

RATE OF SWELLING OF VACUUM-IMPREGNATED WOOD

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(Received April 1995)

ABSTRACT

The swelling rate of wood wafers vacuum-impregnated with water and other swelling agents was measured by a videotaping technique. After an initial period of inhibited swelling, the rate of swelling could be described quantitatively by a simple membrane Fickian diffusion model for solvent penetration into the wood cell walls. Diffuse porous aspen swelled more slowly than red pine as a result of differences in initial distribution of solution in the wood tissue. In red pine, swelling rate increased with increasing degree of saturation of the wood void space, while in aspen the swelling rate was not related to solution absorption. Wood relative density did not affect swelling rate significantly over the range of densities tested. Increased solution temperature had the expected effect of increased swelling rate. The estimated activation energy for bound water diffusion inducing swelling depended on the direction of swelling and the treating solution and ranged from 26.4 to 41.6 kJ/mole. Treatment with 8% monoammonium phosphate (MAP) resulted in slower swelling rates compared to water and 10% polyethylene glycol (PEG) treated wafers under most conditions. The organic swelling solvents dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) initially swelled wood much more slowly than water.

Keywords: Swelling, diffusion, bound water, monoammonium phosphate (MAP), polyethylene glycol (PEG-1000), red pine (*Pinus resinosa* Ait.), trembling aspen (*Populus tremuloides* Michx.), temperature, activation energy, dimethylsulfoxide (DMSO), dimethyl formamide (DMF).

INTRODUCTION

When wood below fiber saturation point (FSP) moisture content is impregnated with waterborne chemicals or other swelling solvents, it swells rapidly as solvent penetrates the unsaturated cell walls. This effect can be used to help our understanding of how solvents and dissolved solutes interact with the wood cell wall/bound water matrix following pressure impregnation. For example, if it is assumed that the amount of swelling is equal to the volume of solvent that has entered the cell wall, diffusion of solvent into the cell wall can be monitored by the rate of swelling. Also, chemicals in solution impregnated into wood will presumably follow the same pathways as the sorbed solvent in penetrating the cell wall. Thus, the rate of swelling gives a relative measure of the rate at which solutes distribute

themselves in the cell-wall matrix following impregnation. This provides information about the likelihood that wood-protecting chemicals are able to completely saturate the wood cell walls to protect against organisms like soft rot fungi (e.g., Dickinson 1974).

By using published values for the bound water diffusion coefficient of water in wood substance, the average distance that solvents and solutes must diffuse to saturate the wood cell-wall matrix, the "effective average diffusion path length" in a given treated block can be estimated from the rate of swelling (Cooper and Churma 1990). The rate of swelling and the effective diffusion path length are related to the wood species anatomy and the resulting distribution of treating solution in the block. Within a wood species, the cell-wall thickness (wood density) and the percent of void space

saturated are also expected to affect the swelling rate.

Most other studies on the rate of swelling of wood involve immersion of large blocks in water or other solvent at atmospheric pressure. The rate of swelling depends on simultaneous penetration into the void structure and diffusion in the cell wall and is relatively slow (e.g., Hittmeier 1967; Rosen 1973; Simpson 1974). Diffusion coefficients calculated from these studies overestimate bound water coefficients because of the combined effects. Also, in some of these studies (e.g., Hittmeier 1967), small specimens are used with relatively large proportions of cut walls. There is evidence that cut cell walls are more permeable to diffusants than the undisturbed cell lumen (Tarkow and Southerland 1964), and the results of such studies could be misleading when applied to movement of materials from treated lumens into the cell-wall matrix.

In this study, rates of swelling of wood, vacuum-treated with water, wood-treating solutions, or other solvents are used to investigate the factors affecting diffusion of water and other swelling solvents from the impregnated void space into the surrounding wood cell walls.

MATERIALS AND METHODS

Swelling rate measurements were made on 25- × 25- × 10-mm along-the-grain sapwood wafers cut in a true radial/tangential orientation to allow measurement of dimensional change in either the radial or tangential direction (Fig. 1). Most swelling measurements were made on samples of red pine (*Pinus resinosa* Ait.) cut from the sapwood of a single new pole section and trembling aspen (*Populus tremuloides* Michx.) from the sapwood of a single tree. The rates of growth were similar in all samples (about 3 rings per cm). Swelling measurements were made with water, 10% polyethylene glycol (PEG-1000), and 8% monoammonium phosphate (MAP) at approximately 4°C, room temperature (about 22°C), and 42°C. Additional evaluations were made at room temperature using the nonaqueous swelling agents dimethylformamide (DMF) and di-

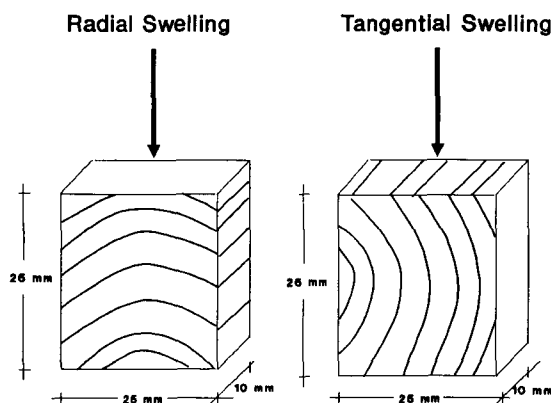


FIG. 1. Sample size and orientation for linear swelling measurements.

methylsulfoxide (DMSO). In most cases, four matched replications were evaluated for each species, direction of measurement, temperature, and treating liquid evaluated.

In addition, room temperature water swelling measurements were made on samples of red pine and aspen from a variety of sources and treated at a range of pressure differentials to provide a data base for evaluating the effect of relative density and fraction of void space saturated on average effective diffusion path length (L_e). For each species, 30 specimens were evaluated in each of the radial and tangential directions.

Each sample, at initial moisture content (u_i) of 5–10% was mounted in a reservoir in a vacuum chamber fitted with a dial gauge extensometer (Cooper and Churma 1990) and a vacuum (24 in. Hg or 21 KPa absolute pressure for the main study and variable vacuums for the additional study) drawn with a vacuum pump for 20 min. The treating solution was drawn into the reservoir until the specimen was submerged. When the vacuum was released, water penetrated the wafer resulting in rapid swelling. To allow precise recording of swelling over the short swelling period, the extensometer and a running stopwatch were videotaped, and the videotape was reviewed frame-by-frame (30 frames per second) to give cumulative swelling (± 0.0025 mm) and elapsed time (± 0.01 sec) simultaneously. The

samples were left submerged in the treating solution for 48 h, and the change in dimension in the direction of interest was measured to provide the equilibrium total swelling value.

For low temperature evaluation, the apparatus and treatment solution were immersed in an ice water bath for the tests. For high temperature evaluation, all tests were conducted in a dry kiln operating at $42^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The actual solution temperature was measured ($\pm 0.1^{\circ}\text{C}$) for each experiment. The Arrhenius temperature dependence relationship $D = D_0 \exp(-Q/RT)$ was applied to cell-wall diffusion coefficients (D in cm^2/s) for water, MAP and PEG treatments, estimated as described below. In this equation, D_0 is the pre-exponential factor, Q is the activation energy (kJ/mole), R is the gas constant ($8.314 \times 10^{-3} \text{ kJ} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$), and T the absolute temperature ($^{\circ}\text{K}$). $\ln D$ values were plotted vs. $1/T$, and the activation energies (Q) were estimated from the slope of the best linear fit of the plots.

For short times, the relationship between diffusion coefficient (D) and the half membrane thickness L_e is (Crank 1956):

$$D = \pi L_e^2 E^2 / 4t \quad (1)$$

where $E = m_t/m_e$ the ratio of the amount of water adsorbed in the cell wall at time t (m_t) to the equilibrium amount of moisture sorbed (m_e). If we assume that the volume adsorbed in the cell wall is equivalent to the amount of swelling, i.e., ignore sorption compression or cell-wall microvoid effects (Weatherwax and Tarkow 1968) and assume no change in the cell lumen volume, E corresponds to the fraction of total swelling that has occurred at time t .

Thus, a plot of E^2 vs. t should be linear with a slope of $4D/\pi L_e^2$ for $E < 0.5$. For samples tested at room temperature, L_e values were estimated using Stamm's (1960a) values of bound water diffusion coefficients for softwoods and hardwoods at 25.5°C corrected to the actual test temperature based on Stamm's (1960b) estimates of temperature dependence. The assumed bound water diffusion coefficients averaged: $D = 12.6 \times 10^{-8}$ and $11.6 \times 10^{-8} \text{ cm}^2/\text{s}$ for radial and tangential diffusion,

respectively, in red pine and $D = 12.8 \times 10^{-8}$ and $9.9 \times 10^{-8} \text{ cm}^2/\text{s}$ for radial and tangential diffusion, respectively, in aspen. It has been shown that the bound water diffusion coefficient depends on the moisture content (e.g., Simpson 1974) so D represents an "integral" diffusion coefficient over the changing cell-wall moisture content during water sorption.

The basic relative density (G_{FSP}) of each specimen was determined from the green volume and dry mass (m_0 in g) of each specimen. The volume (V_s in ml) of solution or solvent absorbed was determined from the mass absorbed and the solution or solvent density at the test temperature (by hydrometer). The percentage of total void space saturated by treatment (F_{VL}) was estimated assuming that the relative density of dry wood substance is 1.53, the fractional fiber saturation point of both species is 0.35, and the relative density of adsorbed water in the cell wall is 1.0 as follows (Siau 1971):

The porosity (V_{ai}) in the test sample at fiber saturation point moisture content is:

$$\begin{aligned} V_{\text{ai}} &= 1 - G_{\text{FSP}}[1/1.53 + 0.35] = \\ &= 1 - 1.004G_{\text{FSP}} \end{aligned} \quad (2)$$

After treatment, the porosity of the wood is:

$$V_{\text{af}} = 1 - G_{\text{FSP}}[0.654 + V_s/m_0] \quad (3)$$

The percentage of void space saturated with water is $F_{\text{VL}} = 100[V_{\text{ai}} - V_{\text{af}}]/V_{\text{ai}}$. The L_e values are expected to be affected by F_{VL} , cell-wall thickness (relative density) and direction of diffusion; thus a multilinear regression analysis was run on the variables to allow prediction of L_e for a given degree of saturation and specific gravity for each orientation of the test specimen.

For other than room temperature conditions and for treating fluids other than water, the expected L_e values were predicted from the above regression, based on the uptake of solvent or solution. Equation (1) was then used to estimate the diffusion coefficient. In all cases, the half swelling time was also determined by extrapolating the linear portion of the E^2 vs. t

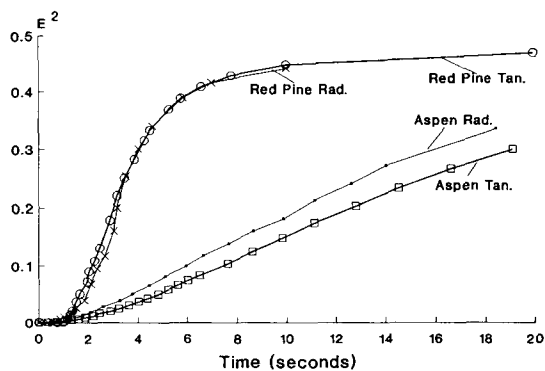


FIG. 2. Comparison of swelling curves for red pine and aspen—water at 22°C.

curve to $E^2 = 0.25$ as a basis of comparison for the different treatments and conditions.

RESULTS AND DISCUSSION

General

The plots of E^2 vs. t are initially concave upwards, then linear to at least $E = 0.5$ ($E^2 = 0.25$ —Figs. 2 to 7). This initial nonlinearity is non-Fickian behavior that can be attributed to restrained swelling (Stamm 1960a), and possibly, to a measurable time delay in swelling as the solution penetrates the accessible void space through the end grain of the samples. The restraint results from the inability of the solvent, as it initially penetrates the S_3 cell-wall layer, to cause the still dry interior S_2 cell layer to swell outwards.

Effect of species

Red pine wafers swelled much faster than aspen (Fig. 2) with half swelling times at room temperature of 4–5 seconds compared to 15–20 seconds for aspen. This shows that the diffusion distances are shorter in the softwood even though the percentage of the void space impregnated (F_{VL}) is similar for the two species. This results from the more uniform initial distribution of solvent in the pine tracheids. Generally 80–90% of the void space is saturated with treating fluid including the longitudinal tracheids and ray tissue. Aspen is

mainly penetrated through the vessels (Stone and Green 1958) leaving larger expanses of untreated fiber and parenchyma tissue between the treated vessels and consequently longer diffusion distances.

These swelling rates correspond to estimated average effective diffusion path lengths (L_e) of 10 to 20 μm for red pine. This is more than double the average cell-wall thickness in red pine and likely results from the incomplete saturation of the void space and the fact that the cell wall is not represented perfectly by a plane membrane. As the solvent diffuses into the secondary cell wall from the lumen side, the diffusion area increases rather than remaining constant as with a simple membrane.

The aspen samples have correspondingly longer diffusion path lengths (20 to 30 μm). This is actually shorter than the average half distance between adjacent vessels suggesting that some impregnation of other tissue, such as rays, occurs.

Supplementary study—Prediction of L_e values from specific gravity and degree of saturation (30 replications per species and direction)

There was no statistically significant correlation between the diffusion path length (L_e) and wood relative density for either species. This probably resulted from the low variability in the G_{FSF} values for the samples selected for this study (Table 1) and does not disprove the hypothesis that higher density woods have higher L_e values. For example, Cooper and Churma (1990) found that denser southern pine had significantly longer L_e values than red pine despite their similar anatomical structures and degrees of saturation.

For red pine, plots of L_e vs. F_{VL} showed an exponential increase in L_e with decreasing percentage of total void space treated. The simplified regression equations giving the best fit of the data were:

For radial swelling:

$$\log L_e = 2.78 - 0.825 \log F_{VL}$$

($r^2 = 0.37$, significant at the 0.05 level)

TABLE 1. Effect of F_{VL} on the rates of swelling of red pine and aspen samples. Water at 22C—30 replications per species and direction (standard deviations in brackets).

Species	Direction	E^2/t	$t_{1/2}$ (s)	G_{FSP}	F_{VL} (%)	$D \times 10^8$ (cm^2/s)*	L_e (μm)
Red Pine	Radial	0.058 (0.036)	15.2 (16.1)	0.381 (0.043)	77.9 (24.5)	12.6	23.3 (18.2)
Red Pine	Tangential	0.105 (0.060)	10.3 (11.5)	0.387 (0.009)	78.8 (23.5)	11.6	18.4 (19.1)
Aspen	Radial	0.020 (0.010)	17.4 (6.33)	0.355 (0.010)	73.3 (14.4)	12.8	30.6 (6.85)
Aspen	Tangential	0.020 (0.006)	17.6 (4.51)	0.353 (0.004)	74.5 (12.2)	9.9	26.0 (3.7)

* Based on Stamm (1960a) values corrected to the actual test temperature.

or:

$$L_e (\mu m) = 605F_{VL}^{-0.825} \quad (4)$$

and for tangential swelling:

$$\log L_e = 3.20 - 1,103 \log F_{VL}$$

($r^2 = 0.87$, significant at the 0.001 level)

or:

$$L_e (\mu m) = 1,596F_{VL}^{-1.103} \quad (5)$$

For combined radial and tangential swelling, the best fit relationship was:

$$L_e (\mu m) = 1,036F_{VL}^{-0.98}$$

($r^2 = 0.57$, significant at the 0.001 level)

(6)

An increased level of saturation by the treating solution (higher F_{VL}) results in a lower estimated diffusion path length and the exponent is close to 1.0, indicating that the diffusion path length varies approximately inversely with the percentage of void space impregnated.

For aspen, there was no statistically significant relationship between the estimated diffusion path length and the percentage of void volume impregnated. Since aspen treats primarily through the large vessel elements, the level of treatment could not be affected significantly by lowering the vacuum differential during treatment and the rate of swelling was more or less independent of level of treatment. The average L_e values for aspen based on the 30 samples were 30.6 μm in the radial direction and 26 μm in the tangential direction.

For both species, the L_e values were higher for the radial direction than for the tangential direction, which is surprising, as rays are expected to facilitate radial bound water diffusion.

Effect of swelling direction

For red pine, the total swelling (S) from the test moisture content (6–10%) to saturation was 4–5% in the radial direction compared to 6–7% tangentially and the radial/tangential ratio about 1.4. Despite the smaller swelling changes in the radial direction, the relative swelling rates (characterized by the E^2/t values in Tables 1–4) were generally lower for radial than tangential swelling, showing that the wood swelled much faster in the tangential direction. This may be attributed to swelling restraint by the rays. However, the fact that the estimated diffusion path lengths were longer in the radial direction as discussed above results in the estimated diffusion coefficients being higher in the radial direction.

In aspen, there is much higher swelling anisotropy with a ratio of total tangential to total radial swelling of about 2.1. Possibly as a result of this, the relative swelling rates (E^2/t) were higher in the radial direction for this species. While the estimated L_e values were higher in the radial direction in the 30 sample study, the estimated L_e values in the radial and tangential directions for the 4 matched samples in Table 2 were similar (26.3 and 26.8 μm respectively), these latter values were used for the calcula-

TABLE 2. Summary of rate of swelling results for red pine and aspen samples vacuum treated with water. Each mean based on 4 replications (standard deviations in brackets).

Species	Temp. °C	Dir.	u_i	V_s/M_0	G_{FSP}	S (%)	E^2/t	$t_{1/2}$ s	F_{VL} %	L_c (μm)	$D \times 10^8$ (cm^2/s)
Red pine	4	Rad	0.091 (.005)	1.74 (.078)	0.385 (.007)	4.65 (0.31)	0.044 (.005)	7.32 (1.07)	87.4 (4.63)	15.18 (0.66)	7.93 (0.96)
Red pine	4	Tan	0.083 (.004)	1.74 (.037)	0.389 (.002)	6.58 (0.70)	0.063 (.008)	5.86 (0.73)	88.87 (3.04)	11.45 (0.45)	6.48 (0.64)
Aspen	4	Rad	0.105 (.007)	1.86 (.177)	0.344 (.004)	3.60 (0.33)	0.0092 (.001)	30.54 (3.90)	79.1 (8.10)	26.3	5.02 (0.48)
Aspen	4	Tan	0.129 (.037)	1.86 (.156)	0.347 (.005)	7.77 (0.86)	0.0075 (.002)	39.31 (10.7)	80.37 (6.75)	26.8	4.23 (1.30)
Red pine	22	Rad	0.086 (.003)	1.55 (0.11)	0.392 (.009)	4.81 (0.63)	0.084 (.037)	4.97 (2.55)	77.8 (8.68)	18.0 (1.68)	14.0*
Red pine	22	Tan	0.091 (.002)	1.66 (0.02)	0.394 (.004)	6.22 (0.60)	0.138 (.034)	3.34 (0.44)	85.1 (1.51)	12.0 (0.23)	10.5*
Aspen	22	Rad	0.080 (.007)	1.65 (0.22)	0.360 (.011)	3.33 (0.49)	0.0277 (.012)	12.75 (5.76)	72.8 (9.96)	26.3	12.6 (0.30)
Aspen	22	Tan	0.073 (.005)	1.91 (0.06)	0.353 (.003)	7.95 (0.85)	0.0178 (.0026)	16.41 (2.57)	85.1 (3.34)	26.8	9.83 (0.22)
Red pine	41	Rad	0.084 (.007)	1.66 (0.03)	0.389 (.006)	4.42 (0.40)	0.303 (.056)	1.27 (0.20)	83.73 (0.96)	15.7 (0.15)	58.4 (10.7)
Red pine	42	Tan	0.085 (.007)	1.63 (0.10)	0.386 (.009)	6.59 (0.60)	0.255 (.033)	1.50 (0.19)	80.37 (5.53)	12.9 (1.04)	33.2 (6.07)
Aspen	41	Rad	0.089 (.007)	1.85 (0.06)	0.342 (.003)	3.91 (0.38)	0.0731 (.020)	4.08 (0.72)	77.93 (2.80)	26.3	39.7 (10.8)
Aspen	42	Tan	0.094 (.008)	1.94 (0.12)	0.340 (.002)	8.43 (0.88)	0.0500 (.014)	6.03 (1.42)	82.2 (6.95)	26.8	28.2 (7.92)

* Stamm's (1960a) values corrected for temperature.

tions of temperature and solute effects discussed below, since these samples were matched.

Effects of solutes

Wafers treated with PEG-1000 solutions swelled at similar rates to matched water-treated wafers except for the low temperature-treated aspen where the rate of swelling of the PEG-treated samples was lower (Tables 2 and 3). Samples treated with the 8% MAP solution generally swelled more slowly than samples treated with water (Figs. 3 and 4). This results in lower average diffusion coefficients for water leaving the MAP solutions (Tables 2 and 4).

These effects may be explained by an osmotic effect; as water is adsorbed into the cell wall, the concentration of solute in the lumens increases, increasing the chemical potential of

the solution and resisting the loss of water to the cell wall. The greater effect for MAP could result from the observed exclusion of phosphates from the cell walls (Cooper and Roy 1994), which would not allow the chemical potential increase to be relieved by diffusion of solute into the cell wall. Alternatively, the higher viscosities of the solutions may slow down the absorption of solution into the void space, retarding the swelling rate.

Effect of temperature

For matched specimens evaluated at other temperatures, it was assumed for red pine that for equivalent relative solution absorption, the effective flow path lengths would be similar to those evaluated at room temperature. To normalize the data to take into account variable solution absorptions, Eqs. (4) and (5) were used

TABLE 3. Summary of rate of swelling results for red pine and aspen samples vacuum treated with 10% PEG-1000. Each mean based on 4 replications (standard deviations in brackets).

Species	Temp. °C	Dir.	u_i	V_s/M_0	G_{FSP}	S (%)	E^2/t	$t_{1/2}$ s	F_{VL} %	L_e (μm)	$D \times 10^8$ (cm^2/s)
Red pine	4	Rad	0.088 (.002)	1.61 (.06)	0.382 (.004)	4.94 (0.35)	0.043 (.016)	8.72 (2.96)	77.9 (4.42)	16.68 (7.26)	9.27 (2.62)
Red pine	4	Tan	0.086 (.003)	1.73 (.033)	0.388 (.004)	6.18 (0.35)	0.057 (.008)	6.33 (0.72)	87.4 (2.58)	11.66 (0.38)	6.07 (1.02)
Aspen	4	Rad	0.104 (.009)	1.76 (.10)	0.351 (.006)	3.61 (0.63)	0.0073 (.001)	39.69 (6.13)	76.2 (7.11)	26.3	2.98 (1.85)
Aspen	4	Tan	0.104 (.007)	1.80 (.14)	0.347 (.003)	7.84 (0.82)	0.0048 (.0013)	61.28 (14.2)	77.2 (6.78)	26.8	2.70 (0.72)
Red pine	21	Rad	0.091 (.001)	1.60 (0.03)	0.393 (.003)	4.39 (0.35)	0.104 (.033)	4.42 (0.78)	80.70 (1.85)	12.0 (6.93)	15.7 (10.6)
Red pine	21	Tan	0.088 (.005)	1.61 (0.03)	0.392 (.003)	6.29 (0.33)	0.112 (.011)	5.83 (2.61)	81.20 (1.83)	12.6 (0.31)	14.0 (1.48)
Aspen	21	Rad	0.079 (.007)	1.76 (0.12)	0.353 (.004)	3.60 (0.39)	0.0220 (.0029)	15.40 (1.68)	76.80 (5.73)	26.3	13.4 (2.50)
Aspen	21	Tan	0.079 (.006)	1.78 (0.12)	0.355 (.005)	7.34 (0.91)	0.0187 (.0019)	15.54 (1.59)	78.90 (6.65)	26.8	10.4 (1.06)
Red pine	43	Rad	0.091 (.001)	1.12 (0.03)	0.430 (.003)	3.85 (0.35)	0.225 (.028)	1.51 (0.14)	84.0 (1.37)	15.6 (0.21)	43.4 (6.47)
Red pine	42	Tan	0.088 (.005)	1.11 (0.03)	0.420 (.003)	6.50 (0.33)	0.289 (.030)	1.43 (0.13)	83.3 (2.34)	12.2 (0.33)	33.7 (3.95)
Aspen	43	Rad	0.090 (.001)	2.05 (0.21)	0.340 (.004)	3.94 (0.35)	0.0690 (.0211)	4.30 (0.76)	88.0 (11.7)	26.3	37.5 (11.5)
Aspen	42	Tan	0.089 (.007)	2.18 (0.26)	0.339 (.004)	8.42 (0.88)	0.0478 (.003)	5.92 (0.33)	94.0 (14.5)	26.8	27.0 (1.82)

to estimate L_e values at these other temperatures. From the slope of the E^2 vs. t curves, diffusion coefficients were estimated using Eq. (1). For aspen, the estimated L_e values of 20.3 μm (radial) and 20.8 μm (tangential) estimated

from matched samples treated with water at room temperature were used, since there is no apparent effect of F_{VL} on diffusion path length.

The rate of swelling is highly temperature-dependent as expected (Figs. 5 and 6). The half

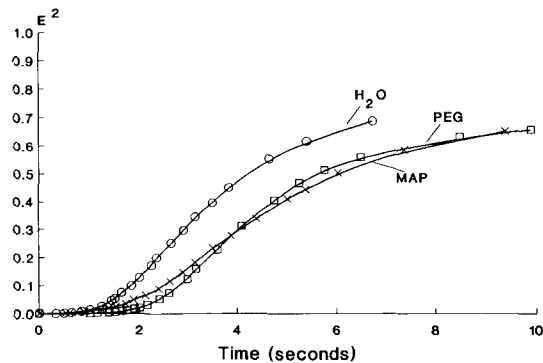


FIG. 3. Effect of solute on the rate of swelling of red pine—22°C.

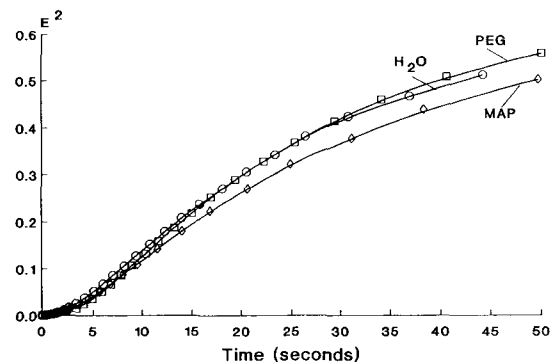


FIG. 4. Effect of solute on the rate of swelling of aspen—22°C.

TABLE 4. Summary of rate of swelling results for red pine and aspen samples vacuum treated with 8% MAP. Each mean based on 4 replications (standard deviations in brackets)

Species	Temp. °C	Dir.	u_i	V_s/M_0	G_{FSP}	S (%)	E^2/t	$t_{1/2}$ s	F_{VL} %	L_e (μm)	$D \times 10^8$ (cm^2/s)
Red pine	4	Rad	.087 (.003)	1.71 (0.13)	.388 (.005)	4.65 (0.40)	0.033 (.009)	11.28 (4.97)	86.52 (7.26)	15.34 (1.12)	6.07 (1.57)
Red pine	4	Tan	.088 (.002)	1.77 (0.15)	.390 (.010)	6.54 (0.31)	0.041 (.006)	8.89 (1.25)	90.6 (2.01)	11.2 (0.27)	4.02 (0.51)
Aspen	4	Rad	.104 (.007)	1.99 (0.13)	.348 (.003)	3.36 (0.24)	0.0070 (.0010)	39.86 (5.33)	87.82 (7.01)	26.3	3.83 (0.54)
Aspen	4	Tan	.104 (.009)	1.97 (0.13)	.348 (.005)	7.58 (1.40)	0.0047 (.0020)	70.32 (23.20)	86.5 (5.20)	26.8	2.65 (1.12)
Red pine	21	Rad	.091 (.001)	1.71 (0.04)	.391 (.002)	4.80 (0.49)	0.091 (.012)	3.74 (0.42)	87.92 (3.75)	15.1 (0.52)	16.1 (1.05)
Red pine	21	Tan	.090 (.003)	1.81 (0.03)	.391 (.005)	6.30 (0.44)	0.106 (.002)	3.47 (0.24)	92.13 (2.76)	11.0 (0.36)	10.1 (0.81)
Aspen	21	Rad	.079 (.007)	1.97 (0.09)	.351 (.006)	3.61 (0.63)	0.0173 (.0023)	17.09 (2.71)	89.42 (4.15)	26.3	9.42 (1.27)
Aspen	21	Tan	.079 (.003)	1.92 (0.14)	.356 (.005)	7.50 (0.44)	0.0164 (.002)	17.90 (2.24)	86.93 (4.76)	26.8	9.09 (0.81)
Red pine	43	Rad	.091 (.001)	1.12 (0.04)	.440 (.005)	3.66 (0.35)	0.298 (.025)	1.26 (0.09)	88.6 (3.42)	15.0 (0.47)	52.9 (7.73)
Red pine	43	Tan	.080 (.003)	1.13 (0.03)	.435 (.005)	6.25 (0.50)	0.206 (.034)	1.81 (0.19)	89.4 (1.81)	11.4 (0.25)	20.7 (2.47)
Aspen	43	Rad	.089 (.007)	2.18 (0.10)	.342 (.003)	3.91 (0.38)	0.0233 (.005)	10.3 (1.61)	92.5 (1.36)	26.3	13.1 (2.83)
Aspen	43	Tan	.094 (.008)	2.25 (0.14)	.340 (.002)	8.43 (0.89)	0.0300 (.004)	9.20 (1.19)	94.3 (1.03)	26.8	16.9 (2.01)

swelling times at 42°C were less than 2 seconds for red pine and less than 10 seconds for aspen (Tables 2–4). The half swelling times approximately doubled between 42°C and room tem-

perature and again between room temperature and 4°C for both species. Results of the Arrhenius plots of $\ln D$ vs. $1/T$ are shown in Table 5. There is considerable variation in the

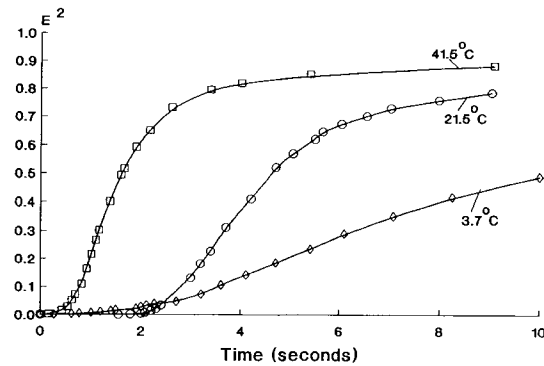


FIG. 5. Effect of temperature on the rate of swelling of red pine—water treatment.

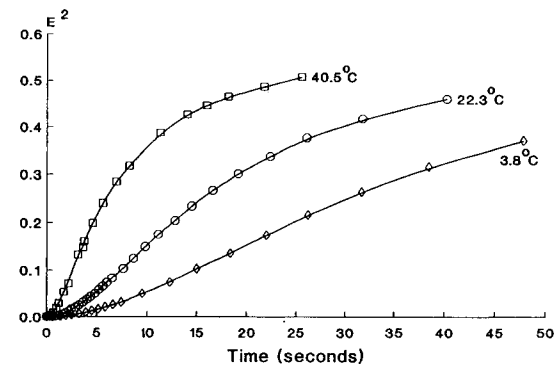


FIG. 6. Effect of temperature on the rate of swelling of aspen—water treatment.

TABLE 5. Arrhenius plots for temperature dependence of bound water diffusion.

Species	Solution	Direction	Equation	r^2	Activation energy (kJ/mole) Mean S.E.
Red pine	water	Radial	$\ln D = 18.8 - 4,657/T$	0.94	38.8 (3.3)
		Tangential	$\ln D = 15.3 - 3,725/T$	0.93	31.0 (2.8)
Red pine	10% PEG	Radial	$\ln D = 15.1 - 3,570/T$	0.85	29.7 (4.2)
		Tangential	$\ln D = 16.4 - 4,042/T$	0.96	33.7 (2.0)
Red pine	8% MAP	Radial	$\ln D = 19.6 - 4,965/T$	0.96	41.4 (2.7)
		Tangential	$\ln D = 14.7 - 3,676/T$	0.97	30.6 (1.9)
Aspen	water	Radial	$\ln D = 18.3 - 4,613/T$	0.96	38.4 (2.5)
		Tangential	$\ln D = 17.3 - 4,416/T$	0.91	36.8 (3.7)
Aspen	10% PEG	Radial	$\ln D = 19.1 - 4,898/T$	0.94	40.8 (3.1)
		Tangential	$\ln D = 19.4 - 5,070/T$	0.94	42.20 (3.5)
Aspen	8% MAP	Radial	$\ln D = 10.9 - 2,615/T$	0.83	21.8 (3.2)
		Tangential	$\ln D = 16.1 - 4,167/T$	0.86	34.7 (4.5)

D values at a given temperature, even after normalization to take into account variable chemical absorptions. This results in relatively low r^2 values and large standard errors of the estimates of the activation energies. There was no consistent effect of species, direction of swelling, or solution on the activation energies. The estimated activation energies in the range from 21.8 to 42.2 kJ/mole are in the general range of that estimated by Choong (1963) for bound water movement of about 35.6 kJ/mole and are lower than the value of 50.2 kJ/mole estimated by Stamm (1960b) for sitka spruce.

Other swelling solvents

Although DMSO and DMF are known "super swelling" agents with wood with larger heats of wetting and % swelling of wood, compared to water (Ashton 1973; Kajita et al. 1979), they initially swell dry wood more slowly than water (Fig. 7). The half swelling times (Table 6) averaged 92 seconds for DMSO, 34 seconds for DMF, and only 13 seconds for water. The diffusion coefficients were correspondingly lower for the two organic solvents. However, with time, the rate of swelling decreased more slowly and total equilibrium swelling was reached more quickly for DMF and DMSO than for water. The slower swelling in DMSO compared to DMF was also observed by Ashton (1973) for blocks immersed in the solvents.

However, it is somewhat surprising considering that DMSO has a smaller molar volume than DMF (71 ml/mole compared to 81 for DMF and 18 for water) and has a greater hydrogen bonding capability and heat of wetting with wood (Kajita et al. 1979).

SUMMARY AND CONCLUSIONS

- (1) The rate of swelling of wood, vacuum-treated with various solutions, could be monitored by means of a video-recording technique allowing the estimation of diffusion path lengths and estimates of cell-wall diffusion coefficients of solvents under different experimental conditions.

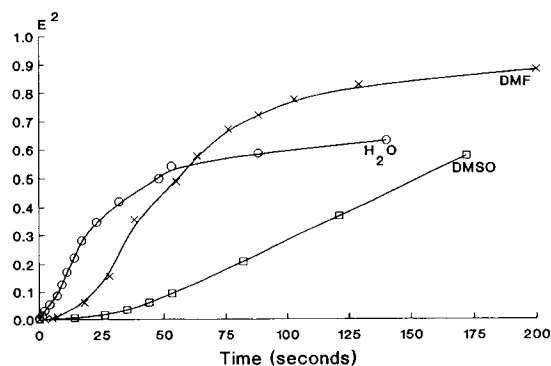


FIG. 7. Comparison of radial swelling rates of aspen treated with water, DMF or DMSO—22°C.

TABLE 6. Comparison of swelling rate of different swelling solvents—aspens samples at room temperature (standard deviations in brackets).

Sol.	Dir.	u_i	u_r	G_{FSP}	S (%)	E^2/t	$t_{1/2}$ s	F_{VL} %	L_e (μm)	$D \times 10^8$ (cm^2/s)
Water	Rad	0.080	1.65	0.360	3.33	0.0277	12.8	72.6	26.3	12.6
		(.007)	(0.22)	(.011)	(0.49)	(.012)	(5.76)	(9.96)		(0.30)
DMSO	Rad	0.091	2.07	0.352	3.30	0.0038	92.1	78	26.3	1.25
		(.003)	(.004)	(.003)	(6.1)	(0.30)	(.001)	(5.5)		(0.30)
DMF	Rad	0.090	1.78	0.353	3.30	0.0091	34.2	80	26.3	2.90
		(.003)	(.003)	(.006)	(.003)	(0.45)	(.003)	(3.4)		(0.45)

- (2) The rate of swelling was greatly affected by the anatomical and physical characteristics of the wood samples, as they influenced the initial distribution of treating solution in the void space and the degree of saturation of the total void space. Diffuse porous aspen swelled at a slower rate than red pine because the solvent was primarily distributed in the dispersed vessel elements of the hardwood, but is well distributed in most of the red pine tracheids.
- (3) The effective diffusion path length in vacuum-treated red pine, as estimated from the rate of swelling of treated wood, increased with decreased % void volume saturated. This relationship was not observed for aspen. L_e depends on the wood structure and for similar solution absorptions is approximately 25 μm in diffuse porous aspen compared to about 15 μm for red pine. In red pine, the relationship was best described by the equations:

$$L_e(\text{radial}) = 605F_{VL}^{-0.825}$$

and

$$L_e(\text{tangential}) = 1,596F_{VL}^{-1.103}$$

- (4) The presence of 8% MAP in the solution inhibited the rate of swelling compared to the water.
- (5) The calculated activation energies for swelling of the cell walls with water varied considerably among the species and treatments and ranged from 21.8 to 42.2 kJ/mole.
- (6) DMF and DMSO swelled wood at a slower

rate than water does under similar treating conditions.

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