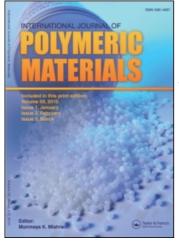
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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713647664

Water Repellency of Several Wood Species Impregnated with Vinyl Monomers

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To cite this Article Alma, M. H., Maldas, D. and Hafizolu, H.(1995) 'Water Repellency of Several Wood Species Impregnated with Vinyl Monomers', International Journal of Polymeric Materials, 30: 3, 159 – 165 **To link to this Article: DOI:** 10.1080/00914039508028594 **URL:** http://dx.doi.org/10.1080/00914039508028594

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Water Repellency of Several Wood Species Impregnated with Vinyl Monomers

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(Received April 15, 1995)

Several hard and soft wood species (e.g., poplar, beech, alder, pine, fir and spruce), originated from Turkey, were prepared to wood plastic composites (WPC) with styrene (St) and a mixture of styrene and methylmethacrylate (St-MMA) monomers by using capillary uptake method. The average water uptake of the monomers-treated wood specimens was approximately between 43 to 64% due to water soaking for 72 h. The average water repellent effectiveness (WRE) of WPC was 54% and 55% for St and St-MMA, respectively. As far as water uptake is concerned, poplar gave the highest WRE values, whereas beech had the lowest one.

KEY WORDS wood species, styrene, methylmethacrylate, wood plastic composites, water repellent effectiveness.

1. INTRODUCTION

Wood is a three-dimensional polymeric composite made up primarily of cellulose, hemicellulose, and lignin, which are responsible for most of physical and chemical properties exhibited by wood. In fact, wood is very susceptible to moisture, and moisture in cell wall have a great influence on the all wood properties, but moisture in voids affects only weight.¹⁻³

Impregnation of wood with vinyl monomers followed by *in situ* polymerization is one of the practical methods to minimize the amount of absorbed water. For example, the water uptake of 81% was reported for methylmethacrylated-wood specimens at 80% WPG.⁴ The water uptake of 60% was found for various wood

species treated with St.⁵ Moreover, a WRE of 85–99% was reported for southern pine impregnated with multifunctional monomers.⁶

However, all accessible sites for water uptake are not completely sealed off even at about 190% WPG of polymer,² and many monomers used to make WPC do not penetrate the cell walls and do not completely fill the voids after polymerization due to shrinkage of the polymer.^{1.7}

The objectives of this research were to polymerize monomer, St and a mixture of St-MMA in several hard and soft wood species, originated from Turkey, and compare to the performance of wood polymer composites in view of water resistance.

2. MATERIALS AND METHODS

2.1 Materials

Both hardwood and softwood species of Turkish origin, such as black poplar (*Populus nigra* L.), black alder (*Alnus glutinosa* Mill. Gaertn.), oriental beech (*Fagus orientalis* L.), scotch pine (*Pinus sylvestris* L.), oriental spruce (*Picea orientalis* L.), and caucasian fir (*Abies nordmanniana* L.), were used as wood samples. Test specimens, having dimensions of $25 \times 25 \times 12.5$ mm, were prepared by sawing sapwood longitudinally.

Styrene (St), and a mixture (5:2 weight ratio) of styrene-methyl methacrylate, (St-MMA) were used as monomers. 2,2'-azobisisobutyronitrile (AIBN) was used as an initiator for the *in situ* polymerization. Both St and MMA were purified from inhibitors, 1,4-benzendiol and monoethyl ether of 1,4-benzendiol, by using CaCl₂.

2.2 Impregnation Process and In situ Polymerization

A capillary uptake method was used for the impregnation of vinyl monomers (i.e., St and St-MMA) into the wood. The samples, which were conditioned previously to about 9% equilibrium moisture content (EMC) in a humidity chamber, were subjected directly to a vacuum of 25-cm Hg for 30 min at ambient temperature to remove air from wood. The free vinyl monomers containing 0.1% (by weight of vinyl monomers) AIBN, were introduced into vacuum chamber containing wood samples until the wood samples were covered. After 1 hour of impregnation, vacuum was released, and the impregnation process continued for another 24 h under atmospheric pressure in order to get sufficient penetration of the monomers into wood samples. Finally, impregnated wood samples were taken out and wiped out to remove excess monomer from wood surfaces. The wood samples were wrapped up in aluminum foil and thermally polymerized at $60-70^{\circ}$ C for 24 h. After polymerization, the unwrapped samples were oven-dried at 50°C for 12 h to remove unreacted monomers. The weight of samples were taken after curing procedure.

All of the samples, both control and treated, were immersed in liquid water for various periods of time. After each soaking period, the excess water were wiped out from wood surfaces and weight of the samples were taken. The water uptake was determined for 2, 4, 8, 24, and 72 h on the basis of oven-dry measurements, and calculated using the following Equation (1):

$$D = \frac{W_1 - W_0}{W_0} \times 100$$
 (1)

where D is the water uptake (%), W_1 is the weight of water-soaked specimen (g), and W_0 is the weight of oven-dried specimens (g).

Water repellency which was measured for various periods as resistance to water uptake is expressed as water repellent effectiveness (WRE), and it was calculated from the Equation (2)³:

$$WRE = \frac{D_c - D_t}{D_c} \times 100$$
 (2)

where D_c is the water uptake of untreated samples immersed in water for various period (g) and D_t is the water uptake of treated samples immersed in water for the same time as control (g).

Scanning electron microscopy (SEM) was performed to examine the distribution of St-MMA co-polymer in poplar wood samples. The samples $(3 \times 3 \times 3 \text{ mm})$ were coated with gold palladium (Au:Pd = 50:50) vapor in a vacuum evaporator (Technics Sputter Coater). The samples were examined in a scanning electron microscope (JEOL SEM) operated at 20 Kev.

3. RESULTS AND DISCUSSION

Table I shows relation between the density of wood species under study and the average weight percent gain (WPG). The WPG values vary between 17 and 39% for the wood samples treated with St only and between 15 and 64% for those

TABLE I

The density of several untreated wood and WPG of St- and a mixture of St and MMA-treated wood species

Wood species	Treatment	Density" (g/cm ³)	
Poplar	St	0.382	39.13
•	St-MMA	0.387	64.17
Alder	St	0.521	27.39
	St-MMA	0.539	39.16
Beech	St	0.638	17.23
	St-MMA	0.629	15.30
Pine	St	0.450	20.70
	St-MMA	0.445	17.22
Spruce	St	0.415	24.81
	St-MMA	0.432	25.20
Fir	St	0.446	28.84
	St-MMA	0.440	25.93

"Density of untreated wood.

TABLE II

Comparison of water uptake percent of St- and a mixture of St and MMAtreated several wood species with those of untreated ones a function of various water soaking times

		Water uptake (%) Soaking time (h)					
Treatment							
	2	4	8	24	48	72	
Poplar							
Control	73.5	103.4	116.4	139.3	162.7	170.3	
St	15.5	26.2	35.4	45.9	56.5	63.9	
St-MMA	07.6	15.2	25.2	32.5	41.3	45.4	
Alder							
Control	43.2	55.5	64.4	78.0	93.3	97.4	
St	09.7	15.1	22.2	33.8	43.0	49.3	
St-MMA	08.4	12.9	20.1	31.1	41.3	48.9	
Beech							
Control	42.1	56.1	61.4	73.2	83.0	85.8	
St	08.1	13.9	21.1	32.0	38.6	45.7	
St-MMA	06.7	13.2	20.6	29.9	37.4	42.9	
Pine							
Control	49.3	69.4	72.5	84.9	97.8	110.8	
St	17.6	25.6	36.1	40.5	50.8	57.0	
St-MMA	12.2	20.7	28.1	39.4	49.6	56.4	
Sprue							
Control	64.4	86.2	90.7	101.8	121.3	132.8	
St	17.2	26.2	30.5	42.1	52.3	60.1	
St-MMA	13.5	22.6	31.6	47.6	55.6	61.4	
Fir							
Control	73.6	87.6	96.7	107.7	128.8	136.4	
St	12.5	22.0	31.2	43.4	52.8	61.0	
St-MMA	10.2	18.6	26.0	35.7	44.1	50.2	

treated with a mixture of St and MMA under the experimental conditions. It is also evident from this table that the highest impregnation yield (64%), i.e., WPG, is found for poplar with a density of 0.38 g/cm³, whereas the lowest one (15%) is for beech with a density of 0.682 g/cm³, suggesting a significant relation between the impregnation yield and the density of wood.

Similarly, WPG of 8-63% were reported for various wood species treated with several vinyl monomers,⁸ and WPG of 25-102% for several monomers were found for pine species.⁹

Table II presents the water uptake values (in percent) of the wood samples. As shown in the table, during the first 2 h of water soaking, the water uptake of untreated samples ranges from about 42 to 74%, whereas that of WPC samples containing St and a mixture of St and MMA ranges from 9 to 18% and 8 to 12%, respectively. As for a 72-h water soaking test, the water uptake values of the untreated wood samples are about 97 to 170%, whilst those of WPC in the presence of St and a mixture of St and MMA are approximately 46 to 64% and 43-61%, respectively.

These results reveal that through the deposition of St-MMA copolymer in voids of wood (as shown in Figure 1), hygroscopicity of wood can be controlled to some

WATER REPELLENCY OF WOOD

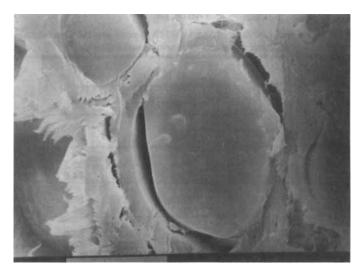
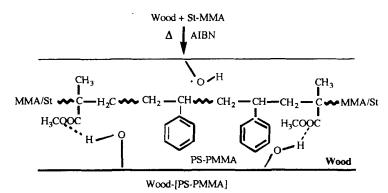


FIGURE 1 SEM micrograph of poplar treated with a mixture of St and MMA (3000×).



SCHEME I Hypothetical reaction of wood-[PS-PMMA] composite.

extent. It is also obvious from Table I that, in general, the performance of Sttreated samples is somewhat higher than that of St-MMA treated ones regardless of wood species even though the amount of polymer loading, i.e., WPG obtained for St treatment is higher than that of a mixture of St and MMA treatment, for example, for pine, fir, and beech. This can be attributed to the hydrogen bonding, which reduce hydrophilic behavior of wood, between MMA and —OH groups of cellulose in wood in the presence of an initiator (as shown in reaction Scheme I).

On the other hand, after a water soaking test of 72 h, the highest water uptake values are observed for St-treated poplar with the lowest density, while the lowest values are for beech with higher density in the case of St-treatment.

The water repellent efficiency (WRE) is listed in Table III. As shown in this table, during the first 2 h of water immersion, the WRE of the samples treated with St ranges from 64 to 87%, while those of ones treated with the mixture of St and MMA ranges from 75 to 90% for the same wood species. On the other hand, during a 72-h water immersion, the wood samples treated with St result in WRE

		<u></u>	WRE (*	%)		
Treatment						
	2	4	8	24	48	72
Poplar						
St	78.9	74.6	69.6	67.0	65.2	62.4
St-MMA	89.6	85.2	78.3	76.6	74.5	73.3
Alder						
St	77.4	72.8	65.3	56.5	53.8	49.3
St-MMA	80.4	76.7	68.7	60.0	55.7	49.7
Beech						
St	80.6	75.2	65.7	56.2	53.5	46.7
St-MMA	83.8	76.7	66.3	59.1	54.8	49.9
Pine						
St	64.2	63.0	50.1	48.7	48.5	47.8
St-MMA	75.1	70.1	61.2	51.1	49.2	49.0
Sprue			·····			
St	73.2	69.5	66.3	58.5	57.2	54.7
St-MMA	79.0	73.7	65.1	53.1	54.1	52.0
Fir						
St	82.9	74.8	67.7	59.7	58.9	55.2
St-MMA	86.6	78.7	73.1	66.8	65.7	63.1

WRE of St- and a mixture of St and MMA-treated several wood species immersed in water for various soaking times

ranging from about 49 to 63%, while for those treated with the mixture of St and MMA, WRE changes from 49 to 73%. Incidentally, WRE of about 33, 45 and 61% was reported for pine, spruce, and beech impregnated with mocroinimeric initiator.¹⁰

As in water uptake measurements, the mixture of St and MMA is found to be more effective than St alone with result to *WRE* evaluation. This phenomenon can also be explained by the reaction Scheme I, that is, hydrogen bonding between MMA and —OH groups in wood.

Poplar wood species has a highest WRE range (between 70 and 90%) in the case of St-MMA treatment, regardless of water immersion time, in comparison with the other species. This is explained by the highest amount of WPG as shown in Table I.

CONCLUSION

The treatment of several soft and hard wood species with St alone and the mixture of St and MMA brought about a considerable reduction in water uptake of wood. St-MMA comonomer treatment was found to be more effective than St alone as far as water uptake and *WRE* are concerned. Furthermore, poplar species showed the best water resistance performance amongst the other species used. Wood polymer composites thus prepared can be used for some special materials, e.g., vases, bowls, desk, caddies, letter holder, bag pipes, ancient abacus, etc.

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