J Wood Sci (2006) 52:490–495
DOI 10.1007/s10086-006-0807-2

ORIGINAL ARTICLE

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Analysis of the temperature dependence of water sorption for wood on the basis of dual mode theory

Received: September 30, 2005 / Accepted: February 13, 2006 / Published online: June 29, 2006

Abstract Isotherm curves of water sorption for wood at various temperatures were analyzed based on the dual mode theory where the total coverage was represented by a linear combination of the Langmuir and Henry equations. The saturation concentration and affinity constant of the Langmuir equation and the parameter of Henry's law had a transition point near 60°C. The analysis based on the dual mode theory found that the constants for whole wood were related to those of wood components and depended more on their glass transition temperatures. That is, it was theoretically demonstrated that the characteristic temperature dependence of water sorption for wood occurs because wood consists of three components (cellulose, hemicellulose, and lignin) with different glass transition temperatures.

Key words Water sorption · Temperature dependence · Glass transition temperature · Dual mode theory

Introduction

The isotherm curve of water sorption for wood is sigmoid and similar to other natural products.[1–3] Skaar[4] introduced various sorption theories and described how the water sorption of wood fit the Hailwood and Horrobin theory,[5] which is a kind of dual mode theory. This dual mode theory has been applied to both natural and chemically modified wood.[6–10] The general dual mode theory, which was proposed by Meares[11,12] and Michaels et al.,[13] has been applied successfully to the gas adsorption of synthetic polymers,[14–17] in which the total coverage is represented by a linear combination of the Langmuir and Flory-Huggins equations. In some cases, Henry's equation is exchanged for the Flory-Huggins equation because the former is the approximate equation of the latter.[18] This theory differs from the Hailwood and Horrobin theory in that the Langmuir sorption process is dependent on the Henry sorption process for the latter theory.

Nevertheless, the characteristic temperature dependence of water sorption for wood has not been examined in detail yet based on the dual mode theory, although it has been applied to various materials. Therefore, this report analyzes the temperature dependence of water sorption for wood based on the dual mode theory considering wood components that have different glass transition temperatures.

Data used in the analysis

The isotherm data for 0°–100°C used in this analysis were taken from the *Wood Handbook* published by the US Department of Agriculture[19] and are probably the standard isotherm data for wood. Figure 1 shows typical isotherm curves from the data.

Results and discussion

Application of the dual mode theory and temperature dependence of its parameters

In the dual mode theory, total moisture content ($\mathrm{cm^3 STP/cm^3}$) is represented by the following equation:[11–13]

$$C = C_D + C_H \tag{1}$$

where C_D and C_H are described by the Henry and Langmuir equations, respectively, that is

$$C_D = K_D h \tag{2}$$

$$C_H = \frac{C'_H b' h}{1 + b' h} \tag{3}$$

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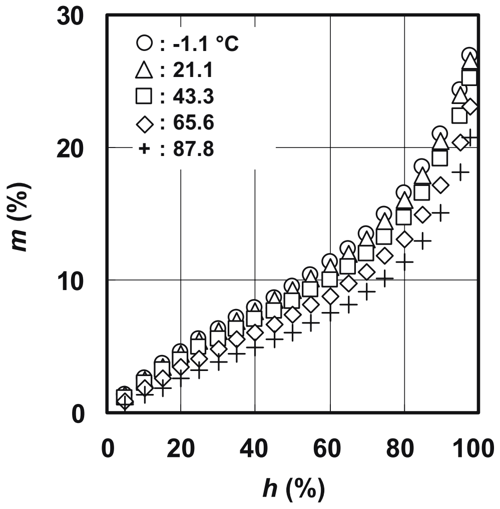

Fig. 1. Typical sorption isotherm curves at various temperatures using data from the *Wood Handbook* published by the US Department of Agriculture.[19] m, Moisture content, h, relative humidity

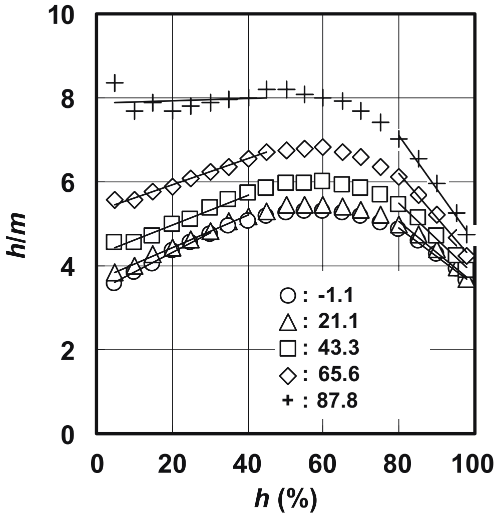

Fig. 2. Relationships between the ratios of relative humidity to moisture content (h/m) and relative humidity (h)

where h is the fractional relative humidity, K_D is Henry's parameter, C'_H and b' are the saturation concentration and modified affinity constant in the Langmuir equation, respectively, such that $b' = bp_0$, where b and p_0 are affinity constant and vapor pressure, respectively. When using the moisture content units (g/g) generally used for wood,

$$m = m_D + m_H \tag{4}$$

with

$$m_D = k\frac{K_D h}{1 - K_D h} \tag{5}$$

$$m_H = \frac{m_0 b' h}{1 + b' h} \tag{6}$$

where k is a constant by unit conversion, and m_0 is the saturation concentration (g/g). Equations 5 and 6 show the linearity of h/m_D vs h and h/m_H vs h. Note that the dual mode theory differs from the Hailwood and Horrobin theory in that m_H and m_D are dealt with independently. In the Hailwood and Horrobin theory, the constants m_0, b', and K_D are calculated by solving a quadratic equation obtained by substituting Eqs. 5 and 6 for Eq. 4.

Figure 2 shows h/m vs h for wood from the *Wood Handbook* published by the US Department of Agriculture[19] and that the plots are not symmetric. This implies that the Hailwood and Horrobin theory cannot be applied to the curves in Fig. 2, because h/m vs h must be a quadratic curve in the Hailwood and Horrobin theory. Nevertheless, in Fig. 2, these curves are linear in both the lower and higher relative humidity regions, i.e., they are approximated by the Langmuir theory at low relative humidity and by Henry's law at high relative humidity. As a result, we can assume that isotherms at various temperatures for wood are described by a linear combination of the Langmuir theory and Henry's law. The isotherm obtained using Eqs. 4–6 is in good agreement with the experimental results without the intermediate region of relative humidity, as shown in Fig. 3, which is example one of the all data. Note, however, that this result is not necessarily valid theoretically, because wood is a multicomponent system. We must consider the effects of the different components.

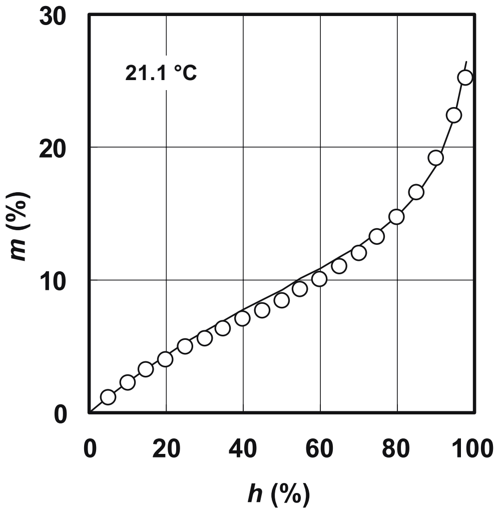

Fig. 3. Comparison of the experimental results (*open circles*) and theoretical calculation (*solid line*) for a sorption isotherm curve

The temperature dependence of parameters m_0, b', and K_D is shown in Figs. 4 to 6, which were calculated from h/m_H vs h for low relative humidity and from h/m_D vs h for high relative humidity. We note that the slope of m_0 vs T is positive because the slope is generally negative for many polymers. Moreover, they have a transition point near 60°C (= 0.003 K^{-1}). This characteristic temperature dependence suggests that the overall water sorption of wood is affected by the glass transition temperature of its components, considering the glass transition effect on gas sorption for various polymers.[15–17] Therefore, we will try to explain the temperature dependence, that is, the appearance of the temperature transition seen in Figs. 4–6, regarding a multicomponent system whose components have different glass transition temperatures.

Dual mode theory and glass transition temperature

It is well known that gas sorption behavior changes abruptly at the glass transition temperature T_g for synthetic polymers. For glassy polymers below T_g, both gas sorption on the surface in the unrelaxed volume, i.e., the sum of microvoids, and dissolution into the matrix proceed during sorption; that is, a sorption isotherm consists of contributions from both Langmuir sorption and Henry dissolution. The unrelaxed volume below T_g decreases with increasing temperature, so that the coverage C'_H, that corresponds to m_0, decreases with temperature according to the following equation:[17]

$$C'_H = \gamma\Delta\alpha\left(T_g - T\right) \tag{7}$$

where γ is a constant, and $\Delta\alpha$ is the difference between the cubic thermal expansion constants above and below T_g. Moreover, T_g also decreases with increasing sorbate concentration, because the flexibility of molecular chains in the matrix increases with the sorbate concentration. As a result, Eq. 7 is reduced to the following equation:

$$C'_H = \gamma\Delta\alpha\left(T_{g_0} - \beta C^* - T\right) = \gamma\Delta\alpha\left[T_g\left(C^*\right) - T\right] \tag{8}$$

where T_{g_0} is T_g at $C^* = 0$, and β and C^* are a constant and the effective sorbate concentration, respectively. Equation 8 is valid for many synthetic polymers.[17] This equation shows that the Langmuir sorption at $T < T_g$ is affected by both the measurement temperature and the sorbate concentration. The result shown in Fig. 4 is in conflict with Eqs. 7 and 8 because the slope of C'_H vs T of equations is negative. This conflict is discussed hereinafter.

For simplicity, we use Eq. 7, because the effect of C^* on T_g is slight at low relative humidity. By contrast, for rubbery polymers above T_g, most microvoids disappear, so that the sorbate dissolves in the matrix, and its dissolution obeys Henry's equation or the Flory-Huggins equation in some cases. That is, the sorption behaviors above and below the glass transition temperature differ because the flexibility of the molecular chains changes.

The glass transition temperatures of wood components differ. Many researchers have reported the glass transition of wood and its components under various wet conditions.[20–27] The reported values differ because of differences in the measurement methods. Furuta et al.[27] reported –40°C for hemicellulose, 50–100°C for lignin, and above 100°C for cellulose using viscoelastic measurements under wet conditions. These values are much lower than those of Goring[20] determined with the softening point apparatus or the mechanical measurements of Salmen and Back.[22,23] Hillis and Rozsa[24] found two peaks below 100°C in the temperature dependence of the rotation rate under a constant torque for wet wood, while Irvine[25] and Kelley et al.[26] reported glass transition temperatures of 60°–70°C for milled wood lignin (MWL). Considering these results, the glass transition temperatures of lignin and hemicellulose are about 60°C and below room temperature, respectively. Therefore, the temperature dependence of m_0, b', and K_D for whole wood is expected to be apparent.

Whole wood as a multicomponent system can be analyzed using dual mode theory to clarify the characteristic temperature dependence of m_0, b', and K_D, as shown in Figs. 4–6. We will use the units $\mathrm{cm^3STP/cm^3}$ and Eq. 8 in the following discussion. The temperature dependence of the saturation concentration, affinity, and Henry's parameter does not change on unit conversion.

Temperature dependence of Langmuir's parameters

First, we examine isotherms for low relative humidity, for which the isotherms should obey the Langmuir equation, as shown in Fig. 2.

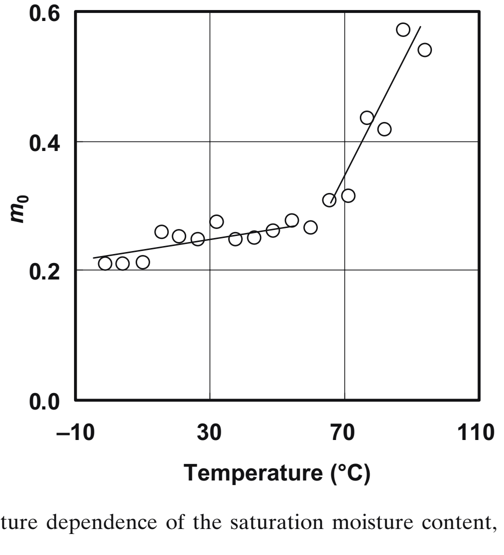

Fig. 4. Temperature dependence of the saturation moisture content, m_0

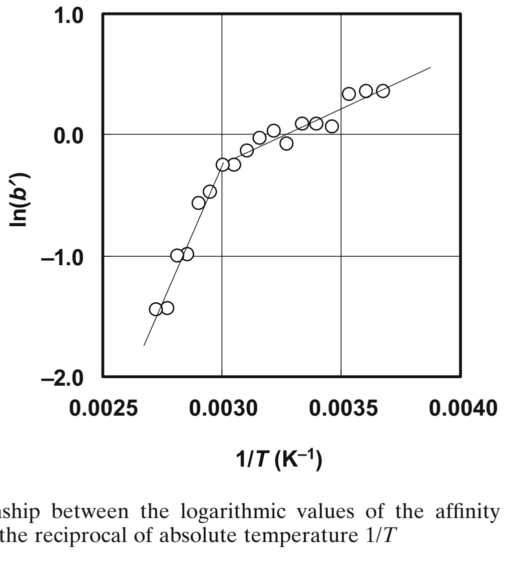

Fig. 5. Relationship between the logarithmic values of the affinity constant b' and the reciprocal of absolute temperature $1/T$

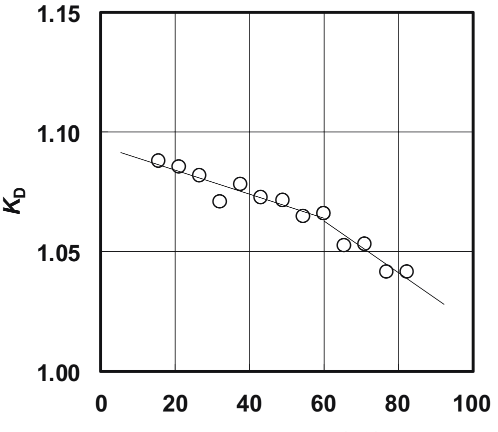

Fig. 6. Temperature dependence of Henry's law parameter K_D

In our discussion, the wood components hemicellulose, lignin, and cellulose are represented by the subscripts 1, 2, and 3, respectively. For example, their respective glass transition temperatures are T_{g_1}, T_{g_2}, and T_{g_3}, and $T_{g_1} < T_{g_2} < T_{g_3}$. Assuming that each component obeys Eq. 1, then Eq. 1 for the entire system of wood is represented by

$$C = \sum_{i=1}^{3} \phi_i C_i = \sum_{i=1}^{3} \phi_i \left(C_{D_i} + C_{H_i} \right) \tag{9}$$

where ϕ_i is the volume fraction of component i.

According to dual mode theory, sorption below T_g causes both Langmuir sorption and Henry dissolution. However, the contribution of the Henry dissolution is small at low relative humidity, so that the sorption is approximated by the Langmuir sorption. By contrast, the Langmuir-type sorption levels off at high relative humidity, so that its contribution is constant, C'_H. Then, the moisture content of component i is represented by

$$C_i = \left(K_{D_i} + C'_{H_i} \right) h \qquad \left(T \leqq T_g \right) \tag{10}$$

where K_{D_i} is Henry's parameter for component i. That is, the sorption for high relative humidity is approximated by Henry's equation. Of course, the moisture content at $T \geqq T_g$ obeys Henry's law for all values of relative humidity.

For low relative humidity, the total moisture content is represented by Eqs. 11–13 in each temperature region using the previous approximation.

$$C = \sum_{i=1}^{3} \phi_i \frac{C'_{H_1} b'_i h}{1 + b'_i h} \cong \left(\sum_{j=1}^{3} \phi_j C'_{H_j} b'_j \middle/ \sum_{i=1}^{3} b'_i \right) \sum_{i=1}^{3} b'_i h \middle/ \left(1 + \sum_{i=1}^{3} b'_i h \right) \qquad \left(T \leqq T_{g_1} \right) \tag{11}$$

$$C = \phi_1 K_{D_1} h + \sum_{i=2}^{3} \phi_i \frac{C'_{H_1} b'_i h}{1 + b'_i h} \cong \left[\phi_1 K_{D_1} \middle/ \sum_{i=2}^{3} b'_i + \sum_{i=2}^{3} \left(\phi_j C'_{H_j} b'_j \middle/ \sum_{i=2}^{3} b'_i \right) \right] \sum_{i=2}^{3} b'_i h \middle/ \left(1 + \sum_{i=2}^{3} b'_i h \right) \qquad \left(T_{g_1} \leqq T \leqq T_{g_2} \right) \tag{12}$$

$$C = \sum_{i=2}^{2} \phi_i K_{D_i} h + \phi_3 \frac{C'_{H_3} b'_3 h}{1 + b'_3 h} \cong \left(\sum_{i=1}^{2} \phi_i K_{D_i} \middle/ b'_3 + \phi_3 C'_{H_3} \right) b'_3 h \middle/ \left(1 + b'_3 h \right) \qquad \left(T_{g_2} \leqq T \leqq T_{g_3} \right) \tag{13}$$

where C'_{H_i}, b'_i, and K_{D_i} are the saturation moisture content, modified affinity constant, and Henry's parameter, respectively. Equations 11, 12, and 13 are derived using $h \ll 1$ and assuming $b'_i h^2 \ll 1$. In general, $b'_i < 1$ for many synthetic polymers.

Note that from Eqs. 11–13, the Langmuir equation is not exactly valid, but is approximately valid in the region of low relative humidity for wood when the T_gs of the components differ. That is, the Langmuir-type isotherm for low relative humidity in Fig. 2 is apparent. The constants C'_H (or m_0), b', and K_D obtained from the isotherm for whole wood reflect those of the components, so that their temperature dependence depends on the glass transition temperatures of the components.

This is why the Langmuir curve in the dual mode theory does not level off for wood,[28] while the curve does level off in the Hailwood and Horrobin theory.[6,7] The former should be valid because one of the components, moist hemicellulose, does not obey the Langmuir equation, but obeys Henry's law at room temperature ($T_{g_1} \leqq T \leqq T_{g_2}$), as shown in Eq. 12, whose contribution is represented by $\phi_1 K_{D_1} h$ in Eq. 12.

Next, we examine the temperature dependence of C'_H and b' for the apparent Langmuir-type isotherm, which is found in the region of low relative humidity. From Eqs. 11–13, the apparent C'_H is represented by

$$C'_H = \left(-\sum_{i=1}^{3} \phi_i \gamma_i \Delta\alpha_i b_i^0 \right) T \middle/ \sum_{i=1}^{3} b_i^0 + \sum_{i=1}^{3} \phi_i \gamma_i \Delta\alpha_i b_i^0 T_{g_t} \middle/ \sum_{i=1}^{3} b_i^0 \qquad \left(T \leqq T_{g_1} \right) \tag{14}$$

$$C'_H = \left(\phi_i K_{D_1}^{o} \exp\left[\left(\Delta H_{H_1} - \Delta H_{b_1} \right) / RT \right] - \left(\sum_{i=2}^{3} \phi_i \gamma_i \Delta\alpha_i b_i^0 \right) T \right) \middle/ \sum_{i=2}^{3} b_i^0 + \sum_{i=2}^{3} \phi_i \gamma_i \Delta\alpha_i b_i^0 T_{g_i} \middle/ \sum_{i=2}^{3} b_i^0 \qquad \left(T_{g_1} \leqq T \leqq T_{g_2} \right) \tag{15}$$

$$C'_H = \left(\sum_{i=1}^{2} \phi_i K_{D_i}^{0} \exp\left[\left(\Delta H_{H_i} - \Delta H_{b_i} \right) / RT \right] - \phi_3 \gamma_3 \Delta\alpha_3 T \right) \middle/ b_3^0 - \phi_3 \gamma_3 \Delta\alpha_3 b_3^0 T_{g_3} / b_3^0 \qquad \left(T_{g_2} \leqq T \leqq T_{g_3} \right) \tag{16}$$

where ΔH_{H_i} and ΔH_{D_i} are the enthalpy of the Langmuir sorption and the Henry dissolution for component i, respectively, and $\Delta H_{H_i} \ll \Delta H_{D_i} < 0$. In the derivation, $C'_{H_i} = \gamma \Delta\alpha_i (T_g - T)$, $b_i = b_i^0 \exp[-\Delta H_{H_i}/RT]$, and $K_{D_i} = \mathrm{K}_{D_i}^0 \exp[-\Delta H_{D_i}/RT]$ are used, where b_i^0 is a constant, R is the gas constant, and T is the absolute temperature.

Equation 14 as a function of T represents a line with a negative slope at $T < T_{g_1}$. Because we are concerned with the appearance of the transition at 60°C, as shown in Fig. 4, we do not deal with Eq. 14 here because $T_{g_1} \ll$ room temperature.

The slopes of Eqs. 15 and 16 depend on the contribution of the exponential term in the equations, that is, the contribution of Henry's dissolution. Given that $\exp[(\Delta H_{\mathrm{H}_i} - \Delta H_{\mathrm{D}_i})/RT]$ is a monotonically increasing function of T because $\Delta H_{\mathrm{H}_i} \ll \Delta H_{\mathrm{D}_i} < 0$, Eqs. 15 and 16 are monotonic functions of T and are approximated by straight lines in the narrow temperature region. Their slopes above and below T_{g_2} differ. If the exponential term in Eqs. 15 and 16 is greater than the term of T, the slopes above and below T_{g_2} (= 60°C) are positive, and the former is less than the latter. This explains the relationship between m_0 and T in Fig. 4, where m_0 corresponds to C'_{H}.

The above discussion explains partly the conflict between Eqs. 7 and 8 and the result shown in Fig. 4. Unfortunately, we cannot clarify that all because the values of most of the constants in Eqs. 15 and 16 is not known. Nevertheless, our discussion explains the appearance of the transition at 60°C in Fig. 4 at least.

Next, we discuss the temperature dependence of b'. The apparent b' for the whole system is obtained from Eqs. 11–13. Considering $b'_i = b'^0_i \exp[-\Delta H_{\mathrm{H}_i}/RT]$ in the Langmuir theory, b' in an each temperature region is represented by

$$b' = \sum_{i=1}^{3} b'_i = \sum_{i=1}^{3} b_i^0 \exp\left[-\Delta H_{\mathrm{H}_i}/RT\right] \qquad \left(T \leqq T_{\mathrm{g}_1}\right) \tag{17}$$

$$b' = \sum_{i=2}^{3} b'_i = \sum_{i=2}^{3} b_i^0 \exp\left[-\Delta H_{\mathrm{H}_i}/RT\right] \qquad \left(T_{\mathrm{g}_1} \leqq T \leqq T_{\mathrm{g}_2}\right) \tag{18}$$

$$b' = b'_3 = b_3^0 \exp\left[-\Delta H_{\mathrm{H}_3}/RT\right] \qquad \left(T_{\mathrm{g}_2} \leqq T \leqq T_{\mathrm{g}_3}\right) \tag{19}$$

The affinity b' as a function of $1/T$ is a monotonically increasing function considering $\Delta H_{\mathrm{H}_i} < 0$ so that $\ln(b')$ is also monotonically increasing. Then, we derive the following equations as a slope when $\ln(b')$ is differentiated by $1/T$.

$$\frac{d\ln(b')}{d(1/T)} = \sum_{i=1}^{3} b'_i \Big/ \left(-\Delta H_{\mathrm{H}_i}/R\right) \Big/ \sum_{i=1}^{3} b'_i \qquad \left(T \leqq T_{\mathrm{g}_1}\right) \tag{20}$$

$$\begin{aligned} \frac{d\ln(b')}{d(1/T)} &= \left(b'_2 \Big/ \sum_{i=2}^{3} b'_i\right)\left(-\Delta H_{\mathrm{H}_2}/R\right) + \left(b'_3 \Big/ \sum_{i=2}^{3} b'_i\right)\left(-\Delta H_{\mathrm{H}_3}/R\right) \\ &\quad \left(T_{\mathrm{g}_1} \leqq T \leqq T_{\mathrm{g}_2}\right) \end{aligned} \tag{21}$$

$$\begin{aligned} \frac{d\ln(b')}{d(1/T)} &= \left(-\Delta H_{\mathrm{H}_3}/R\right) = \left(\sum_{i=2}^{3} b'_i \Big/ \sum_{i=2}^{3} b'_i\right)\left(-\Delta H_{\mathrm{H}_3}/R\right) \\ &= \left(b'_2 \Big/ \sum_{i=2}^{3} b'_i\right)\left(-\Delta H_{\mathrm{H}_3}/R\right) + \left(b'_3 \Big/ \sum_{i=2}^{3} b'_i\right)\left(-\Delta H_{\mathrm{H}_3}/R\right) \\ &\quad \left(T_{\mathrm{g}_2} \leqq T \leqq T_{\mathrm{g}_3}\right) \end{aligned} \tag{22}$$

where ΔH_{H_2} and ΔH_{H_3} are the enthalpy of water sorption for lignin and cellulose, respectively. The affinity of water for cellulose is greater than that for lignin, and water sorption is an exothermic process, $\Delta H_{\mathrm{H}_3} < \Delta H_{\mathrm{H}_2} < 0$. Thus, comparing Eqs. 21 and 22, we have

$$0 < \left.\frac{d\ln(b')}{d(1/T)}\right|_{\left(1/T_{g_2}\right) \leq (1/T)} < \left.\frac{d\ln(b')}{d(1/T)}\right|_{(1/T) \leq \left(1/T_{g_2}\right)} \tag{23}$$

Equation 23 reveals that the slope at $1/T_{\mathrm{g}2} \leq 1/T$ is less than that at $1/T \leq 1/T_{\mathrm{g}2}$ for $\ln(b')$ vs $1/T$. This equation explains the transition at $1/T = 0.003\ \mathrm{K}^{-1}$ (= 60°C) in Fig. 6, if T_{g_2} = 60°C, which is the glass transition temperature for MWL according to Irvine[25] and Kelley et al.[26]

Therefore, we conclude that Figs. 4 and 5 reflect the temperature dependence of C'_{H} (or m_0) and b' for wood components whose glass transition temperatures differ.

Temperature dependence of Henry's parameter

Even in the region of high relative humidity, the isotherm obeys the Langmuir sorption at $T < T_{\mathrm{g}}$ and the Henry dissolution at $T_{\mathrm{g}} < T$. However, the Langmuir sorption apparently levels off at high relative humidity. Therefore, the moisture content at $T < T_{\mathrm{g}}$ is represented by Eq. 10, as mentioned above. Of course, it is represented by Henry's equation at $T_{\mathrm{g}} < T$. Accordingly, the moisture content of the entire system is represented by

$$\begin{aligned} C &= \sum_{i=1}^{3} \phi_i \left[K_{\mathrm{D}_i} + \left(C'_{\mathrm{H}_i} b'_i h\right)/\left(1 + b'_i h\right)\right] \cong \sum_{i=1}^{3} \phi_i \left(K_{\mathrm{D}_i} + C'_{\mathrm{H}_i}\right) h \\ &\quad \left(T \leqq T_{\mathrm{g}_1}\right) \end{aligned} \tag{24}$$

$$\begin{aligned} C &= \left[\phi_1 K_{\mathrm{D}_1} h + \sum_{i=1}^{3} \phi_i \left(C'_{\mathrm{H}_i} b'_i h\right) \Big/ \left(1 + b'_i h\right)\right] h \\ &\cong \left[\phi_1 K_{\mathrm{D}_1} + \sum_{i=2}^{3} \phi_i \left(K_{\mathrm{D}_i} + C'_{\mathrm{H}_i}\right)\right] h \qquad \left(T_{\mathrm{g}_1} \leqq T \leqq T_{\mathrm{g}_2}\right) \end{aligned} \tag{25}$$

$$\begin{aligned} C &= \sum_{i=1}^{2} \phi_i K_{\mathrm{D}_i} h + \phi_3 \frac{C'_{\mathrm{H}_3} b'_3 h}{1 + b'_3 h} \cong \left[\sum_{i=1}^{2} \phi_i K_{\mathrm{D}_3} + \phi_3 \left(K_{\mathrm{D}_3} + C'_{\mathrm{H}_3}\right)\right] h \\ &\quad \left(T_{\mathrm{g}_2} \leqq T \leqq T_{\mathrm{g}_3}\right) \end{aligned} \tag{26}$$

Equations 24–26 show that Henry's law apparently holds for the region of high relative humidity and that Henry's parameter K_{D} for the entire system reflects the sorption and dissolution properties of wood components. As a result, K_{D} is represented by

$$K_{\mathrm{D}} = \sum_{i=1}^{3} \phi_i \left(K_{\mathrm{D}_i} + C'_{\mathrm{H}_i}\right) = \sum_{i=1}^{3} \phi_i K_{\mathrm{D}_i} + \sum_{i=1}^{3} C'_{\mathrm{H}_i} \qquad \left(T \leqq T_{\mathrm{g}_1}\right) \tag{27}$$

$$\begin{aligned} K_{\mathrm{D}} &= \phi_1 K_{\mathrm{D}_1} + \sum_{i=2}^{3} \phi_i \left(K_{\mathrm{D}_i} + C'_{\mathrm{H}_i}\right) = \sum_{i=1}^{3} \phi_i K_{\mathrm{D}_i} + \sum_{i=2}^{3} C'_{\mathrm{H}_i} \\ &\quad \left(T_{\mathrm{g}_1} \leqq T \leqq T_{\mathrm{g}_2}\right) \end{aligned} \tag{28}$$

$$\begin{aligned} K_{\mathrm{D}} &= \sum_{i=1}^{2} \phi_i K_{\mathrm{D}_i} + \phi_3 \left(K_{\mathrm{D}_3} + C'_{\mathrm{H}_3}\right) = \sum_{i=1}^{3} \phi_i K_{\mathrm{D}_i} + C'_{\mathrm{H}_3} \\ &\quad \left(T_{\mathrm{g}_2} \leqq T \leqq T_{\mathrm{g}_3}\right) \end{aligned} \tag{29}$$

Here, the temperature dependence of C'_{H_i} and K_{D_i} are represented by $C'_{\mathrm{H}} = \gamma\Delta\alpha(T_{\mathrm{g}} - T)$ presented in Eq. 7 and $K_{\mathrm{D}_i} = K^0_{\mathrm{D}_i}\exp[-\Delta H_{\mathrm{D}_i}/RT]$, respectively.

Now, we examine K_{D} as a function of T above and below T_{g}. From Eqs. 27–29, the slope dK_{D}/dT of K_{D} vs T is derived as follows:

$$\frac{dK_{\mathrm{D}}}{dT} = \sum_{i=1}^{3}\left(\phi_i K^0_{\mathrm{D}_i}\Delta H_{\mathrm{D}_i}/RT^2\right)\exp\left[-\Delta H_{\mathrm{D}_i}/RT\right] - \sum_{i=1}^{3}\phi_i\gamma_i\Delta\alpha_i b_i^0 \quad \left(T \leqq T_{\mathrm{g}_1}\right) \tag{30}$$

$$\frac{dK_{\mathrm{D}}}{dT} = \sum_{i=1}^{3}\left(\phi_i K^0_{\mathrm{D}_i}\Delta H_{\mathrm{D}_i}/RT^2\right)\exp\left[-\Delta H_{\mathrm{D}_i}/RT\right] - \sum_{i=2}^{3}\phi_i\gamma_i\Delta\alpha_i b_i^0 \quad \left(T_{\mathrm{g}_1} \leqq T \leqq T_{\mathrm{g}_2}\right) \tag{31}$$

$$\frac{dK_{\mathrm{D}}}{dT} = \sum_{i=1}^{3}\left(\phi_i K^0_{\mathrm{D}_i}\Delta H_{\mathrm{D}_i}/RT^2\right)\exp\left[-\Delta H_{\mathrm{D}_i}/RT\right] - \phi_3\gamma_3\Delta\alpha_3 b_3^0 \quad \left(T_{\mathrm{g}_2} \leqq T \leqq T_{\mathrm{g}_3}\right) \tag{32}$$

As $K_{\mathrm{D}_i} = \phi_i K^0_{\mathrm{D}_i}(\Delta H_{\mathrm{D}_i}/RT^2)\exp[-\Delta H_{\mathrm{D}_i}/RT]$ is a monotonically decreasing function of T, from Eqs. 31 and 32 we find

$$\left.\frac{dK_{\mathrm{D}}}{dT}\right|_{T \leq T_{\mathrm{g}_2}} < \left.\frac{dK_{\mathrm{D}}}{dT}\right|_{T_{\mathrm{g}_2} \leq T} < 0 \tag{33}$$

Equation 33 shows the appearance of the transition at T_{g_2} for K_{D} vs T. As $K_{\mathrm{D}_i} = \phi_i K^0_{\mathrm{D}_i}(\Delta H_{\mathrm{D}_i}/RT^2)\exp[-\Delta H_{\mathrm{D}_i}/RT]$ is approximated by a straight line with a negative slope in the narrow region of T, K_{D} vs T in $T_{\mathrm{g}_1} \leqq T \leqq T_{\mathrm{g}_3}$ consists of two straight lines with a transition point at T_{g_2}. This is in agreement with the result shown in Fig. 6. Therefore, the K_{D} for whole wood depends on the thermal properties of its components.

Conclusions

The isotherm curves of water sorption at various temperatures for wood were analyzed using the dual mode model. The saturation concentration and affinity constant of Langmuir's equation and Henry's parameter as a function of temperature had a transition point at 60°C, which is the glass transition temperature of lignin. The analysis considering a multicomponent system using the dual mode model found that the constants for whole wood are related to those of its components and depend on their glass transition temperatures. That is, the characteristic temperature dependence of water sorption for wood occurs because wood consists of components with different glass transition temperatures.

In this report, the slopes of C'_{H} and K_{D} near and below T_{g_2} could not be discussed in detail because the change in the microvoid volume plasticity with water sorption and the values of most of the constants in the derived equation are not known for wood. Therefore, a strict discussion of this is expected after these values are clarified.

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