MOISTURE ADSORPTION AND SWELLING IN POLYETHYLENE GLYCOL AND POLYMETHYL METHACRYLATE TREATED WOOD AT HIGH RELATIVE HUMIDITY

Howard N. Rosen
Research Chemical Engineer, USDA Forest Service,
North Central Forest Experiment Station, Carbondale, IL 62901

(Received 15 September 1975)

ABSTRACT

The rates and amounts of swelling and moisture adsorption at 97% relative humidity and 24 C in untreated, polyethylene glycol of molecular weight 1000 (PEG-1000)-treated, and polymerized methyl methacrylate monomer (MMA)-treated yellow-poplar and silver maple were compared. Swelling and moisture adsorption were 60 to 90% slower in MMA-treated wood than in untreated wood. Antishrink efficiencies of MMA-treated wood ranged from 9 to 21%. The rate of moisture adsorption in PEG-1000-treated wood was faster than in untreated wood. Considerable moisture was adsorbed by the PEG-1000 in the cell cavities of the PEG-1000-treated wood. Antishrink efficiencies ranged from 82 to 92%.

Additional keywords: Adsorption, *Liriodendron tulipifera*, *Acer saccharinum*, diffusion, antishrink efficiency.

INTRODUCTION

Two of the most popular commercial chemicals for modification of the swelling characteristics of wood are polyethylene glycol of molecular weight 1000 (PEG-1000) and methyl methacrylate (MMA). PEG-1000 is usually added in aqueous solution to wood used for such items as wood carvings and gunstocks as well as to deteriorated archeological specimens as a preservative. MMA is impregnated and polymerized in wood to form wood-plastic composite materials that are made into such items as flooring and billiard cues.

The swelling and moisture adsorption characteristics of PEG-1000- and MMA-treated dry wood are reflected in three ways: (1) rate of dimensional change: by the rate of moisture adsorption; (2) degree of dimensional change: by the bulking of the cell walls by the treatment chemical; and (3) amount of moisture adsorption: by the hygroscopicity of the treated wood.

Although PEG-1000 has been shown to impart considerable dimensional stability to wood, varying results have been found for MMA. Stamm (1959b) was able to obtain an 82% reduction in shrinkage of southern pine by soaking the wood for one week in a 30% aqueous PEG-1000 solution. Antishrink efficiencies of several MMA-treated wood species at full loading were found by Ellwood et al. (1969) to range from 32 to 54%, but Siau and Meyer (1966) reported antishrink efficiencies of less than 14%.

PEG-1000 is more hygroscopic than untreated wood at high humidity, and wood treated with PEG-1000 becomes damp with moisture above 80% relative humidity (Stamm 1956; Schneider 1969). Few data exist on moisture content of MMA-treated wood at various relative humidities, although MMA is known to retard the rate of moisture adsorption by wood. Ellwood et al. (1969) found the rate of moisture diffusion in several wood species at high MMA loadings to be 20 to 30% of the rate of untreated wood.

The object of this paper is to compare the rate and amount of swelling and the moisture uptake for untreated, PEG-1000-treated, and MMA-treated dry wood at high relative humidity. These comparisons will illustrate the advantages and possible disadvantages achieved in dimensional stability and moisture resistance by adding MMA or PEG-1000 to wood.

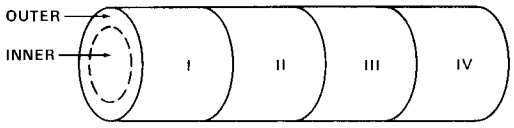

FIG. 1. Sections for PEG-1000 distribution.

EXPERIMENTAL PROCEDURES

Straight-grained and clear sections of yellow-poplar (*Liriodendron tulipifera* L.) sapwood and silver maple (*Acer saccharinum* L.) heartwood 5 by 5 by 40 cm along the grain were cut from the bolts of trees found locally in southern Illinois and kiln-dried to 6 to 8% moisture content. Square sections were turned on a lathe to cylinders 3.6 cm in diameter and 5 cm along the grain before conditioning at 29 C and 28% relative humidity to approximately 6% equilibrium moisture content (EMC).

From the approximately 40 cylinders of each species, 12 cylinders of yellow-poplar and 12 cylinders of silver maple were treated with MMA monomer (0.2% Vazo catalyst), 8 cylinders of yellow-poplar, and 8 cylinders of silver maple with a 50% aqueous PEG-1000 solution, and 8 cylinders of yellow-poplar with a 30% aqueous PEG-1000 solution. A full cell pressure treating method (150 psi with pressure applied for 90 min at 22 C) was used. Cylinders treated with MMA were cured at 67 C for 5 h. All cylinders were then conditioned at 29 C and 28% relative humidity until EMC.

Initial moisture contents based on the weight of oven-dry wood were determined on two cylinders of each species and treatment (including untreated cylinders) by oven-drying at 103 C. Also, PEG-1000 distributions were determined in duplicate for each treatment and species treated with aqueous PEG-1000 solution. To accomplish this, the cylinders were cut into 8 sections of equal volume, 4 along the grain to establish longitudinal PEG-1000 distribution and 2 along the radius to establish radial PEG-1000 distribution (Fig. 1). The PEG-1000 content of each section was determined by water extraction (Rosen 1975).

To determine swelling and moisture adsorption, cylinders were placed on a table in the center of a humidity box so that their ends faced fans located on opposite ends of the box. These fans forced humid air across the end faces of the cylinders at a velocity of 650 ft/min. The box contained a saturated solution of potassium sulfate to maintain the relative humidity at 97% at 24 C.

Three separate moisture adsorption runs were made in the humidity box—the first on the untreated samples, the second on MMA-treated samples, and the last on PEG-1000-treated samples. For the runs made on the untreated and MMA-treated samples, the rate of volumetric swelling was determined by enclosing the cylinders in a swelling cell as described by Rosen (1973). This cell has a rubber gasket that encircles the cylinder so that moisture cannot penetrate radially; thus, moisture diffusion is restricted to the longitudinal direction. Moisture adsorption could not be measured on the samples in the swelling cells; therefore, the rate of moisture adsorption was determined simultaneously with volumetric swelling by using "matched" samples. Cylinders that matched those in the swelling cell as closely as possible, in terms of specific gravity and degree of treatment, were wrapped in a latex liner so that the ends were exposed to the humid air. These matched cylinders were placed alongside their respective swelling cells. This permitted the rapid removal of the wood cylinder from the latex liner so that weights could be taken at intervals during a run.

The swelling cells were not used for PEG-1000-treated samples because the swelling of the samples was too small to obtain accurate results from the swelling cell. PEG-1000-treated cylinders for each treatment condition (yellow-poplar treated with 30 and 50% aqueous PEG-1000 solution and silver maple treated with 50% aqueous PEG-1000 solution) were wrapped in latex liners, and weights were taken at time intervals during the run to determine moisture adsorption. A final swelling value at the completion of the run was determined for these cylinders from direct measurement with calipers.

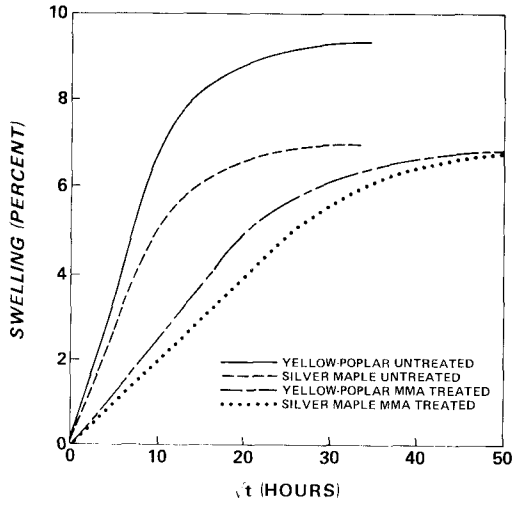

FIG. 2. The rates of volumetric swelling of untreated and MMA-treated yellow-poplar and silver maple.

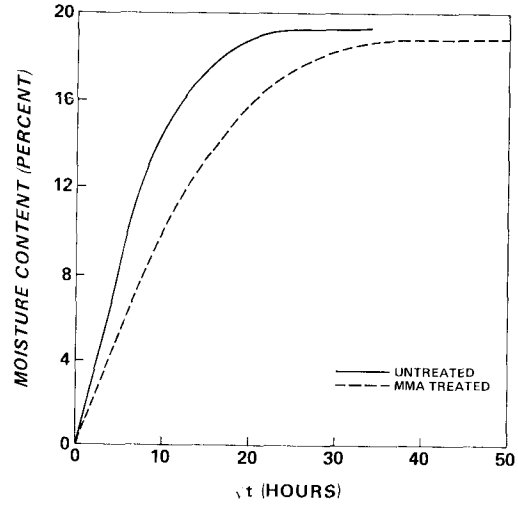

FIG. 3. The rates of moisture adsorption in untreated and MMA-treated yellow-poplar.

The runs in the humidity box were terminated after swelling and moisture adsorption reached a constant value or after approximately 2,000 h. The cylinders were weighed and measured before and after pressure treatment, after conditioning (prior to placing in the humidity box), and at the completion of a run. From these measurements, final moisture content, antishrink efficiency (ASE),[1] and other physical parameters were calculated.

RESULTS AND DISCUSSION

The rate of moisture adsorption and accompanying swelling were significantly decreased in the MMA-treated wood (Figs. 2 and 3). Moisture content was based on the oven-dry weight of the untreated wood. It took three times as long to reach 10% moisture adsorption for MMA-treated yellow-poplar. The retardation of the movement of moisture in the MMA-treated wood is reflected in the diffusion coefficient, D, shown in Table 1; the values of diffusion coefficients were 5 to 7 times greater for untreated wood than for MMA-treated wood.

A careful examination of the order of magnitude of the moisture diffusion coefficients of the cell wall and MMA polymer components of the MMA-treated wood can help to explain why moisture movement is reduced by treating wood with MMA to form a wood-plastic composite. The order of magnitude of the diffusion coefficient through cell-wall substance is 10^{-7} cm^2/sec (Stamm 1959a), through MMA polymer is 10^{-8} cm^2/sec (Crank and Park 1968), and through the untreated wood of this study was 10^{-5} cm^2/sec (Table 1). The greatest portion of diffusion in the gross wood occurs through the cell cavities-cell wall combination (Stamm 1964). Consequently, partially filling the cell cavities with a material that has a very low diffusion coefficient would retard the diffusion of moisture through the gross wood. The fiber cavities in this study were only partially filled with MMA polymer for several reasons: first, because of incomplete impregnation during treatment as indicated by K_{11}[2]

[1] $$\text{ASE} = \frac{(\text{Swelling of control}) - (\text{Swelling of treated sample})}{\text{Swelling of control}} \times 100.$$

[2] Defined as the percentage of weight of treating solution impregnated into the wood compared to the theoretical maximum amount of solution that could possibly be impregnated into the wood.

TABLE 1. *Physical parameters for adsorption of moisture in untreated and MMA-treated yellow-poplar and silver maple at 97% relative humidity*

Specimen	Oven dry Specific gravity	MC, %[a] Initial	MC, %[a] Final	Maximum Swelling %	D[b] $cm^2/sec \times 10^6$	K_D %	ASE %
			Untreated cylinders[c]				
Silver maple							
Cell[d]	0.47	5.0	23.2	7.2	8.4	-	-
Liner[e]	0.49	5.0	23.6	7.9	-	-	-
Yellow-poplar							
Cell	0.51	5.6	24.5	9.0	9.0	-	-
Liner	0.50	5.6	25.2	9.0	-	-	-
			Treated cylinders[f]				
Silver maple							
Cell	0.50	5.0	24.1	6.7	1.2	96	9
Liner	0.51	5.0	24.2	7.0	-	96	9
Yellow-poplar							
Cell	0.50	6.0	24.5	7.1	1.7	96	21
Liner	0.51	6.0	25.3	7.1	-	93	21

[a]Based on weight of oven dry untreated wood.

[b]$D = \frac{\pi L^2 E^2}{16t}$, where D is the integral diffusion coefficient for the average moisture content, L is the longitudinal thickness of the cylinder, and E is the fraction of final swelling at time, t.

[c]Average of 2 samples.

[d]Swelling cell cylinders.

[e]Matched latex liner cylinders.

[f]Average of 3 samples.

less than 100; second, because of a 20% shrinkage of the monomer upon polymerization; and last, because of monomer loss during polymerization (approximately 15%). The diffusion coefficients on the order of 10^{-6} cm^2/sec (Table 1) found for MMA-treated wood are consistent with the above argument.

Small values of ASE's (Table 1) indicate low bulking of the cell wall by MMA. The ASE of 21% obtained for yellow-poplar treated with MMA was lower than the value of 33% obtained by Ellwood et al. (1972); but differences in polymerization techniques (radiation instead of heat-catalyst), polymer loading, and moisture content could explain the discrepancy.

Differences in rates and amounts of moisture adsorption between PEG-1000 (Fig. 4) and untreated or MMA-treated wood (Fig. 3) are more pronounced above 80% relative humidity because, as stated previously, water begins to condense on the surface of the PEG-1000-treated wood above this humidity. At 97% relative humidity, PEG-1000-treated cylinders went above the approximately 30% fiber saturation point of the wood, indicating that PEG-1000 had adsorbed considerable moisture. Condensed water was observed on the surface of the cylinders during the runs, and some PEG-1000 was leached from the cylinders.

Condensed water was probably formed inside the PEG-1000-treated wood during exposure to 97% relative humidity. Although the cell cavities were almost completely filled with aqueous PEG-1000 solution after pressure treatment (K_D greater than 90%), part of the cavities were emptied by the removal of moisture during conditioning to approximately 6% moisture content. Upon exposure of the dry treated wood to the high humidity, considerable moisture was adsorbed by the wood. Part of the moisture entered the cell walls (30%),

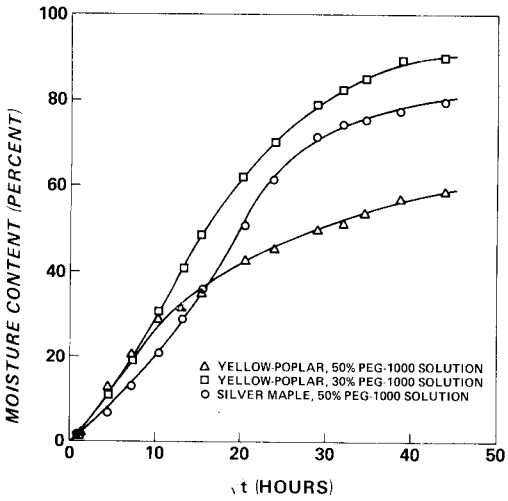

FIG. 4. The rates of moisture adsorption in PEG-1000-treated yellow-poplar and silver maple.

but the remainder of the moisture was adsorbed by the PEG-1000. Since PEG-1000 forms a saturated solution with water at less than 50% water (Anon 1971), aqueous solutions of PEG-1000 and water were formed in the cell cavities of the wood. For example, Table 2 shows that the 90% moisture content of 30% PEG-1000-treated yellow-poplar after 2,000 h is more than enough to saturate the cell walls and form an aqueous solution with the 52% PEG-1000 content of the wood.

The moisture content of the cylinders appears to be approaching that of complete saturation (maximum MC—Table 2); i.e., the moisture content of the *treated* wood at which the cell walls and void space are completely filled with moisture. At 2,000 h, the moisture content of the silver maple samples was 90% of that at maximum MC; the moisture content of the yellow-poplar samples was about two-thirds that of maximum MC.

The yellow-poplar cylinders treated with 30% PEG-1000 had a higher amount of moisture adsorption than cylinders of the same species treated with 50% PEG-1000. Since the PEG content of 30% PEG-1000-treated wood was lower than the 50% PEG-1000-treated wood, more void space was available for greater adsorption of moisture in the wood with the lower PEG content.

Although equilibrium moisture contents were not reached for PEG-1000-treated cylinders after 2,000 h exposure to 97% relative humidity, the moisture contents were enough above the fiber saturation point to assume maximum swelling had occurred. The swelling of these cylinders at 2,000 h, listed as "final swelling" in Table 2, was less than 1.5% giving ASE's of 82% or greater.

Moisture uptake and swelling rate of treated wood cylinders can be affected by the distribution of treatment chemical. The cylinders were treated at conditions to achieve complete penetration so the treating chemical would be evenly distributed throughout the wood. K_D was over 90% for all treatments (Tables 1 and 2).

The distribution of PEG-1000 in the cyl-

TABLE 2. *Physical parameters for adsorption of moisture in PEG-1000-treated yellow-poplar and silver maple at 79% relative humidity*

Specimen[a]	Oven dry specific gravity	MC, %[b]			Maximum swelling %	K_D %	PEG content %	ASE %
		Initial	At 2,000 hr	Maximum				
				50% PEG				
Silver maple	0.52	5.3	76	85	1.4	91	76	82
Yellow-poplar	0.50	6.2	59	92	0.7	96	87	92
				30% PEG				
Yellow-poplar	0.50	5.6	90	124	0.9	98	52	90

[a] Averages of four samples.

[b] Based on weight of oven dry untreated wood.

TABLE 3. *PEG-1000 distribution in wood*

Section[a]	PEG-1000 content, %		
	Silver maple	Yellow-poplar	
	50% PEG	50% PEG	30% PEG
I-outer cylinder	75	84	49
I-inner cylinder	78	75	32
II-outer cylinder	79	86	47
II-inner cylinder	68	75	32
III-outer cylinder	77	85	53
III-inner cylinder	70	77	37
IV-outer cylinder	113	110	75
IV-inner cylinder	112	103	66

[a]See Fig. 1.

inders prior to exposure to 97% relative humidity showed slightly lower PEG-1000 content in the outer portion of the cylinder and a higher PEG-1000 content in section IV (Table 3) of the wood. Replicate analyses reflected the same trends. The variation of PEG-1000 in the radial direction occurred because the surface was more easily penetrated than the center of the wood. The high content of PEG-1000 in section IV of the sample was surprising. The cylinders filled with aqueous PEG-1000 solution were inadvertently tilted slightly while drying to 5 to 6% moisture content, so that section IV was the lowest section of the cylinder. Since the PEG contents in section IV of the cylinders were 10 to 20% higher than theoretically possible with pressure impregnation alone, some PEG-1000 must have migrated from the upper portion of the wood during drying.

Even though the treatment chemicals were not evenly distributed in the wood, MMA because of surface loss and PEG-1000 because of migration of PEG-1000 during conditioning, the trends and phenomena found in this study are not thought to be greatly dependent on chemical distribution in the wood.

The widely varying characteristics of PEG-1000- and MMA-treated wood to moisture adsorption and swelling lead the author to believe that a combination of both chemicals might produce a superior wood product. Future studies might be directed at a combined treatment of wood with PEG-1000 to dimensionally stabilize the wood and MMA polymer to lower the hygroscopicity of the treated product.

CONCLUSIONS

1. At 97% relative humidity, MMA monomer impregnated and polymerized in yellow-poplar sapwood and silver maple heartwood retards the rate of moisture adsorption and swelling compared to untreated wood by 60 to 90%.

2. MMA monomer impregnated and polymerized in yellow-poplar sapwood and silver maple heartwood produces little dimensional stabilization of the wood.

3. At 97% relative humidity, the rate of moisture adsorption increases in PEG-1000-treated yellow-poplar sapwood and silver maple heartwood compared to untreated wood. Moisture is adsorbed by the PEG-1000 in the cavities of the PEG-1000-treated wood.

REFERENCES

ANONYMOUS. 1971. Polyethylene glycols handbook. Dow Chemical Company, Midland, Mich. 24 pp.

CRANK, J., AND G. PARK, eds. 1968. Diffusion in polymers. Academic Press, New York. Pp. 275, 296.

ELLWOOD, E., R. GILMORE, J. A. MERRILL, AND W. K. POOLE. 1969. An investigation of certain physical and mechanical properties of wood-plastic combinations. U.S. Atomic Energy Comm. Rep. ORO-638 (RTI-2513-T13).

ELLWOOD, E., R. GILMORE, AND A. STAMM. 1972. Dimensional stabilization of wood with vinyl monomers. Wood Sci. 4(3):137–141.

ROSEN, H. N. 1973. Continuous measurement of the swelling of wood. For. Prod. J. 23(3): 55–57.

———. 1975. How to determine polyethylene glycol 1,000 content in treated wood. USDA Forest Serv. Res. Note NC-191, 3 pp.

SCHNEIDER, A. 1969. Contributions on the dimensional stabilization of wood with polyethylene glycol, Part I. Holz Roh-Wehkst. 27(6):209–224.

SIAU, J. F., AND J. A. MEYER. 1966. Comparison of the properties of heat and radiation cured wood-polymer combinations. For. Prod. J. 16(8):47–56.

STAMM, A. J. 1956. Dimensional stabilization of

wood with Carbowax. For. Prod. J. 6(5):201–204.

———. 1959a. Bound-water diffusion into wood in the fiber direction. For. Prod. J. 9(1):27–32.

———. 1959b. Effect of polyethylene glycol on the dimensional stability of wood. For. Prod. J. 9(10):375–381.

———. 1964. Wood and cellulose science. Pp. 410–440. Ronald Press, New York.