×T) (mm).

The samples were dried at 105°C for 24 hr before the heat treatment and then heated at 200°C for 0 (untreated control sample), 1, 2, 3, 5, 20, 48, 72, 120, 240, and 360 hr. The heating times were determined to allow the 11 data points to be plotted at nearly regular intervals on a logarithmic scale (expressed as the natural logarithm the times are 0, 0.69, 1.10, 1.61, 3.00, 3.88, 4.28, 4.79, 5.48, and 5.89, respectively). The weight loss due to heat treatment was estimated relative to the weight of the untreated sample.

Each sample was subsequently conditioned at 20°C for 3 weeks to determine the extent of moisture adsorption, by placing samples in sealed containers conditioned by ten different saturated solutions: LiCl (11% RH), CH_3COOK (22% RH), $MgCl_2$ (33% RH), K_2CO_3 (43% RH), $LiNO_3$ (47% RH), $Mg(NO_3)_2$ (53% RH), NaBr (57% RH), NH_4NO_3 (62% RH), $SrCl_3$ (71% RH), NaCl (75% RH), $(NH_4)_2SO_4$ (80% RH), KCl (84% RH), $BaCl_2$ (88%RH), KNO_3

(92% RH), $Pb(NO_3)_2$ (95% RH), and K_2SO_4 (97% RH). The results were analyzed in terms of Hailwood and Horrobin theory (Hailwood, Horrobin. 1946) and Dubinin and Radushkevich theory (Dubinin. 1960, 1965).

Results and Discussion

Figure 1 shows the weight loss of the mousouchiku blocks heated at 200°C for 0 to 360 hr in air. The weights decrease rapidly for the samples heated for less than 120 hr, while the decrease was more gradual for those heated for longer than 120 hr. This same trend occurs for wood (Nakano. 2003).

The samples were then placed in sealed containers, along with saturated solutions, at 20°C for 21, 30, 60, and 90 days. The results differed slightly for the different adsorption periods and this paper considers only the sorption results over 21 days. The isotherms are shown in Figure 2 and were sigmoidal, with the moisture content for a given relative humidity varying with heating time over a wide variety of relative humidities. The relationship between heating time and moisture content at RH 0.93 is shown in Figure 3, which demonstrates that the hygroscopicity of a heated sample decreases for up to 5 hr, and then increases thereafter. A similar trend has been reported for heated wood (Nakano. 2003). Over a fixed heating time of 2 hr, the hygroscopicity of a sample decreased as the heating temperature was increased to 250°C, but increased at higher temperatures. For the same sample, the adsorption of nitrogen gas began at 250°C and increased with heating temperature. Fourier transform infrared (FT-IR) measurements suggest that hydroxyl groups provide adsorption sites for water and control adsorption of samples heated below 250°C. A comparison of the adsorption of water vapor with that of nitrogen showed a decrease in adsorption until 250°C, caused by a reduction in the number of hydroxyl groups. At above 250°C, the adsorption increases as a result of the formation of capillaries in the wood due to gasification (Nakano. 2003). In the light of the above discussion by Nakano, the results plotted in Figure 3 are consistent with a decrease in adsorption sites and a lowering in hygroscopicity on heating for up to 5 hr, followed by an increase in capillaries upon the gasification or volatilization of bamboo after heating for more 5 hr, which increases the hygroscopicity.

The hygroscopic behavior was evaluated in terms of the Hailwood and Horrobin theory used to describe the behavior of hydrophilic polymers. This theory has been applied successfully to wood and chemically modified wood. The theory assumes that the adsorbent is an ideal solid solution and invokes three constants: K_1, K_2, and W. K_1 and K_2 are equilibrium constants used to describe the interaction of dissolved water and the anhydrous polymer to form hydrous polymer, and the relationship between the dissolved water and the water vapor, respectively. W is defined as the molecular weight of polymer substances per adsorption site. The relationships between K_1, K_2, $1/W$, and weight loss are shown in Figures 4 to 6.

The relationships between the sample weight loss for a given heating time and the parameters K_1K_2 and $1/W$ are shown in Figure 4. The product K_1K_2 is the equilibrium constant for the reaction of water vapor with heated bamboo to form hydrous bamboo via monolayer adsorption. Figure 4 shows that K_1K_2 increases up to the heating time of 2 to 5 hr, after which it decreases linearly with further heating. This implies that adsorption ability peaks at 2 to 5 hr and decreases thereafter, implying that the area of the internal surface is reduced on heating beyond 2 to 5 hr.

Figure 5 shows that the variation in $1/W$ with weight loss is opposite of that for K_1K_2. That is, the number of sorption sites per mass $1/W$ shows the minimum after heating for 2 to 5 hr, but increasing linearly over the same time.

The relationships between K_1K_2 and $1/W$ and the heating time are shown in Figure 5. Hailwood and Horrobin theory gives $K_1K_2 = C_1 + C_2/(1/W)$, where C_1 and C_2 are constant and K_1K_2 is inversely proportional to $1/W$. However, the direction of the plot varies before and after

2 to 5 hr. Clearly both the chemical composition and physical structure of the internal surface contribute to the water adsorption changes upon heating time.

Hailwood and Horrobin theory is based on the presence of a specific adsorption site. Consequently, it is impossible to discuss those samples for which the condensation of water in capillaries dominates over adsorption at specific sites, although appropriate parameters can be derived. For example, $1/W$, the number of adsorption sites per unit mass of bamboo, shows the most adsorption after heating for 360 hr with a weight loss of over 60%. At this point, those components in the bamboo contributing to water adsorption, especially hemicellulose, are decomposed, but there will have been an increase in capillaries as a result of a loss of the bamboo components. The increase in the number of adsorption sites and change in the equilibrium constants for adsorption imply that Hailwood and Horrobin theory can be used only for samples with short heating times.

Saturated adsorption, arising from capillary condensed water, can also be modeled using the empirical equation of Dubinin and Radushkevich, which is used to describe the adsorption of vapors on microporous carbons (Dubinin. 1960, 1965). The amount of adsorption is:

$$m = m_0 \exp[-(\frac{\varepsilon}{E_0})^2]$$

where m_0 is the moisture content of capillary condensed water, ε is Polanyi' s adsorption potential, and E_0 is a parameter related to the interaction energy. Here, ε=RTln[1/h] (R is the gas constant, T is the absolute temperature, and h is the relative humidity).

With microporous carbons, this equation is invalid over a wide pressure range (Rand. 1976). We applied Dubinin and Radushkevich equation to our adsorption data and also confirmed that this theory is not useful for the full range of relative humidities, but applies at lower relative humidities. Therefore, the linear plot of $(\mathrm{RTln}[1/h])^2$ vs. ln(m) for the adsorption data obtained at lower relative humidities was extrapolated to obtain its slope, $(1/E_0)^2$, and intercept, ln(m_0), allowing the characteristic adsorption energy E_0 and saturated adsorption m_0 to be derived. Note that the obtained values are reliable for low relative humidities and lower moisture contents only, and not over a wide pressure range, including the fiber saturation point.

The relationship between parameter m_0 or E_0 in the Dubinin and Radushkevich theory and the measured weight loss is shown in Figure 6 with m_0 peaking after heating for 2 to 5 hr and increasing linearly over longer heating times. This behavior is similar to that of parameter 1/W in Hailwood and Horrobin theory, as shown in Figure 4. m_0 represents the moisture content when all of the capillaries are filled with water molecules. Like the results for 1/W, those for m_0 imply that heating for 2 to 5 hr leads to the formation of capillaries upon gasification or volatilization. Conversely, E_0 decreased after peaking with heating for 2 to 5 hr. This is the same trend shown by Hailwood and Horrobin's parameter K_1K_2, the equilibrium constant for the interaction between the adsorbate and adsorbent, *i.e.*, the formation of hydrous bamboo. Considering weight loss, parameter E_0 describes not only the formation of capillaries but also the adsorption mechanism of the bamboo on heating for 2 to 5 hr.

As illustrated by Hailwood and Horrobin theory, Figure 7 shows how the adsorption capacity of heated bamboo varies with the heating time from 2 to 5 hr. In this regard, m_0 shows little variation for heating for 1 to 5 hr. Subsequently, the only interaction change that occurs upon further heating is between water molecules and bamboo substances.

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Captions

Fig. 1. Weight loss of mousouchiku bamboo with heating time at 200°C.

Fig. 2. Isothermal curves of wood heated for various times.

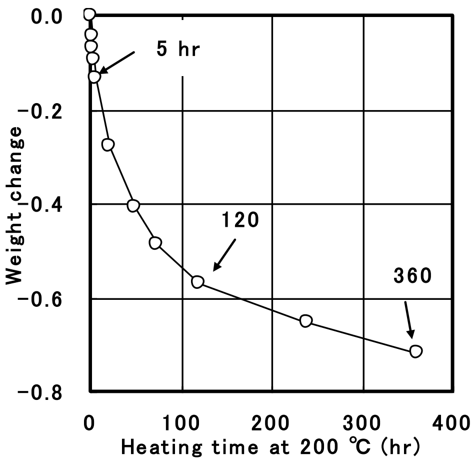
Fig. 3. Relationship between the moisture content and weight loss with heating time.

Fig. 4. Variation in the Hailwood and Horrobin parameters K_1K_2 and $1/W$ with weight loss.

Fig. 5. Relationship between the Hailwood and Horrobin parameters K_1K_2 and $1/W$.

Fig. 6. Variation in the Dubinin and Radushkevich parameters m_0 and E_0 with weight loss.

Fig. 7. Relationship between the Dubinin and Radushkevich parameters E_0 and m_0.



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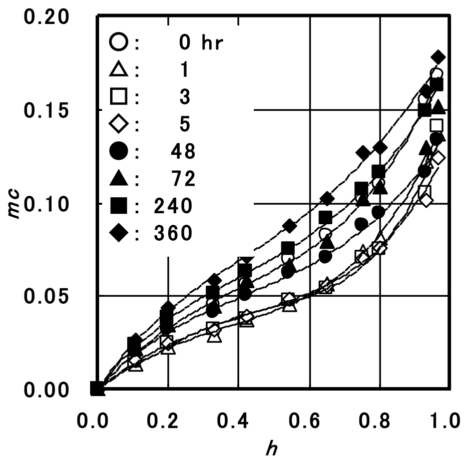

Fig. 2. Isothermal curves of wood heated for various times.

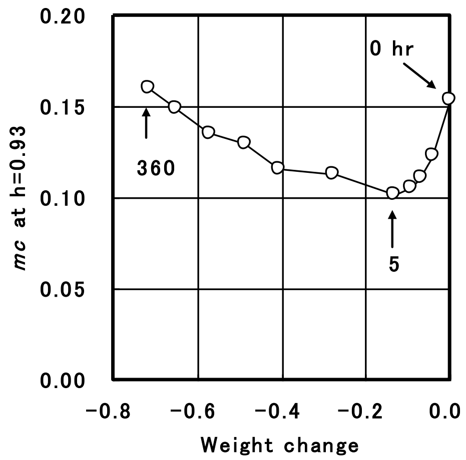

Fig. 3. Relationship between the moisture content and weight loss with heating time.

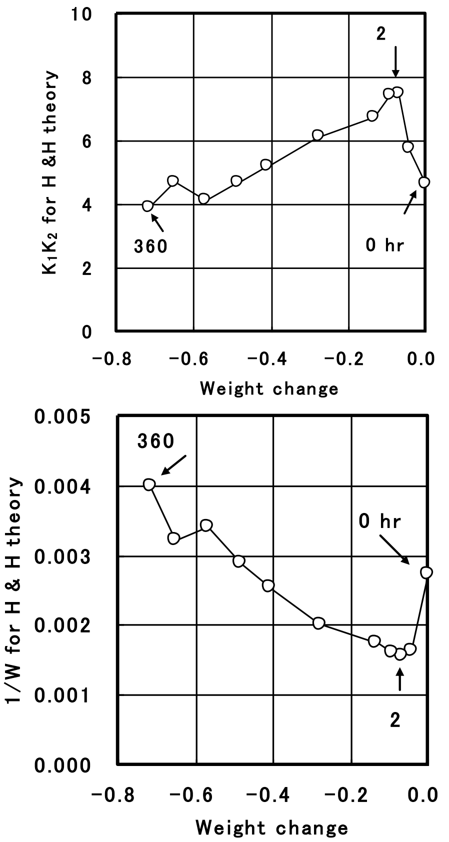

Fig. 4. Variation in the Hailwood and Horrobin parameters K_1K_2 and $1/W$ with weight loss.

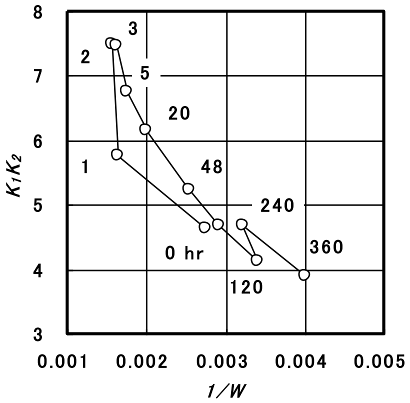

Fig. 5. Relationship between the Hailwood and Horrobin parameters K_1K_2 and $1/W$.

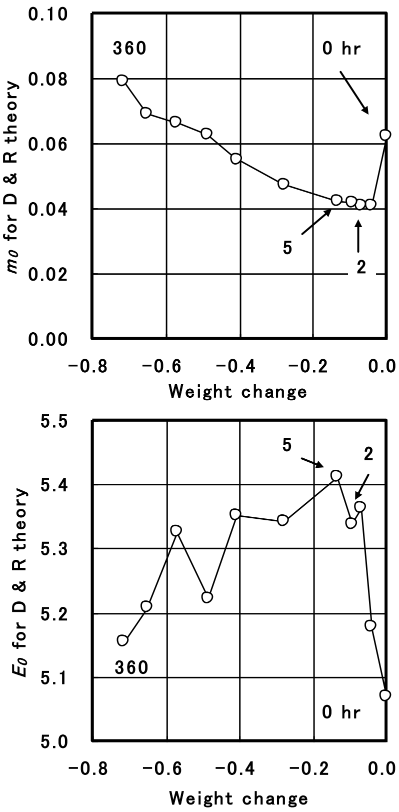

Fig. 6. Variation in the Dubinin and Radushkevich parameters m_0 and E_0 with weight loss.

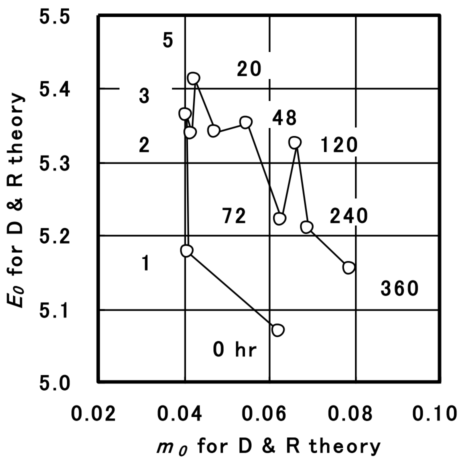

Fig. 7. Relationship between the Dubinin and Radushkevich parameters E_0 and m_0.