Study on the sorption of water vapour by softwood hemicelluloses

By TAKESI SADOH

Introduction

In the previous paper[6] the auther have reported on the some sorption behaviours of water vapour by hardwood hemicelluloses. It was shown that the hardwood hemicelluloses take up water vapour and swell much more than wood and cellulose do.

The hemicelluloses of softwood are different in their components from those of hardwood. The former consists of mannan besides xylan, containing greater amounts of hygrophilic uronic acid group, though the latter contains xylan only, with less amounts of uronic acid.

In this paper the water sorption and the volumetric swelling were measured for some softwood hemicelluloses, and the calculation was made on the hysteresis ratio, the area of sorptive surface, the free-energy change during adsorption, and the interaction coefficient of adsorbent-water system. The results were compared with those for hardwood hemicelluloses, cellulose, and wood.

Materials

The samples used in this study were the filmy specimens of hemicelluloses prepared from wood meal of three conifers, Hinoki (*Chamaecyparis obtusa* S. et Z.), Sugi (*Cryptomeria japonica* D. DON), and Akamatsu (*Pinus densiflora* S. et Z.), by the following procedures.

The wood meal was delignified with sodium chlorite and acetic acid at 75°C for five hours. A part of the holocellulose obtained was extracted with 20 times its volume of 5 percent potassium hydroxyde for three hours, after pre-extraction with 0.5 percent potassium hydroxyde for an hour, and another part was extracted without the pre-extraction. However the sample without the pre-extraction hornified during the redrying after conditioning shown below, giving no reproduciable data.

The solution obtained by filteration was poured into three times its volume of methanol with acetic acid. The precipitate was centrifuged. The supernatant was decanted, and the residue was resuspended in 85 percent methanol and centrifuged. The supernatant on the residue was replaced with pure methanol, and ethyl ether, successively. The resulting precipitate was suspended in ethyl

---

Contribution from the Laboratory of Wood Technology, Kyoto Prefectural University, Kyoto.

ether, then, added into hot water. The aqueous solution of hemicelluloses, obtained here, was condensed and dried on a glass plate in oven to make transparent film.

Experimental procedures

Both the adsorption and desorption isotherms were determined at 20°C by changing the relative humidity in steps. The samples were exposed in the atmosphere, the relative humidities of which were controlled by the saturated solution of the salts shown in Table 1, and when the equilibrium was established the samples were weighed and the sorbed water was calculated from the increment of the weight. Two to four days were necessary to attained the equilibrium from the results of preliminary experiments. Any differences were not observed between the results on the same samples obtained by the previous method (in the absence of air)⁶⁾ and the present one (in the presence of air).

Table 1. Relative humidities over saturated solution of the salts. (at 20°C)

Salt	Relative humidity(%)
$ZnBr_2 \cdot 2aq.$	10.0
$MgCl_2 \cdot 6aq.$	33.5
$K_2CO_3 \cdot 2aq.$	44.0
$Mg(NO_3)_2 \cdot 6aq.$	54.0
$NaNO_3$	66.0
NaCl	76.0
KCl	86.0
$Na_2SO_3 \cdot 7aq.$	92.5

The volumetric swelling at a course of adsorption was measured by change in the volume which was calculated from the buoyancy of specimen in benzene.

Before each of the experiments, the specimen was sufficiently conditioned, exposing in an atmosphere controlled at room temperature and 85.5 percent relative humidity for a month. The sample, pre-treated by 0.5 percent potassium hydroxyde, gave reproduciable data after the conditioning.

Results

The adsorption isotherms for the softwood hemicelluloses obtained in this study are shown in Figure 1. Figure 2 shows an example of the sorption isotherms for the softwood hemicelluloses in contrast with the adsorption isotherms for hardwood hemicelluloses and softwood. To represent the hysteresis effect for these materials the desorption ratio is plotted against the relative humidity in Figure 3. The volumetric swelling is plotted against the moisture content in Figure 4. Above 35 percent moisture content, for softwood hemicelluloses, the measurement was not made as the specimens became too soft to operate

To facilitate numerical comparison of the sorption behaviours among these materials, parameters of some of the theoretical equations were calculated from the isothems obtained by this and previous experiments.

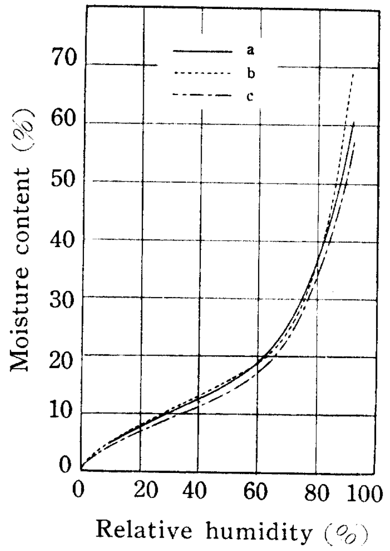

Fig. 1. Adsorption isotherms for softwood hemicelluloses at 20°C. (a, b, and c : see Table 2)

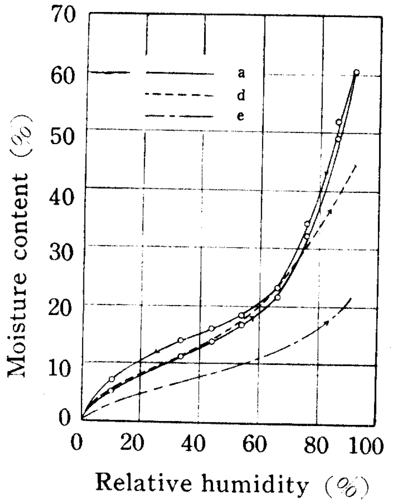

Fig. 2. Comparison of sorption isotherms among hemicelluloses and wood. (a, d, and e : see Table 2)

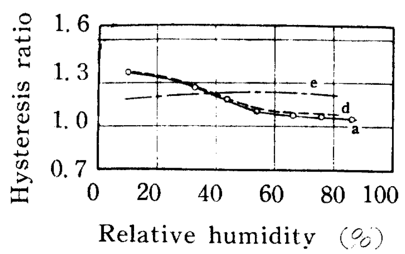

Fig. 3. Variation of hysteresis ratio, des./ads., with relative humidity. (a, d, and e : see Table 2)

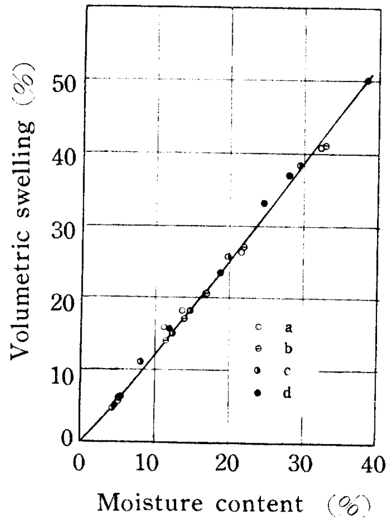

Fig. 4. Volumetric swelling of hemicelluloses.
(a, b, c, and d: see Table 2)

The equation used are as follows :

Area of sorptive surface. The adsorption isotherm is analyzed with the following equation,[2]

$$u = \frac{v_m c x}{1+cx} \cdot \frac{1-x^n}{1-x}, \qquad (1)$$

where u is the moisture content, x the relative vapour pressure, and c, v_m, and n are the parameters of the equation. Among the parameters, v_m and nv_m show the number of grams of adsorbed water per gram of sorbent on the primary and the total sorption sites, respectively. The area of sorptive surface is calculated from nv_m with use of the equation,

$$A = \frac{sN}{M} nv_m, \qquad (2)$$

where N is Avogadro number, s the projected area of one water molecule, and M the molecular weight of water.

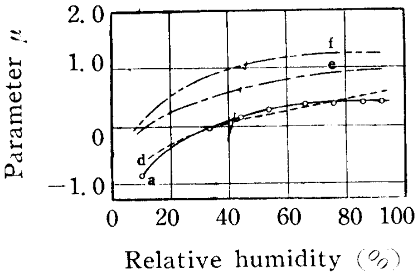

Fig. 5. Variation in parameter μ with relative humidity.
(a, d, e, and f : see Table 2)

Free-energy change. By PALMER and coworkers³⁾ the free-energy change from dry state to saturation, ΔF(cal /gram of sorbent), can be calculated from the adsorption isotherm with the equation,

$$\Delta F = \frac{-RT}{M}\int_0^1 \frac{x}{u}dx, \quad (3)$$

where R is the gas constant, T the absolute temperature, M the molecular weight of water, u the moisture content, and x the relative vapour pressure. From the equation the free-energy cange is given by the area below the curve u/x vs. x multiplied by $-RT/M$.

Interaction coefficient. In the view point that the sorption behaviour is treated as a solution phenomenon of the sorbate in a sorbent, SIMHA and ROWEN⁴·⁷⁾ have written the equation,

$$\ln p/p_0 = \ln v_1 + v_2 + \mu (v_2)^2, \quad (4)$$

where p/p_0 is the relative vapour pressure of sorbate, v_1 and v_2 the volume fraction of the sorbate and sorbent respectively, and μ the parameter of the equation. In this paper v_1 and v_2 are respectively given from the equation,

$$v_1 = 1 - v_2, \quad (5)$$

and

$$v_2 = \frac{1}{\rho u + 1}, \quad (6)$$

where u is the moisture content, and ρ the density of sorbent. The values of μ so obtained are plotted against the relative vapour pressure in Figure 5, and the limiting value of μ at saturation vapour pressure is determined by extrapolation.

The values calculated with the equations for the softwood hemicelluloses and others are given in Table 2.

Discussion

No reproduciable data were given for the softwood hemicelluloses prepared without pre-extraction with 0.5 percent potassium hydroxyde solution because of hornification of the specimen when redried after the conditioning. The hornification may be due to the hygrophilic uronic acid groups which are removed by the pre-treatment with a dilute alkali solution.

General shape of the sorption isotherm for the softwood hemicelluloses is such a typical sigmoid curve as those for other cellulosic materials. Among species of original wood only little difference in the isotherm is obserbed as shown in Figure 1. In Figure 2, the isotherm for softwood hemicelluloses

Table 2. Parameters of hygroscopicity. (at 20°C)

	Letter in figures	n	v_m	nv_m	A (cm^2/g)	ΔF (cal/g)	Limit-μ
Hemicelluloses							
Softwood							
Hinoki(*Chamaecyparis obtusa* S. et Z.)	a	6.7	10.4	69.7	18.7×10^6	14.3	0.44
Sugi(*Cryptomeria japonica* D. DON)	b	6.2	10.8	67.0	18.0	14.5	0.36
Akamatsu(*Pinus densiflora* S. et Z.)	c	6.8	9.7	66.0	17.8	13.9	0.47
Hardwood*							
Buna(*Fagus crenata* BLUME)	d	5.8	10.7	62.0	16.6	13.8	0.63
Shina(*Tilia japonica* SIMK.)		6.0	10.4	62.4	16.7	12.8	0.66
Makanba(*Betula maximowicziana* REGEL)		6.0	9.9	59.4	15.9	12.7	0.71
Wood							
Hinoki	e	4.1	6.8	27.2	7.3	7.3	1.01
Makanba		4.0	7.8	31.4	6.5	8.3	0.92
Buna		3.8	6.4	24.1	8.2	6.6	1.09
Cellulose							
Cotton	f	4.1	4.0	16.4	4.4		1.25
Regenerated		4.9	5.7	28.0	7.5	9.3	0.92

* The hardwood hemicelluloses samples used in previous experiments6) were also extracted with 5 percent potassium hydroxyside from the holocellulose without pre-treatment described here.

accords with that for hardwood hemicelluloses except at high relative humidities, where the isotherm shows an appreciable deviation to the higher moisture content. The fact indicates that the softwood hemicelluloses, even if prepared after the pre-treatment, are more hygrophilic than hardwood hemicelluloses prepared without the pre-treatment.

The differences between the two kinds of hemicelluloses are found in the following points, i.e., the softness of specimen described above, the area of sorptive surface, the free-energy change during adsorption, and the limiting. μ-value. On the hysteresis effect and the swelling behaviour, however, there is good agreement between both kinds of hemecelluloses as shown in Figures 3 and 4.

The area of sorptive surface of the softwood hemicelluloses is about 18×10^6 cm^2/g against about 16×10^6 cm^2/g for hardwood hemicelluloses. The difference depends on n-effect rather than v_m-effect. The value of the area are approximately 2.0 to 2.6 times of those for wood.

RUNKEL and LÜTHGENS5) suggested that the value of free-energy change is available as a measure for affinity of materials to adsorbate. They have determined the free-energy change during desorption from saturation, on the samples of delignified wood of beech and spruce, containing various contents of hemicelluloses. They have concluded that the hygroscopicity of hemicellulose is greater for softwood than for hardwood. The present results show that the free-energy change to saturation in hemicelluloses-water system is also greater for softwood than for hardwood. The difference in free-energy change, however, is somewhat less than that in the area of sorptive surface. Among hemicelluloses, cellulose, and wood, hemicelluloses are the highest in the free-energy change during adsorption of water vapour as in the case of the heat of wetting of these systems found by Christensen and Kelsey.[1] This is probably due to the difference in the area of sorptive surface among these materials.

Simha and Rowen[4,7] have proposed that the semi-empirical parameter, μ, of the equation (4) shows a characteristic of interaction of the system, and found that phase separation of the system is possible when the limiting value of μ exceeds 0.5. The limiting μ-values of hemicelluloses-water systems for softwood and for hardwood range from 0.36 to 0.71 though the former are slightly less than the latter. The both are approximate to the critical value (0.5) of complete solution. For wood and cellulose which are insoluble in water, the values exceed 0.9.

As mentioned above, the differences in the sorption behaviours between hemicelluloses from softwood and ones from hardwood are less evident than those between hemicelluloses and wood or cellulose. The slight differences in the sorption behaviours between the softwood hemicelluloses and hardwood hemicelluloses may be based on the content of hygrophilic uronic acid group. The softwood hemicelluloses contain greater amount of uronic acid group than hardwood hemicelluloses. The mol ratio of uronic acid unit/xylose unit is 0.20 to 0.26 in softwood hemicelluloses, and 0.06 to 0.08 in hardwood hemicelluloses. On the contrary, the difference between these hemicelluloses and wood or cellulose is affected by their structures and arrangement of the molecules, for example, crystallinity and combination with lignin.

Summary

The water sorption and the volumetric swelling are measured on the hemicellulose prepared from three species of softwood. The hysteresis ratio, the area of sorptive surface, the free-energy change during adsorption, and the interaction coefficient of the system calculated from the sorption isotherms are compared with those for hardwood hemicelluloses, cellulose, and wood.

Amomg species of the original wood only little difference in the sorption behaviours is observed. The softwood hemicelluloses take up slightly greater amount of water than hardwood hemicelluloses only at high relative humidities.

Except the hysteresis effect and swelling, the differences on the sorption behaviours between softwood-and hardwood-hemicelluloses are found. However these differences among the hemicelluloses are less evident than those among hemicelluloses, cellulose, and wood.

Literature cited

1) CHRISTENSEN, G. N. and K. E. KELSEY (1959) : Holz a. Roh- u. Werkst., **17**, 189.
2) KADITA, S. (1960: Wood Research (Kyoto Univ.), No. 23, 1.
3) PALMER, J. H., C. R. MERRILL, and M. BALANTYNE (1948) : J. Am. Chem. Soc., **70**, 570.
4) ROWEN, J. W. and R. SIMHA (1949) : J. Phys. Colloid. Chem:, **53**, 921.
5) RUNKEL, R. O. H. and M. LÜTHGENS (1956) : Holz a. Roh- u. Werkst., **14**, 424.
6) SADOH, T. (1961) : Sci. Rept. of Kyoto Pref. Univ., Agr., No. 13, 85.
7) SIMHA, R. and J. W. ROWEN (1949) : J. Am. Chem. Soc., **70**, 1663.

針葉樹ヘミセルロースの吸湿に関する研究

佐道 健

要 約 3種の針葉樹（ヒノキ，スギ，アカマツ）から抽出し，膜状に調整したヘミセルロースについて，20°C における吸湿，および膨潤の測定を行なつた．吸湿等温線から計算したヒステレシス比，吸着表面積，吸湿による自由エネルギーの変化，および系の相互作用係数（μ）について，広葉樹ヘミセルロース，セルロース，および木材で得られた値と比較した．

針葉樹ヘミセルロースの吸湿性は，原木の樹種による差がほとんどない．針葉樹ヘミセルロースと広葉樹ヘミセルロースを比較すると，前者の吸湿量はとくに高関係湿度において高い．しかし，このような吸湿挙動の差はヘミセルロースとセルロース，または木材との差に比較すると小さい．