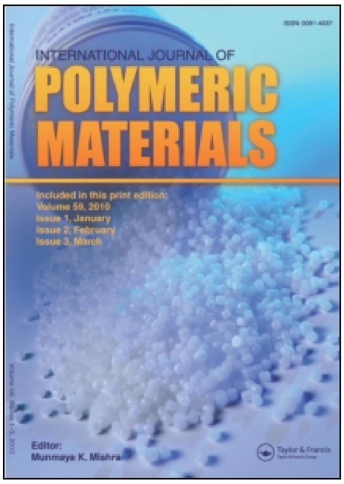

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Dimensional Stability of Several Wood Species Treated with Vinyl Monomers and Polyethylene Glycol-1000

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Several wood species (e.g., poplar, beech, alder, pine, fir and spruce) were successfully treated with three agents (e.g., styrene (St), a St and methylmethacrylate mixture (St-MMA), and polyethylene glycol (PEG)-1000). The polymerization of St and St-MMA monomers *in situ* was performed using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The maximum weight percent gain (WPG), 64.17%, was obtained for a lowest density wood species, e.g., poplar in the case of St-MMA copolymer. On the other hand, lowest value in WPG (about 15%) was obtained for beech with highest density. PEG-1000 treatment gave the highest antishrink efficiency (ASE) (about 84%) for poplar, followed by St and MMA mixture and St ones, respectively. However, maximum increase in density was achieved with St-MMA treatment. In general, the lower density, the better performance in dimensional stability.

KEY WORDS Wood, St and St-MMA, PEG-1000, polymerization, ASE.

1. INTRODUCTION

The poor dimensional stability of wood has been improved by reducing the hygroscopicity of wood,[1] through the formation of cross-links between the inter-fiber structural units in order to minimize separation of these units and stabilize dimensions,[2] and by the deposition of bulking agent within the swollen structure to reduce shrinkage.[1]

However, in the recent years the use of some agent like polyethylene glycols (PEGs), and also vinyl monomers (e.g., styrene, methylmethacrylate, etc.), has shown considerable interest. For instance, spruce saturated with 25% solutions of PEG, having molecular weights of 1000 or less, gave an antishrink efficiency of 100%.[3]

Similarly, vinyl monomers, e.g., methylmethacrylate, has been incorporated into wood samples with up to 100% weight gain, and then polymerized in the lumens, improved wood's dimensional stability.[4] Generally speaking, vinyl polymers simply bulk the wood structure by filling the capillaries, vessels, and other void spaces.[5]

Present study has been undertaken in order to compare the dimensional stability of several hard and soft wood species, which were grown in Turkey, treated with St monomer and St-MMA co-monomer with that of PEG-1000.

2. MATERIALS AND METHODS

2.1 Wood 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 × 25 × 12.5 mm, were prepared by sawing sapwood longitudinally.

2.2 Chemicals

Styrene (St), and a mixture (5:2 weight ratio) of styrene and methylmethacrylate, (St-MMA), and 30% aqueous solution of PEG-1000 (Dow's carbowax) were used as bulking agents 2,2'-azobisisobutyronitrile (AIBN) was used as an initiator for the polymerization. Both St and MMA were purified from inhibitors, 1,4-benzendiol and monoethyl ether of 1,4-benzendiol, by using $CaCl_2$.

2.3 Impregnation Processes

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 (25-cm Hg) for 30 min at ambient temperature to remove the air from wood. The vinyl monomers containing 0.1% AIBN (by weight of vinyl monomers) were introduced into vacuum chamber until the wood samples were covered. After 1 hour of impregnation, vacuum was released, and the impregnation process was carried out for another 24 h under atmospheric pressure. 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°C for 24 h. After polymerization, the unwrapped samples were oven-dried at 50°C for 12 h to remove unreacted monomers. Both weight and dimensions of samples were taken after curing procedure.

However, the wood species saturated with water were treated with PEG-1000 by using Gillwald-Jonat's method, i.e., stepwise increasing pressure method, in order to accelerate treatment. The detail of the treatment was reported in a previous study.[6]

2.4 Characterization

Both untreated and treated wood samples were subjected to water soaking test. Volume of the sample (i.e., WPC) was calculated from the outside dimensions measured to the nearest 0.001 cm with a microcaliper. Ten samples for each treatment as well as control were evaluated, and the averages of the results were reported.

Dimensional stability of the impregnated wood samples was evaluated with antishrink efficiency (ASE) values measured after 7 days of soaking in distilled water, and calculated according to following Equations 1 and 2[4]:

$$S(\%) = \frac{V_2 - V_1}{V_2} \times 100 \tag{1}$$

where S is the volumetric shrinkage coefficient, V_1 is the volume of wood oven-dried samples (for 24 h at 103 ± 2°C), and V_2 is the volume of wood after water soaking test.

$$\text{ASE}(\%) = \frac{S_c - S_t}{S_t} \times 100 \tag{2}$$

where S_c is the volumetric shrinkage of untreated wood and S_t is the volumetric shrinkage of treated wood.

Furthermore, following physical values were also calculated[4]:

$$\text{WPG}(\%) = \frac{W_t - W}{W} \times 100 \tag{3}$$

$$\text{BC}(\%) = \frac{V_t - V}{V} \times 100 \tag{4}$$

$$\Delta d(\%) = \frac{d_t - d}{d} \times 100 \tag{5}$$

where WPG is the weight percent gain of the treated wood samples, W_t is the oven-dry weight of the treated samples, W is the oven-dry weight of the untreated sample, BC is the bulking coefficient (%), V_t is the oven-dry volume of treated sample, V is the oven-dry volume of untreated sample, Δd is the increase in density (%), d_t is the density of the treated sample, d is the density of untreated one.

Scanning electron microscopy (SEM) was conducted to examine the distribution of the polystyrene (PS) and St-MMA co-polymer in poplar wood samples. The wood specimens were firstly soaked in water to soften and small cubic samples (3 × 3 × 3 mm) were cut using a sharp razor blade to yield smooth cross-sectional surfaces. After air drying for 24 hours, samples were glued to aluminum stubs using silver paste so that the cross-sectional surfaces were accessible for examination. The samples 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

The physical characteristics of six different wood species are presented in Table I. Table I reveals that for all types of treatments, the highest chemical loading, i.e., WPG, (64.17%) was obtained for poplar, due to its porous structure and lower density (0.38 gr/cm^3), while the lowest WPG (17.23%) was obtained for beech specimen with a density of 0.64 g/cm^3; suggesting that the lower the density of wood, the higher WPG values. In other words, WPG is strongly dependent upon the permeability of wood.

TABLE I

Characteristics of six wood species treated with St, St-MMA, and PEG-1000

Treatments	(WPG) (%)	Bulking coefficient (%)	Increase in density (%)	Shrinkage (%)
Poplar				
PEG-1000	43.43	7.25	33.16	1.73
St-MMA	64.17	0.69	54.84	10.54
St	39.13	3.65	30.59	10.24
Control (0.38)*	-	-	-	11.48
Alder				
PEG-1000	29.38	9.12	33.16	3.61
St-MMA	39.16	0.87	57.84	8.66
St	27.39	0.19	30.59	11.06
Control (0.52)*	-	-	-	12.17
Beech				-
PEG-1000	19.54	6.61	12.08	6.86
St-MMA	15.30	-1.88	16.95	14.30
St	17.23	-0.49	16.16	14.09
Control (0.64)*	-	-	-	12.78
Pine				
PEG-1000	34.05	8.24	22.66	3.74
St-MMA	17.22	4.76	11.55	7.14
St	20.70	0.65	17.33	10.16
Control (0.45)*	-	-	-	11.48
Fir				
PEG-1000	33.79	6.97	24.10	4.19
St-MMA	25.93	0.26	20.31	11.66
St	28.84	0.76	25.22	11.34
Control (0.44)*	-	-	-	11.84
Spruce				
PEG-1000	38.40	8.23	27.21	3.64
St-MMA	25.20	1.12	18.31	12.00
St	24.81	1.41	16.38	11.43
Control (0.42)*	-	-	-	13.00

*Density (gr/cm^3).

Table I also indicates that bulking coefficients of wood species are 6.61 to 8.24%, −1.88 to 3.65, −0.49 to 1.415 in the presence of PEG-1000, St-MMA, and St, respectively. Because of higher penetration of PEG-1000 into cell wall structure, PEG-1000 had the highest bulking coefficient values compared to two other vinyl monomers irrespect to the wood species used. For the vinyl monomers, however, it was reported that when the vinyl monomers in this study were treated by the solvent exchange method under vacuum and dried after curing, some internal checks could be improved in the samples.[4]

Once again, it is seen from Table I that the highest increase in density value (around 58%) is found for poplar species in the case of St-MMA due to its highest loading level of 64.175%. Moreover, it is also found that the increase in density is directly proportional to WPG value. The volumetric shrinkage data for the treated and untreated specimens are also presented in Table I. It is obvious that the higher vinyl monomer loading in the wood specimen results in lower dimensional stabilization. The lowest shrinkage value, i.e., 1.73% was obtained for poplar by using PEG-1000 agent. Furthermore, PEG-1000 offers the lowest volumetric shrinkage value in comparison with those of St and St-MMA.

Figure 1 shows the antishrink efficiency (ASE) of six types of wood species due to impregnation with three bulking agents. Figure 1 reveals that PEG-1000 is found to be a most effective bulking agent regardless of wood species with ASE values ranging from 46.28 to 83.97%. Our present observation is in a good agreement with the literature.[4] Mixture of St and MMA treatment gives somewhat better ASE values than that of St only. For St and St-MMA treatment, low ASE values are obtained due most probably to lower bulking efficiency (as shown in Table I) in comparison with that of PEG-1000. As more chemical could get into the cell wall structure of wood, it results in better ASE values for PEG-1000.

For St-MMA, ASE values range from −11.83 to 32.00%, while for St only ASE values range from −10.19 to 12.07%. It is also evident from this figure that the highest ASE values for each of the three bulking agents were: 83.97% for poplar

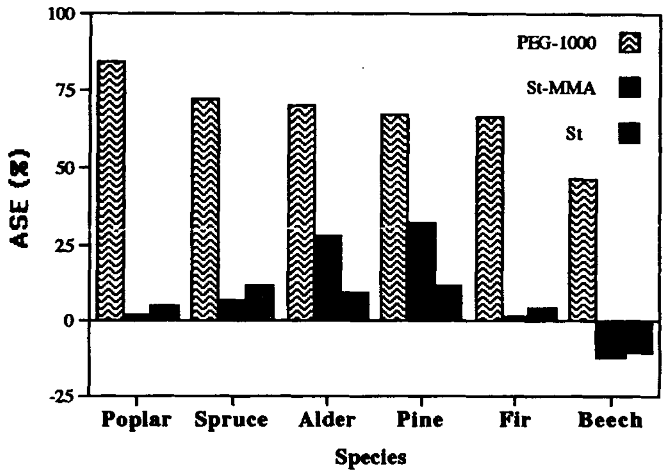
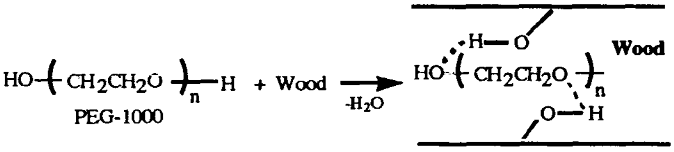


FIGURE 1 Comparison of antishrink efficiency (ASE) of several wood species treated with St and St-MMA with those of PEG-1000.

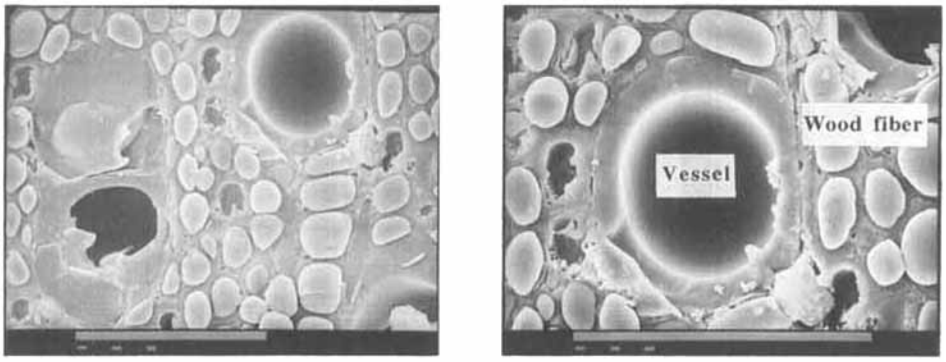
in case of PEG-1000; 32.00% for pine in case of St-MMA; 12.07% for alder in case of St. Furthermore, for all bulking agents, the lowest ASE values are obtained from beech species because of its higher density, which resulted in higher WPG values as listed in Table I. In the case of beech, negative antishrinkage phenomenon was observed for the treatment with St and St-MMA.

The reason for this phenomenon is not clearly understood. However, the shrinkage of the system happened due to crosslinking of the vinyl monomers with the cellulose, thus causing the entire system to shrink upon polymerization of the monomer, or due to some type of internal stress.[4]

The above-mentioned results indicate that in order to prepare WPC with better dimensional stability PEG-1000 is more effective in comparison with those of the vinyl monomers under the study. This fact can be explained by the following hypothetical reaction Scheme I and good deposition of PEG-1000 in the wood cell. As shown in the scheme PEG-1000 is a polar substance, which is compatible to hydrophilic cellulose present in wood. Moreover, PEG-1000 can be fitted into the wood structure due to intermolecular hydrogen bonding between PEG-1000 and cellulose. On the other hand, vinyl monomers like St and St-MMA in the presence of initiator, AIBN, and heat may have the possibility to bulk the inside of the wood through grafting into wood along with ungrafted homopolymer and copolymers. Although polymers are non-compatible to wood, their hydrophobic behavior assists to decrease the hydropic behavior of wood and at the same time to increase the dimensional stability. Once again, St-MMA is more effective than that of St alone, because similar to PEG-1000 MMA can form to some extent hydrogen bonds with —OH groups of cellulose.[7]



SCHEME I Hypothetical chemical structure of interfacial area of wood-PEG-1000.



(a) (b)

FIGURE 2 SEM micrographs of poplar treated with St (1000×) (a) and St-MMA (3000×) (b).

In addition, SEM micrographs of poplar wood-polymer composites show very high and uniform filling in fibers by St and St-MMA copolymer as illustrated in Figures 2a and 2b, respectively. However, it is also demonstrated in the figures that in the samples, volume shrinkage on polymerization as well as loss of monomer during curing led to hallow cylinder, i.e., partially filling the vessels.

CONCLUSIONS

The wood samples treated with PEG-1000 resulted in significant reduction in shrinkage during drying in comparison with those of St and St-MMA treatments. Poplar species gave the highest ASE value (83.97%) in the case of PEG-1000, followed by spruce, alder, pine, fir, and beech, respectively. The lower the density of a wood species, the higher weight percent gain. Through treatment PEG-1000, wood could be dried in safe, i.e., without drying defects. As a result, PEG-1000 would largely be used in the treatment of wood for some special uses, such as wooden statue, parquet, pencil, historical items, etc.

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