

LOW TEMPERATURE INTERNAL FRICTION AND DYNAMIC MODULUS FOR BEACH WOOD¹

Erik J. Sellevold, Fariborz Radjy², Preben Hoffmeyer,
and Lars Bach³

Building Materials Laboratory, Technical University of Denmark,
2800 Lyngby, DENMARK

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ABSTRACT

The dynamic elastic modulus and the internal friction of beech wood beams conditioned to various equilibrium moisture contents have been measured in the temperature range from 25 C to -130 C. The response curves show a marked transition around -90 C for wood with moisture contents at or above the fibre saturation level. The transition is similar to those found for other microporous water-adsorbing materials such as hardened cement paste and porous glass. Decreasing moisture contents in the wood reduce the magnitude of the transition and shift the transition to higher temperatures. We believe the transition to be caused by a gradual solidification ("glass transition") of the adsorbed water.

Additional keywords: *Fagus silvatica*, dynamic elastic modulus, internal friction, temperature effects, moisture content, moisture effects.

INTRODUCTION

The dynamic mechanical response—elastic modulus (E) and internal friction ($\tan \delta$)—of microporous water-adsorbing materials at low temperatures promises to become a new and useful indicator of the pore structure and of the adsorbent-water interaction in such materials. Early work by Radjy (1968) and Radjy and Richards (1969) on hardened cement paste, the binder phase in concrete, demonstrated that two transitions are present in the dynamic mechanical response: 1) the "adsorbate" transition at about -92 C associated with the water adsorbed near the surface of the adsorbent, and 2) the "capillary" transition in the temperature range from 0 C to about -40 C associated with freezing (melting) of water in the larger pores.

Radjy showed that the adsorbate peak height increased with increasing internal

surface area for water-saturated hardened cement pastes, and that the removal of about one-half of the saturated water content did not change the adsorbate $\tan \delta$ peak. Further removal of water resulted in progressively smaller adsorbate peak heights. Since the water first removed is mostly capillary condensed water, Radjy concluded that the adsorbate transition is mainly associated with the water adsorbed near the solid surface.

The elastic modulus increase associated with the capillary transition is caused by a gradual ice-formation (melting) in the pores. The freezing temperature of pore water depends on the pore size (Dufay et al. 1966); the modulus (E)-temperature (T) curve for a saturated specimen is therefore related to the pore size distribution function.

Helmuth (1972) continued the work on hardened cement paste and concluded that the adsorbate transition is caused by a "glass transition" in the adsorbed water, a conclusion later supported by Radjy and Sellevold (1976), who also demonstrated that both the adsorbate and the capillary transitions are general phenomena, existing for such diverse water adsorbing microporous materials as bentonite clay, silica gel,

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²Now at: Geomat Consulting Engineers, Abbas Abad, Kh. Nilofar, K. Nastarin no. 70, Tehran, IRAN.

³Now at: MacMillan Bloedel Research Limited, 3350 East Broadway, Vancouver, B.C., CANADA.

porous Vycor glass, beech wood and possibly alumina (Radjy and Sellevold 1973). A low temperature transition has also been observed for birch wood by Bernier and Kline (1968) and for black cherry wood by Blankenhorn et al. (1972). The characteristics of the low temperature transition (-88 C to -48 C) for black cherry wood were investigated as a function of moisture content by Blankenhorn et al. (1973).

The present paper reports the low temperature dynamic mechanical response for beech wood, preconditioned to various equilibrium moisture contents and using specimens with two different grain orientations.

EXPERIMENTAL ASPECTS

Materials preparation

Two types of slender beech wood (*Fagus sylvatica*) beams were cut as shown in Fig. 1: "parallel to grain" about $4 \times 8 \times 180$ mm and "perpendicular to grain" about $6 \times 10 \times 160$ mm. The two types of beams were cut from different logs. The beams were machined in the "as received" condition—then placed in vacuum desiccators and dried at room temperature, first one week over silica gel, then two weeks over magnesium perchlorate dihydrate (vapor pressure 8×10^{-3} torr). Sets of two companion beams were then placed in vacuum over appropriate salt solutions for moisture conditioning before the test runs. A fully saturated state was obtained by submerging beams in water and then applying vacuum.

Testing procedure

The elastic modulus and the internal friction were measured according to the resonance method. The slender beams were subjected to transverse vibrations in the fundamental mode. E was calculated from the resonance frequency, and $\tan \delta$ from the width of the resonance curve (amplitude versus frequency) at a level of 70.7% of the maximum amplitude (the 3-db level). The beams were supported at their nodes on thin wires and located in a small plexiglass chamber to minimize moisture losses to the walls of the oven during cooling. Magnetic,

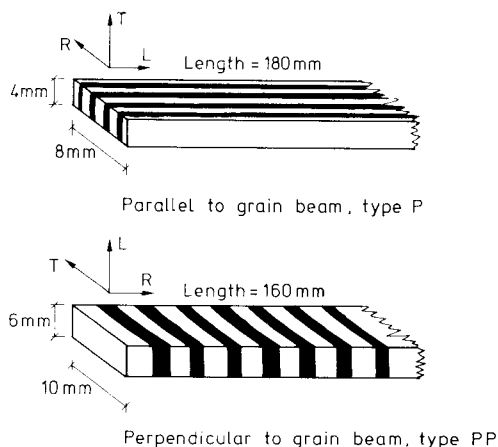


FIG. 1. The two types of beech wood beams.

nontouching transducers placed outside the plexiglass chamber were used to excite and detect the vibrations. The magnetic transducers were coupled to the wood beams via small metal discs, glued to the ends of the beams. The temperature (T) was measured by a platinum resistance thermometer located inside the plexiglass chamber. The entire assembly was supported in a sealed circular oven that could be cooled by the application of liquid nitrogen. Measurements reported here were performed during heating, obtained automatically, recorded digitally, and analyzed by computer.

Details of the experimental apparatus and procedures are given elsewhere (Sellevold and Radjy 1976). The minimum temperature was usually -130 C. The heating rate was set to 9 C/h, although in a few cases the nitrogen supply ran out, causing faster heating rates as shown in Table 1.

EXPERIMENTAL RESULTS

The room temperature adsorption isotherm data are given in Table 1 and plotted in Fig. 2. Table 1 identifies the parallel-to-grain beams with the prefix P in the beam number; the perpendicular-to-grain beams are given the prefix PP. Figures 3a, 3b, 4a, and 4b show the dynamic mechanical response on heating for the parallel- and perpendicular-to-grain specimens at differ-

TABLE I. *Experimental data for beech wood beams*

1) Beam no.	2) p/p _s	3) MC (g/g)	4) SG _t	5) Δ(MC) (g/g)	E(25°C) · 10 ⁻⁵ (kgf/cm ²)	E(-130°C) · 10 ⁻⁵ (kgf/cm ²)	tan δ (25°C)	tan δ max. (%)	6) T _p (°C)	7) $\left[\frac{dT}{dt} \right]_p$ (°C/hr)	8) f _r (25°C) (hz)
P1	0	0	0.77	+0.007	1.73	2.09	0.87	1.36	-36	7	530
P3	0.11	0.025	0.76	+0.003	1.83	2.25	0.78	1.46	-48	10	541
P5	0.23	0.041	0.76	+0.007	1.74	2.20	0.82	1.61	-58	22	537
P7	0.58	0.096	0.71	0	1.65	2.19	0.90	1.89	-83	15	530
P10	0.83	0.148	0.68	0	1.49	2.17	1.06	2.19	-93	20	528
P13	0.97	0.266	0.62	-0.016	1.30	2.07	1.15	2.86	-96	9	538
P3	0.97	0.263	0.61	-0.010	1.30	2.04	1.18	2.73	-97	9	543
P17	1.00	0.98	0.60	-0.069	1.26	2.51	1.29	2.70	-96	9	443
P13	1.00	0.96	0.60	-0.029	1.30	2.60	1.17	2.63	-95	8	449
PP3	0.23	0.038	0.60	+0.002	0.18	0.30	1.62	3.38	-60	9	427
PP3	0.97	0.269	0.52	-0.019	0.11	0.38	4.10	6.56	-96	9	293

1) P refers to parallel to grain beams; PP refers to perpendicular to grain beams.

2) Relative vapor pressure at which moisture conditioning took place at 25°C.

3) Moisture content; gram water per gram dry wood.

4) Specific Gravity at test = the dry beam weight divided by the beam volume at the start of a test.

5) MC before test minus MC after test.

6) Temperature of tan δ peak.

7) Heating rate at tan δ peak temperature.

8) Resonance frequency of beams at the start of a test.

ent equilibrium moisture contents. Experimental points are shown for tests only where they deviate significantly from the drawn lines.

According to Fig. 3b, melting is complete not at 0 C, but at about +3 C. This error is probably caused by the fact that the temperature probe is located a few millimeters away from the beam, and therefore does not measure the beam temperature during melting. The relative modulus change values are calculated as fractional changes relative to the initial room temperature elastic moduli E (25 C) listed in Table I. The calculation assumes that beam weight and dimensions are constant throughout the test.

Table I lists a number of other materials properties and test parameters; the adsorbate peak temperatures and heights are also plotted versus moisture content in Fig. 5. Figure 6 shows the E-moduli for both types of beams at room temperature and -130 C.

In order to obtain different equilibrium moisture contents in a short time, none of

the beams was conditioned and tested at all moisture content levels. However, Table I shows that at each of the two highest moisture contents (0.26 and 0.98) tests were made on two different beams. The results for the two beams in each set agreed very well. A companion beam to P10 was also tested at MC = 0.148, and the tan δ peak at -93 C reproduced that found for P10. The results are not reported since complete test data were not obtained with this beam because of apparatus breakdown.

Several beams were tested more than once. The results demonstrated excellent reproducibility. The response was also shown to be independent of the stress amplitude within the range of our apparatus.

The weight of the metal discs glued to the specimens (0.15 g each) was considered as evenly distributed along the length of the beams when calculating the E-moduli. Such a procedure introduces a small error, but a more elaborate procedure was not considered justified since the main concern of this work was relative, and not absolute, values for the E-modulus.

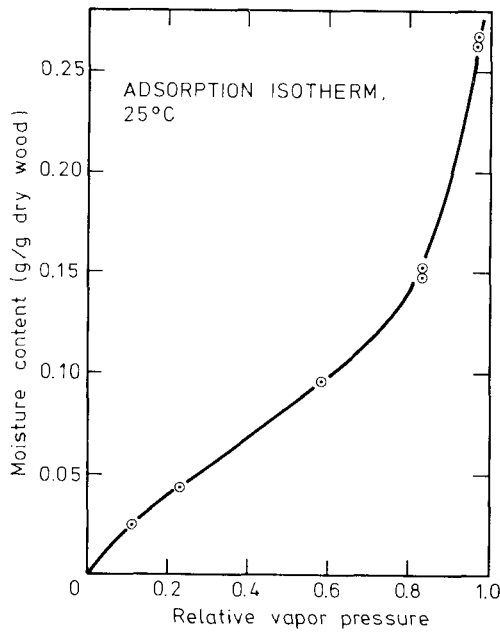


FIG. 2. Adsorption isotherm for beech wood beams.

DISCUSSION AND CONCLUSIONS

The experimental results at 25 C given in Table 1 and Fig. 6 are in general agreement with the observations of other investigators (Pentoney 1955). E (25 C) decreases with increasing moisture content up to fibre saturation, while $\tan \delta$ increases; E (25 C) for PP beams are about one order of magnitude smaller than for the P beams while the internal friction of the former is much larger. The two types of beams are not strictly comparable since the specific gravity at a given moisture content is considerably lower for the PP beams than for the P beams because of different spacings of the annual rings. E (25 C) displays a maximum value and $\tan \delta$ (25 C) a minimum value at a moisture content of about 0.03 g/g; this agrees with the results of Kollmann and Krech (1960) and is supposed to reflect the effect of water molecules bridging the gap between hydroxyl groups of neighbouring microfibrils.

Before discussing the two transitions, it is necessary to consider the influence of changes in specimen dimensions and weight

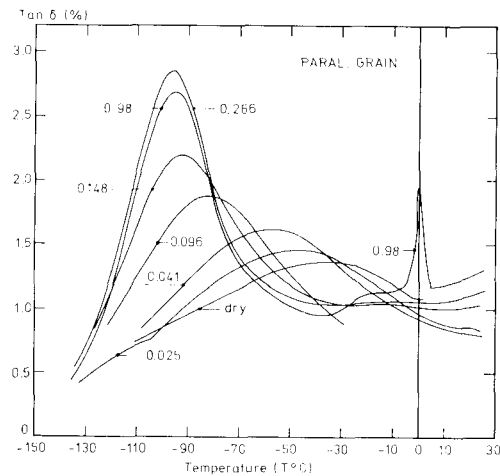


FIG. 3a. Internal friction response of parallel-to-grain (P) beams. Numbers give the moisture contents in units of g/g dry wood.

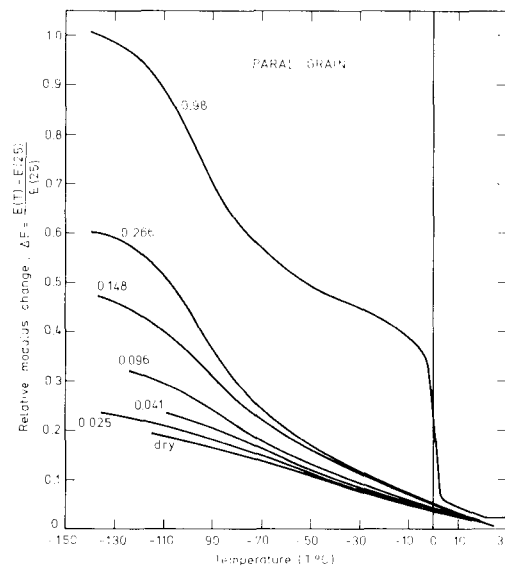


FIG. 3b. Relative modulus change of parallel-to-grain (P) beams. Numbers give the moisture content in units of g/g dry wood.

during a test. Any changes in those quantities are recorded as changes in the E -modulus since we measure only the resonance frequencies of the beams as a function of temperature, and then calculate the E -modulus using the formula:

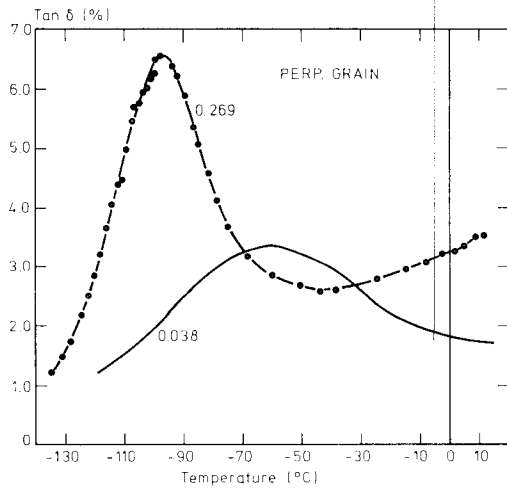


FIG. 4a. Internal friction response of perpendicular-to-grain (PP) beams. Numbers give the moisture content in units of g/g dry wood.

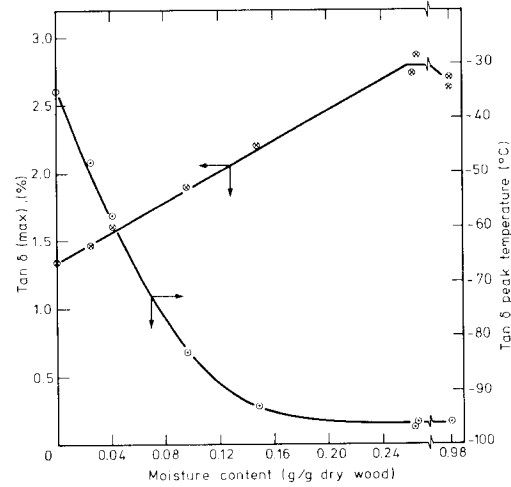


FIG. 5. Tan δ peak height and temperature at different moisture contents for parallel-to-grain (P) beams.

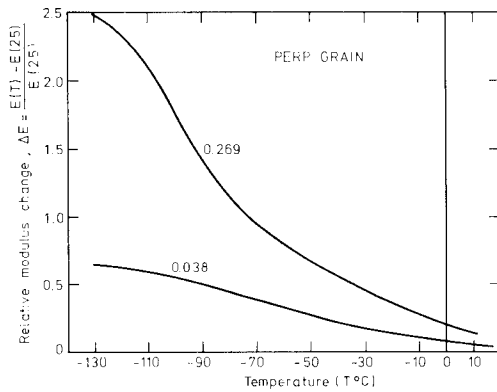


FIG. 4b. Relative modulus change of perpendicular-to-grain (PP) beams. Numbers give the moisture content in units of g/g dry wood.

$$E = (0.9655 \times 10^{-6}) (W) (f_r^2) \left(\frac{L^3}{bh^3} \right) \quad (1)$$

where W = beam weight in grams
 f_r = resonance frequency in hz
 L = beam length in cm
 b = beam width in cm
 h = beam thickness in cm
 E = elastic modulus kgf/cm²

Table 1 shows that the moisture change during a test is small except for the fully saturated beams. We therefore assume that W is a constant for a given test. However,

any radial or tangential shrinkage-swelling can have important influences. For example, a 2% shrinkage in the tangential direction, affecting the thickness h , of the P-beams is, according to Eq. 1, recorded as an increase of about 6% in the E-modulus. Kübler (1962) has demonstrated that cooling of wood specimens below 0 C

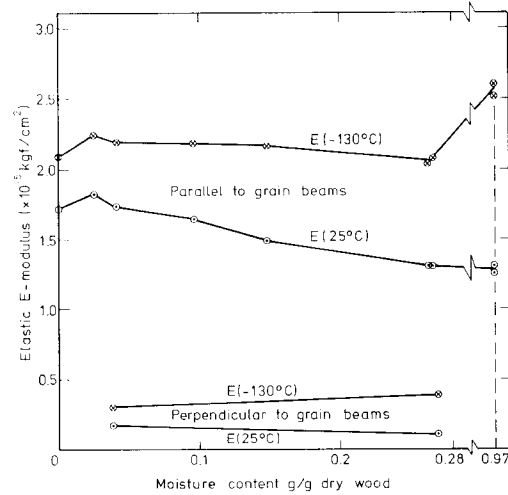


FIG. 6. E-moduli at +25 C and -130 C at different moisture contents for the two beam types.

can result in pronounced shrinkage, a phenomenon referred to by him as "coldness-shrinkage." We will consider this point later.

The capillary transition temperature range

The only beam displaying a capillary transition is the fully saturated one, Fig. 3b. The large modulus change for this beam near 0 C is clear evidence that ice has formed in the cell lumens. Moisture contents at or below the fibre saturation point do not produce a capillary transition. This observation implies that if ice forms, it is in such locations that the ice does not contribute to the stiffness of the beams. This appears quite likely when one considers the pore structure of wood; at the fibre saturation point the cell lumens are empty and here ice can nucleate and grow without space restrictions. As the temperature is lowered, the growth is fed by desorption of interfibrillar adsorbed water from the cell walls. The desorption process leads to a lower moisture content in the cell walls, and thereby to an increase in the E-modulus since E (25 C) increases with decreasing moisture content, Fig. 6. The desorption process will also lead to coldness-shrinkage, and therefore, according to Eq. 1, further increase the calculated E-modulus. Before discussing this point further, we will consider the amount of freezable water in wood.

Experimental values of entropy and enthalpy for water adsorbed at high relative vapor pressures in wood (Skaar 1972) are close to the values for bulk water. Assuming the entropy of adsorbed water to be equal to that of bulk water, the freezing temperature of water adsorbed at a given relative vapor pressure can be predicted (Sellevoid and Radjy 1976). At -20 C, for instance, all the water adsorbed above a relative vapor pressure of 0.85 can freeze, which, according to Fig. 2, corresponds to about 0.1 gram of ice per gram of dry wood for the fibre-saturated beams. Ice formation therefore probably takes place, but not necessarily the amounts predicted because of, for example, kinetic factors.

Consider the results in Fig. 3b. At -50 C

the fibre-saturated beam has increased its E-modulus by about 17%, while the increase for the dry beam is about 11%—a difference of 6%. This 6% "excess" E-modulus increase for the fibre-saturated beam is presumably caused by desorption to the ice phase as discussed above. The beam with a moisture content of 14.8% also shows substantial "excess" E-modulus increase while the effect is small for lower initial moisture contents. This observation agrees with predicted freezing considerations; for instance, a moisture content of 9.6% was obtained by conditioning at $p/p_s = 0.58$ and the predicted freezing point for this water is lower than -50 C. Therefore we expect no ice formation at -50 C for this beam, and therefore no "coldness-shrinkage." The fact that E (-50 C) is higher for the beam with moisture content of 9.6% than for the dry one (Fig. 3b) may therefore mean that the temperature coefficient of the E-modulus is higher for moist wood than for dry.

It is of interest to make a numerical estimate of E-modulus increase for the fibre-saturated beam based on the coldness-shrinkage data of Kübler (1962). He found a maximum equilibrium shrinkage in the tangential direction of about 2.5% for beech wood with 56% moisture content. This value was reached at -45 C, and little additional shrinkage took place between -45 C and -60 C. According to Eq. 1, a 2.5% decrease in the thickness h corresponds to about an 8% increase in E. Assuming the shrinkage in the radial direction to be one-half of that in the tangential, the shrinkage in the width b increases E by about 1%. The total expected ΔE value is thus about 9%. In addition, the desorption from the cell wall would further increase E (25 C) according to Fig. 6, and therefore also E (-50 C). We observe only a 6% excess E-modulus increase for the fibre-saturated beam at -50 C. We therefore believe that Kübler's shrinkage value of 2.5% is greater than that realized in our experiments.

It follows that the amount of ice formation also is smaller than that predicted from thermodynamic considerations. Our con-

clusion, based on experimental data under nonequilibrium conditions, is not inconsistent with Kübler's results, since he found that coldness-shrinkage values were both a function of cooling rates and initial moisture contents. We conclude that the E-modulus response of the wood beams in the temperature range down to -50°C is in qualitative agreement with the desorption-to-the-ice-phase mechanism, but that a quantitative check requires that coldness-shrinkage measurements are performed under the same conditions as the resonance frequency measurements.

The adsorbate transition

Figures 3a, 3b, 4a, 4b and 5 show that both specimen types undergo a marked adsorbate transition. The transition strength is a strong function of moisture content and grain orientation, while the $\tan \delta$ peak temperature is a function of moisture content only. The transition characteristics as a function of moisture content are different from those observed for hardened cement paste or porous Vycor glass. The two latter materials have an adsorbate transition that decreases in strength and shifts to lower temperatures with decreasing moisture content until the transition essentially disappears for a dry specimen. The adsorbate transition strength also decreases for wood with decreasing moisture content, but the peak temperature increases and a dry specimen displays a significant $\tan \delta$ peak. Note that the moisture contents given in the figures are nominal; as already discussed, the actual moisture contents in the cell walls of the beams with high nominal moisture contents are smaller at low temperatures.

The main features of our results agree with those found for cherry wood by Blankenhorn et al. (1973). In the 0 to 6% moisture content range, however, Blankenhorn et al. found the $\tan \delta$ peak temperature to be independent of moisture content, while we (Figs. 3a and 5) found the peak temperature to decrease in the same range. We offer no explanation for this difference, but note that it is not caused by the variation in heating rates (Table 1), since the effect

of an increased heating rate is to shift the $\tan \delta$ peak to higher temperatures.

Bernier and Kline (1968) observed a $\tan \delta$ peak centered around -13°C for dry birch wood and suggested that the peak is "associated with rather small molecular segments undergoing motion or hindered rearrangement under the applied stress."

The dynamic mechanical response of wood at very high moisture contents is similar to that of hardened cement paste; the large difference in moisture content between fibre saturation and full saturation has only a small influence on the $\tan \delta$ peak—indicating that the ice in the cell lumens plays only a small part in the adsorbate transition.

By analogy to the results for porous Vycor glass and hardened cement paste, we believe the adsorbate transition for fibre-saturated wood to be caused mainly by a gradual solidification ("glass transition") of the adsorbed water. Kimura et al. (1972) studied the Broad-Line NMR of linter cellulose containing 24.2% water and inferred from their results that "the proton movement of adsorbed water changes markedly over the approximate range 180–200 K." This temperature range corresponds to the position of the adsorbate transition—it therefore seems extremely likely that the two experimental phenomena are different manifestations of the same physical process.

In our view then, the low temperature transition in the dynamic mechanical response of wood is caused by two related mechanisms: At high moisture contents the "glass transition" in the adsorbate dominates; at low moisture contents a mechanism associated with the adsorbent structure plays the larger role.

Bernier and Kline (1968) also observed a low temperature transition for birch wood with 6% moisture content, and suggested it was "associated with the hydrogen bonding of water molecules to the cellulose structure." On the basis of our experience with other microporous watersorbing materials (Radjy and Sellevold 1973), we conclude that the characteristics of the adsorbate

transition depend on the nature of the adsorbate-adsorbent interaction.

The adsorbate transition temperatures are the same for P and PP beams, but the strength of the transition is much greater for the latter (Figs. 3 and 4). We believe that this behavior supports our view that the "glass transition" of the adsorbate takes place *in situ* in the cell walls for the following reason: Using a rough analogy, one can view a P beam as a two component composite beam of adsorbate and adsorbent where the two components are in parallel, while in a PP beam the two components are in series. It is easy to demonstrate that when the adsorbate component changes from a very soft state (at temperatures above the "glass transition") to a rigid state (below the "glass transition"), the per cent increase in the E-modulus of the composite is much greater for the series model (PP beams) than for the parallel model (P beams).

In conclusion we want to emphasize that the two low temperature transitions reported here are not peculiar to wood, but exist for all the microporous water-adsorbing materials that have been tested. Furthermore, unpublished results obtained in our Laboratory show that the transitions also exist for other adsorbates (cyclohexane and benzene).

We believe that the general nature of these phenomena greatly enhances the potential of the internal friction technique as a tool to investigate adsorbate-adsorbent interactions in porous materials.

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