DETERMINATION OF DIMENSIONAL STABILIZATION OF WOOD USING THE WATER-SOAK METHOD

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ABSTRACT

Erroneous results can be obtained by the water-soak method in determination of dimensional stability of chemically treated wood. Leaching of bulking chemicals results in a loss of dimensional stability that can be determined only after an initial soaking cycle. After a first soaking cycle, values for percent dimensional stabilization are more realistic for those treatments where the bulking chemical has reacted with cell-wall components. Where the bulking chemical is not bound to cell-wall components, leaching during the first soaking cycle removes most of the chemical, so that in the second soaking cycle, values for percent of dimensional stability are very low. It is important that the test method used be tailored to fit the end use of the product. For products stabilized only against changes in humidity, a second soaking cycle should not be used to determine dimensional stability. Treatments that only fill cell lumens and do not bulk the cell wall result in a low degree of dimensional stability.

Keywords: Pinus spp., southern pine, dimensional stability, antishrink efficiency, bonded chemicals, leaching, test methods, bulking, water soaking, cell walls, chemical modification.

INTRODUCTION

When moisture comes into contact with wood, the water molecules penetrate the cell wall and become bound to cell-wall components through hydrogen bonding. With addition of water to the cell wall, wood volume increases nearly proportionately to the volume of water added. Swelling increases until the fiber saturation point has been reached. Water added beyond this point remains as free water in the lumen and does not cause further swelling. This process is reversible and accounts for the dimensional changes that occur when wood comes into contact with moisture (Stamm 1964).

Many treatments have been devised to reduce swelling of wood in contact with moisture. These treatments are, in most cases, based on bulking the wood cell walls with some material to keep wood in the swollen state as long as the chemical is retained. In this swollen condition, wood cannot expand or contract further in response to contact with water.

Inorganic salts, sugars, polyethylene glycol (Mitchell 1972) and various other organic materials that do not react with the cell wall have been used to bulk the wood cell wall. Because there is no permanent attachment of these bulking chemicals to cell-wall components, when liquid water comes in contact with them, they can be leached out of the cell wall. After leaching and drying, the wood is no longer bulked and no longer dimensionally stabilized. Dimensional stability by bulking with nonreactive chemicals is useful for products such as carvings, which are not generally exposed to liquid water, but which may be damaged by shrinking and swelling resulting from changes in relative humidity.

Chemicals that have been chemically reacted with cell-wall components also bulk the cell wall. Permanence depends on chemical stability of the bonds formed. When liquid water comes in contact with wood that has bulking materials chemically bonded in the cell wall, there is little or no leaching. On drying, the wood is still bulked and dimensionally stabilized.

Some chemicals do not bulk the wood cell wall or bond with cell-wall components, but rather fill lumens and offer little or no dimensional stability. An example of this type of chemical is monomeric methyl methacrylate (Meyer 1977) which, when impregnated into wood and polymerized, can increase the weight of the wood considerably. Although polymerized chemical cannot be leached by water, very little dimensional stability results from this treatment. The small amount of stability that is achieved may be due to some cell-wall penetration by the chemical or to physical blocking of moisture (water repellency) from the cell wall.

The purpose of this paper is to describe a method for determining the dimensional stability resulting from bonded and nonbonded cell-wall bulking treatments as well as lumen fill treatments.

BACKGROUND

There is a variety of terms used to describe the degree of dimensional stability given to wood: antishrink efficiency, swelling percent, dimensional stabilization efficiency, antiswelling efficiency, and percent reduction in swelling. Regardless of the name, generally, they are calculated as follows (Stamm 1964):

$$S = \frac{V_2 - V_1}{V_1},$$ (1)

where

S = volumetric swelling coefficient
V_2 = wood volume after wetting with liquid water
V_1 = wood volume of oven-dried sample before wetting,

or

$$R = \frac{S_2 - S_1}{S_1},$$ (2)

where

R = reduction in swelling or antishrink efficiency resulting from a treatment
S_2 = treated volumetric swelling coefficient
S_1 = untreated volumetric swelling coefficient.

Both the R and S values are usually reported as percent. In that case, the R and S values from Eqs. (1) and (2) are multiplied by 100.

When green wood is oven-dried, wood volume decreases by about 7–16%. When oven-dried wood is treated with chemicals that bulk or add to the cell wall, increase in wood volume is proportional to the volume of chemical added. At chemical loadings in the cell wall of about 20–25 weight percent gain (WPG), the volume of dry treated wood is nearly equal to its green volume. As long as the wood stays in this swollen state, it cannot become larger upon water soaking.

Swelling beyond green volume has been reported under certain conditions, but does not occur to any great extent unless cell walls rupture (Rowell et al. 1976).

Let us examine a hypothetical case of a green water-soaked wood sample of green volume V_G which, upon oven-drying, becomes smaller and has a new oven-dry volume, V_{OD}. This untreated sample is then bulked with a nonbonding but cell-wall-penetrating chemical. After treatment to about 30–50 WPG and re-oven-drying, the sample volume increases to a new treated oven-dry volume, V_{TOD}. At this point, assume V_G to equal V_{TOD}. This sample is then subjected to a water-soaking dimensional stability test and, after 7 days of leaching, wet volume is again measured. Even though most of the bulking chemical has been removed during this time, the treated wet sample volume (V_{TW}) after the test will still be equal to V_G or V_{TOD} because the sample was already in a completely swollen state. This extracted sample, however, upon re-oven-drying, having lost its bulking chemical, will have a new volume nearly equal to the original V_{OD}. Now considering Eq. (1), the volumetric swelling coefficient will be very low for this sample because V_2 (V_{TW}) and V_1 (V_{TOD}) are nearly the same. Using this S value in Eq. (2) will result in a very high R value even though the treating chemical has been leached out. If, at this point, the sample is again given the water-soaking dimensional stability test, the S value would be very high and R would be low. When the leached sample is reweighed, most—if not all—of the weight gain achieved by the treatment will be lost.

If, on the other hand, the sample is treated with a chemical that chemically bonds to the cell walls and is then subjected to the same repeated water-soaking dimensional stability test, the S value would remain low and the R high.

The difference, therefore, between a nonbonded and bonded cell-wall-bulking agent can be determined by the R value resulting from the second water-soaking dimensional stability test. Maintaining a high R value through several water stability tests is an indication of dimensional stabilization due to nonleachable bonded cell-wall bulking.

Considering treatments with noncell-wall-bulking chemicals such as methyl methacrylate, addition of chemical to wood does not result in a proportional increase in wood volume. The treated oven-dry volume (V_{TOD}) is nearly equal to the original untreated oven-dry volume (V_{OD}). Because little or no cell-wall-bulking occurs when this treated sample is subjected to the water-soaking dimensional stability test, water will penetrate the cell wall and cause it to swell close to its original green volume. Now the S value will be large and the resulting R value small. This is similar to the effect of nonbonded bulking chemicals during the second wetting except that when the oven-dried samples are reweighed after test, very little weight loss is observed. The treatment is nonleachable, but does not give dimensional stability.

EXPERIMENTAL

Southern pine samples, ¾-inch radially by ¾-inch tangentially by 1 to 6 inches longitudinally were prepared from freshly cut green logs. The green volume of these samples was determined using a flatbed micrometer; all were then oven-dried and their volume was again determined.

The dry wood blocks were reacted separately with propylene oxide/triethylamine, butylene oxide/triethylamine, methyl methacrylate, methyl isocyanate, acry-

TABLE 1. *Reaction of southern pine with organic reagents.*

Chemical	Catalyst	Ratio chemical/ catalyst	Temperature (°C)	Pressure (psi)
Propylene oxide	Triethylamine	95/5	120	150
Butylene oxide	Triethylamine	95/5	120	150
Methyl methacrylate	Heat	—	80	—
Methyl isocyanate	None	—	120	150
Acrylonitrile	NaOH	96/4	60	150
Acrylonitrile	NH_4OH	90/10	60	150
Acetic anhydride	None	—	120	150

TABLE 2. *Changes in volume of southern pine upon drying and chemical treatment.*

Green volume (in.^{3})	O.D. volume (in.^{3})	ΔV%	Treatment	After treatment O.D. volume (in.^{3})	WPG[1]
3.48	3.24	6.9	Propylene oxide	3.42	15.9
3.60	3.24	10.0	Propylene oxide	3.60	21.1
3.66	3.42	6.6	Propylene oxide	3.66	26.1
3.60	3.30	8.3	Propylene oxide	3.66	34.1
3.60	3.36	6.7	Propylene oxide	3.72	41.0
2.33	2.11	9.4	Acetic anhydride	2.30	13.9
2.39	2.15	10.0	Acetic anhydride	2.33	17.5
2.41	2.17	9.9	Acetic anhydride	2.39	19.5
2.37	2.13	10.1	Acetic anhydride	2.37	22.8

[1] Weight percent gain.

TABLE 3. *Volume changes in southern pine upon chemical treatment.*

Treatment	WPG[1]	Increase in wood volume with treatment[2] (cm^3)	Calculated volume of chemical added[3] (cm^3)
Propylene oxide	26.5	7.1	7.5
	28.8	6.4	7.2
	34.3	8.4	8.0
	36.2	8.9	9.0
Methyl isocyanate	12.4	.16	.14
	25.7	.21	.27
	47.7	.46	.54
	51.2	.54	.58
Acetic anhydride	17.5	3.0	2.9
	19.5	3.6	3.3
	22.8	3.9	4.0
Acrylonitrile	25.7	.46	.77
	28.7	.26	.39
	36.0	.74	1.2
Methyl methacrylate	58.0	.6	7.6
	91.4	.9	10.1

[1] Weight percent gain.
[2] Difference in volume between treatments due to different sample size.
[3] Density used in volume calculations: Propylene oxide. 1.01; methyl isocyanate. 0.967; acetic anhydride. 1.049; acrylonitrile. 0.806; methyl methacrylate, 0.94.

lonitrile in sodium hydroxide or ammonium hydroxide, and acetic anhydride. One set of samples was first reacted with propylene oxide/triethylamine and then impregnated with methyl methacrylate followed by polymerization. Reaction conditions are shown in Table 1. Samples of different weight percent gains were achieved by varying reaction times.

After treatment, samples were oven-dried and volumes determined. Results are shown in Tables 2 and 3. Each result is an average of three samples.

The volumetric swelling coefficient for each separate reaction system was determined on $^3/_4$-inch by $^3/_4$-inch by $^5/_{16}$-inch (radial by tangential by longitudinal) blocks. Samples were submerged in distilled water and evacuated in a vacuum desiccator. Vacuum was continued for 30 min, released for 1 h, reapplied for 30 min, then released for 24 h. Fresh distilled water was then added and this process repeated. After each 24 h, wet volume of the block was determined. This was continued for 7 days. The volumetric swelling coefficient (S) and the antishrink efficiency (R) were calculated using Eqs. (1) and (2), respectively.

Samples were then re-oven-dried, O.D. volume was determined, and the S and R values were again calculated. The samples were then resoaked for 7 days, volume was determined, and then they were re-oven-dried followed by a final volume determination. The values of S and R in these repeated swelling tests are given in Table 4. The rate of water swelling is shown in Table 5.

DISCUSSION

Oven-drying untreated southern pine caused a shrinkage of 6–10% from the original green volume (Table 2). At a WPG of about 20, the oven-dry volume of the treated wood was equal to the original untreated green volume. Table 3 shows that, for propylene oxide, methyl isocyanate, and acetic anhydride, volume expansion in the wood was nearly equal to the volume of chemical added. Although this is strong evidence that the bulking chemicals have ended up in the cell wall, these results do not indicate whether or not the chemical is bonded. For acrylonitrile, there was a greater volume of chemical added than there was an increase in wood volume. This means that not all the chemical in the wood is located in the cell wall. This is very evident in the methyl methacrylate samples, where there was a very large addition of chemical volume with very little increase in wood volume. The methacrylate polymer is mainly in wood lumens.

Table 4 shows the results of a repeated water wetting test for determining dimensional stability. Acetylation with acetic anhydride gave the most consistent results. In this case, R remained constant during two soaking/drying cycles. This indicates strong bonding with little or no loss of chemical during the leaching cycles. Propylene and butylene oxides and methyl isocyanate samples show an R of about 70 on the first wetting cycle. Because of a small loss of chemical upon leaching, R drops during the second wetting cycle. The R value calculated from the first wet volume to the second oven-dry volume is almost always a lower value than any subsequent R values. This is because the new oven-dry volume is smaller than original oven-dry volume because of leached chemical that had bulked the original sample. In the case of acrylonitrile, R value for the first wetting cycle is high but, upon redrying, the R value is negative. This means the bulking chemical in the original oven-dry sample has now been leached out, and the new oven-dry volume is close to or smaller than the volume of the oven-dry sample

TABLE 4. *Volumetric swelling coefficients (S) and antishrink efficiency (R) as determined by the water-soaking method.*

Treatment	WPG[1]	S_1[2]	R_1[3]	S_2[4]	R_2[5]	Wt. loss (%)[6]	S_3[7]	R_3[8]	S_4[9]	R_4[10]	Add. wt. loss (%)[11]
Propylene oxide	0	15.8	—	15.8	—	<.6	15.9	—	15.9	—	2.3
	29.2	6.0	62.0	9.0	43.8	4.0	7.8	50.9	7.9	50.3	1.7
Butylene oxide	0	13.6	—	12.4	—	<.5	12.4	—	12.9	—	2.4
	26.7	3.5	74.3	5.5	55.6	1.6	5.0	59.7	5.4	48.1	3.0
	27.0	3.6	73.5	5.7	54.0	1.6	5.2	58.1	5.6	56.6	2.6
Acetic anhydride	0	13.8	—	13.3	—	<.2	13.6	—	13.3	—	<.2
	16.3	5.1	63.0	5.1	61.7	<.2	5.3	61.0	5.3	60.2	<.2
	21.1	4.2	69.6	4.1	69.2	<.2	4.3	68.4	4.6	65.4	<.2
	22.5	4.1	70.3	3.8	71.4	<.2	4.0	70.6	4.1	69.2	<.2
Acrylonitrile	0	14.1	—	13.9	—	<.5	14.0	—			<.2
NH$_4$OH	26.1	2.7	80.9	15.3	neg.	21.7	14.4	neg.			.9
	0	20.3	—	16.8	—	<.2	16.7	—			<.2
NaOH	25.7	10.5	48.3	18.8	neg.	13.5	17.5	neg.			1.2
Methyl isocyanate	0	14.0	—	13.8	—	<.5	13.7	—	13.5	—	4.5
	10.9	7.2	48.3	8.1	40.4	<.2	8.3	39.4	8.9	34.1	4.5
	21.6	5.5	60.4	6.6	52.0	<.2	6.5	52.6	6.3	53.3	3.9
	26.0	4.2	69.7	5.1	62.8	<.2	4.8	65.0	5.3	60.7	4.3
	29.9	4.7	66.4	6.0	56.8	1.6	4.8	65.0	5.3	60.7	4.1
	41.5	3.2	77.1	8.1	41.3	9.7	8.0	41.6	7.6	43.7	1.4
Methyl methacrylate	75.7	16.2	0	16.0	0	1.7	16.0	0	16.0	0	<.6
Propylene oxide	29.2	7.0	55.7	9.4	41.3	1.7	9.0	43.4	9.0	43.4	1.6
Methyl methacrylate	48.8										

[1] Weight percent gain. Samples recorded at 0 WPG are controls.
[2] Volumetric swelling coefficient determined from initial O.D. volume and first waterswollen volume. Equation (1).
[3] Antishrink efficiency based on S_1. Equation (2).
[4] Determined from first waterswollen volume and re-oven-drying.
[5] Based on S_2.
[6] Percent weight loss based on the difference between initial O.D. weight and O.D. weight after first water soaking.
[7] Determined from re-oven-dry volume and second waterswollen volume.
[8] Based on S_3.
[9] Determined from second waterswollen volume and second re-oven-drying.
[10] Based on S_4.
[11] Additional weight loss based on O.D. weight.

TABLE 5. *Rate of water swelling of southern pine.*

Treatment	WPG[1]	Volumetric swelling coefficient, S			
		1 day	2 days	4 days	7 days
Control	0	18.9	18.9	19.0	19.0
	0	15.8	15.8	15.8	15.8
Acetic anhydride	21.1	4.1	4.1	4.2	4.1
Propylene oxide	29.2	6.1	6.1	6.0	6.0
Methyl methacrylate	75.7	16.1	16.1	16.1	16.2
Propylene oxide Methyl methacrylate	29.2 48.8	6.9	7.0	6.9	7.0

[1] Weight percent gain.

before chemical modification. The negative R value is probably due to the degradative effects of the catalyst and heat on cell-wall components. In samples treated with methyl methacrylate, very little dimensional stability is observed.

These data show clearly the difference between bonded and nonbonded cell-wall-bulking agents and between cell-wall and lumen treatments. These differences are apparent after the first water leaching. Thus, in the calculation of the percent dimensional stability in the water leaching test, it is recommended that the oven-dry volume after the first water leach be used for V_1 in Eq. (1) and the waterswollen volume in the second wetting be used as V_2. This will be a more meaningful measurement of dimensional stability in liquid water of a bonded treatment.

In almost all tests described for water swelling, a soaking time of 1 week is used. Within 24 h, the volumetric swelling coefficient is within experimental error of what it will be in 7 days (Table 5). Soaking beyond 24 h will not increase the swelling coefficient, but it will influence the amount of material leached out.

All samples used in these soaking tests were $^5/_{16}$-inch in the longitudinal direction, permitting easy access of the water into the interior of the sample. This insured rapid swelling and rate of leaching. All samples had parallel sides and annual rings parallel to two faces. If the rings were not parallel to two faces, the sample would have gone out of square during water swelling. Attempts to measure an out-of-square wet block with the flatbed micrometer introduce a very large error in volume measurements.

Since determination of dimensional stability is based on a comparison between an untreated and a treated sample, it is critical that the treated sample come from the same source as the control. The blocks can serve as their own controls if they are subjected to a soaking-drying cycle prior to treatment. The swelling coefficient (S) for pure southern pine earlywood is 6–9, while pure latewood is 17–20 (Rowell 1978). The average swelling coefficient for a sample will, therefore, depend on the proportion of latewood to earlywood. If a different control is used to compare with a treated sample and they differ in the percent of latewood, then the values obtained for the antishrink efficiency are nearly useless.

CONCLUSIONS

For wood products that will be exposed only to changes in humidity and not the leaching effects of liquid water, the value for the antishrink efficiency (R)

obtained prior to the first leaching cycle of the water-soaking test method is most applicable. This method applies to both bonded and nonbonded cell-wall-bulking treatments. For wood products that will come in contact with liquid water where leaching can occur, the data used to calculate the R should be those derived from the second leaching cycle of the water-soaking test method. This value for R more nearly represents the continuing stability of treated wood when exposed to liquid water. High continuing R values result only from bonded cell-wall-bulking treatments or entrapped, nonleachable polymer formed within the cell walls. Those chemical treatments that do not bulk the cell wall but add weight in wood lumens do not result in dimensional stability to any great extent.

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