Improvements of White Pine Wood Properties by Impregnation with Unsaturated Polyesters in Admixture with Styrene

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ABSTRACT: Four unsaturated polyester resins based on poly(ethyleneglycol-maleate-phthalate) (PE) with different bromine contents were used for the impregnation and coating of oven-dried white pine wood samples in admixture with styrene (St). Curing was affected by the initiator–heat technique by using 0.2 wt % of benzoyl peroxide (Bz_2O_2). It was found that the use of the four prepared unsaturated polyester/styrene (PE/St) mixtures resulted in the formation of wood plastic combinations (WPC) with a higher percentage retention, higher percentage crosslinking, water repellent effectiveness, and antiswelling efficiency. ASE properties are excellent for wood samples impregnated with resin without bromine. Water absorption was decreased and a good water uptake was obtained by wood samples impregnated by resin of lower bromine content. Compressive strength was increased for all samples, especially for the wood samples impregnated with resin without bromine. The flammability test for the prepared plastics showed that the samples without bromine are classified as burning substance and the other three samples contain bromine are classified as self-extinguishing samples from ASTM D635-68T (1956). On the other hand, impregnated wood samples with PE/St mixtures show no fire retardancy after carrying ASTM E160-50 (1965), whereas coated wood samples with the same mixtures show excellent fire-retarding properties. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1410–1416, 2001

Key words: white pine wood; impregnation; unsaturated polyesters; water repellent; antiswelling; compressive strength; fire retardancy

INTRODUCTION

Wood may be modified in various ways to change its physical,[1] chemical[2] and biological properties.[3] One of the techniques for altering the properties of wood that has received considerable attention in the last few years is the formation of wood plastic combination (WPC), by incorporating into the wood matrix, either monomers (such as methylmethacrylate,[4] vinyl chloride,[5] vinyl acetate,[1] a mixture of different monomers,[6] urea formaldehyde[7]) or epoxy resin.[8] Various types of unsaturated polyester resins have been successfully used for wood impregnation in admixture with styrene because the volatilization of the impregnating mixture is significantly reduced from the wood matrix, and thus WPC may be produced either by radiation[9,10] or by thermal curing.[11]

The aim of the present work was to strengthen weakness of grade, low density, and fire retardancy of white pine wood by impregnating and coating several samples of white pine wood with four kinds of PE/St resins. The physicomechanical and fire-retarding properties of the resulting WPC are studied and the effect of variation of bromine content (in wt %) in PE/St resins on such properties is also

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discussed. The final goal is to improve dimensional stability, reduce water absorption, increase compression strength, and enhance fire retarding property of the white pine wood.

EXPERIMENTAL

Wood Samples

Samples of as high homogeneity as possible of white pine were chosen from several defect-free boards of white pine wood. They were cut into blocks of 0.5 × 0.5 × 1.0 in. for measurement of water absorption and dimensional change, into blocks of 0.787 × 0.787 × 1.181 in. for measurements of compression strength, and into blocks of 0.5 × 0.5 × 3.0 in. for measurements of fire retardancy. The surface was smoothed carefully to avoid blocking of the pores.

Polyester Resins

Different samples from polyester resins were prepared and purified following the procedure reported[12] by the polycondensation of ethylene glycol (0.3 mol), maleic anhydride (0.279 mol), and phthalic anhydride (0.021 mol). The other samples were prepared by the same procedure by polycondensation of ethylene glycol (0.3 mol), maleic anhydride (0.2864, 0.2790, and 0.2700 mol), and tetrabromophthalic anhydride (0.0136, 0.0210, and 0.0300 mol). After that the four prepared polyester resins were admixed with 30 wt % of styrene monomer to give the final impregnated resins with bromine concentrations 0.0, 5.3, 7.8, and 10.6 wt %, respectively.

Impregnation Technique

The wood samples (density 0.386 gm/cm^3 at approximately 9% moisture content) were oven-dried at 105°C for 9 h, after which they were placed in a desiccator and held under reduced pressure for 0.5 h. The desiccator was then flooded with sufficient PE/St mixture (after diluting the resin by a sufficient quantity of chloroform) from a dropping funnel to completely immerse the wood samples. After 1 h of soaking under reduced pressure, the system was then vented to atmospheric pressure and the samples were allowed to soak for a further 2 h to ensure maximum PE/St mixture uptake. The wood samples were dried in air and curing was then achieved at 60°C for 24 h, at 80°C for 2 h, and finally at 105°C for 2 h to ensure maximum crosslinking. They were then put in a desiccator under vacuum for 0.5 h to ensure removal of uncured products.

Other samples of white pine wood sheets 0.40 in. in thickness, 0.50 in. in width, and 5.00 in. in length were treated by PE/St mixtures (0.0, 5.3, 7.8, and 10.6 wt %, respectively) by a simple dipping process. Polymerization was achieved by an initiator–heat technique at 85°C for 2 h and wood sheets were dried at 105°C for 12 h.

Measurements

The following values were obtained:

$$\% \text{ PE/St retention } (R) = [(W_1 - W_0)/W_0] \times 100$$

$$\% \text{ Crosslinking} = [1 - (W_1 - W_2)/W_1] \times 100$$

$$\% \text{ Total volumetric swelling}[13] = [(V_1 - V_0)/V_0] \times 100$$

$$\% \text{ Antiswell efficiency}[13] = [(S - S_1)/S] \times 100$$

$$\% \text{ Weight gain of WPC} = [(W_2 - W_0)/W_0] \times 100$$

$$\% \text{ Volume change} = [(V_t - V_0)/V_0] \times 100$$

where W_0 and W_1 are oven-dry weights of wood samples before and after impregnation, respec-

Table I Effect of Changing Bromine Content in PE/St Resin on Percentage Retention (R) and Percentage Crosslinking of WPC

Sample Number[a]	Bromine Content (wt %)	W_0	W_1	W_2	Retention (R) (%)	Crosslinking (%)
1	0.0	1.54	3.75	3.69	143	98
2	5.3	1.61	3.85	3.74	139	97
3	7.8	1.60	3.51	3.37	120	96
4	10.6	1.79	3.63	3.42	103	94

[a] All weights are average of six samples.

Table II Effect of Changing Bromine Content in PE/St Resin on Wood Percentage Gain of WPG, Volume Change (%), and Density Change

Sample Number	Bromine Content (wt %)	WPG (%)	V_0 (cm^3)	V_t (cm^3)	Volume Change (%)	d_0[a] (gm/cm^3)	d[a] (of WPC)
1	0.0	139	4.23	4.23	0.09	0.37	0.87
2	5.3	132	4.24	4.29	1.29	0.38	0.87
3	7.8	110	4.23	4.31	2.04	0.38	0.78
4	10.6	91	4.24	4.41	3.90	0.42	0.77

[a] d_0 and d are average densities of untreated and treated wood samples after drying at 105°C for 12 h (average data from six samples).

tively; W_2 is the weight of WPC after soaking in chloroform for 6 days; V_0 and V_1 are the total volumes of untreated and treated wood samples before and after the water-soaking test, respectively, for 7 days; V_t is the final volume of impregnated wood samples after drying at 105°C for 12 h; and S and S_1 are the percentage total swellings before and after treatments, respectively.

Water Absorption and Dimensional Change

Specimens of 0.5 × 0.5 × 1.0 in. were used for this study. Treated and untreated samples were oven-dried at 105°C for 12 h and then submerged in distilled water for different time intervals (2, 4, 8, 24, 48, 72, 144, and 168 h). After soaking, the surfaces of the wood samples were dried roughly with a towel. The percentage water absorbed, percentage volumetric swelling coefficient, and the ASE were calculated.

Compression Strength

Compression strength parallel and perpendicular to grain was measured by a Universal Testing Machine using samples of 2 × 2 × 3 cm for treated and untreated wood samples. Compression strength was performed according to the procedure of Egyptian Standard[14] (ES-650-1965). Samples were placed on a testing machine under a constant deformation rate of 0.0635 cm/min (accuracy in sample dimensions must not be lower than 0.3%). Compression strength in parallel and perpendicular directions was calculated from the equation $\sigma_c = P/A$, where P is the maximum external force (kg) and A the cross-sectional area of the sample (cm^2).

Flammability Test

ASTM D635-68T (1956) (for Rigid Plastics)

This method covers a laboratory procedure for determining the relative flammability of rigid plastic in the form of sheets or molded bars over 0.050 in. in thickness.

ASTM E160-50 (1965) (Crib-Test for Treated Wood)

This method covers a Crib-test procedure for fire tests for combustible properties of treated wood to reduce flammability. The Crib-test specimens cut from the selected sample consisted of 24 pieces 0.5

Table III Effect of Soaking Time on Percentage Water Absorption of WPC Compared to That of Untreated Wood

Sample Number	Bromine Content (wt %)	Water Uptake[a] (%) at Various Soaking Times							
		2 h	4 h	8 h	24 h	48 h	72 h	144 h	168 h
Control	—	84	86	90	98	107	112	126	130
1	0.0	39	45	52	62	66	68	71	74
2	5.3	7	11	15	24	27	28	29	30
3	7.8	7.5	15	21	36	41	43	45	46
4	10.6	10	16	23	40	45	47	50	51

[a] Average data from six samples.

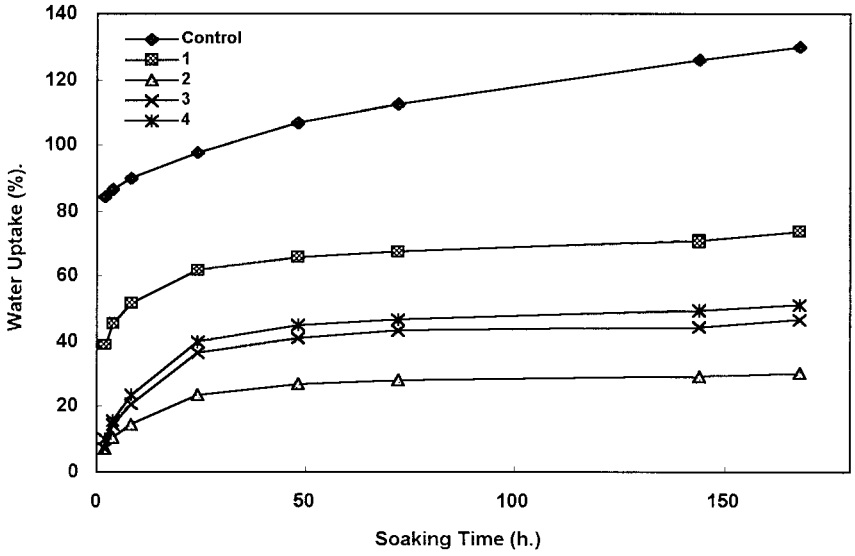

Figure 1 Effect of soaking time on percentage water uptake of treated and untreated wood samples.

$\times$ 0.5 in. in cross section and 3 in. in length, with surfaces smooth-sawed to dimensions within $\pm$0.0794 in. and moisture content of specimen when tested should be 7 $\pm$ 3 wt % of dry material.

Flame-Spread Test for Coated Wood Samples

The flame-spread test for the combustibility of materials was used to determine the rate of flame spread and to measure the ability of assemblies to act as a barrier to the further spread of flame.

RESULTS AND DISCUSSION

Effect of Changing Bromine Content in the PE/St Resins on Percentage Retention (*R*) and Percentage Crosslinking

Data in Table I indicate high percentage retention values for all four samples (103–143%), especially for the samples without bromine. Table I also shows high percentage crosslinking for all WPC (94–98%), especially for impregnated wood samples by resin without bromine content.

The wood percentage gain (WPG) (after the removal of uncured monomers), volume change (%), and density of treated wood samples are given in Table II. The highest WPG values (139.00%) were obtained for impregnated wood samples with the PE/St mixture without bromine content, which decreased with increasing bromine content to reach its lower value (91%) for PE/St mixture of higher bromine content of 10.6 wt %. The density of the whole polymerized wood was found to be from 0.87 g/cm^3 (for impregnated wood samples with PE/St without bromine content) to 0.77 g/cm^3 (for impregnated wood samples with PE/St mixture of 10.5 wt % bromine). In addition, the values of average volume change of wood samples were found to be 0.09, 1.29, 2.04, and 3.90% for impregnated wood sam-

Table IV Water Repellent Effectiveness (WRE) of Wood Polymer Composites

Sample Number	Bromine Content (wt %)	WRE[a] (%) at Various Soaking Times							
		2 h	4 h	8 h	24 h	48 h	72 h	144 h	168 h
1	0	27	17	6	0.66	3	5	12	12
2	5.3	82	73	63	47	45	45	49	49
3	7.8	78	67	53	27	24	24	30	31
4	10.6	76	63	46	19	16	17	21	21

[a] Average data from six samples.

Table V ASE of Wood Polymer Composites After 7 Days of Immersion in Water at 18°C

Sample Number	Bromine Content (wt %)	Swelling Coefficient (S)	ASE[a]
Control	—	15.26	—
1	0.0	13.52	13
2	5.3	11.80	29
3	7.8	11.02	39
4	10.6	10.28	48

[a] All samples were dried at 105°C for 12 h, average data from six samples.

ples with resins containing 0.0, 5.3, 7.8, and 10.6 wt % bromine, respectively. There is a good agreement between our results and those in the literature.[15,16]

The water uptake values (%) of the wood specimens are shown in Table III. During the first 2 h of water soaking, the control samples took up about 84% water and WPC took up about 39, 7, 8, and 10% water for impregnated samples with PE/St mixture of bromine content of 0.0, 5.3, 7.8, and 10.6 wt %, respectively. After 168 h of water soaking the control samples took up about 130% water, whereas wood polymer composites took up about 74, 30, 46, and 51% water for impregnated wood samples with PE/St mixture of 0.0, 5.3, 7.8, and 10.6 wt % bromine respectively, for the prepared PE resins containing bromine. The highest water uptake value of treated samples with PE/St mixture without bromine content was attributed to the higher impregnation yield, as measured by WPG after final cure and drying, for all of the other three impregnated wood samples. As the bromine concentration increased from 5.3 to 10.6 wt % in the impregnating mixture, the average water uptake values of all treated wood samples increased, as seen in Figure 1. It was found that there was good agreement between our result obtained for water uptake and that of the literature.[16]

Dimensional stability and water repellency were measured using a simple water-soaking test. The test estimates not only water repellency (from data obtained for various periods) but also provides a measure of dimensional stability (from data obtained for long-term water soaking). As shown in Table IV, water repellent effectiveness (WRE) was greatly improved for the samples containing bromine.

WRE values for the 2-h period were 82, 78, and 76% for the samples containing 5.3, 7.8, and 10.6 wt % bromine, respectively, and 27% for the free-bromine WPC (compared to samples containing bromine), whereas those for a period of 168 h were found to be 12% for the free-bromine WPC but 49, 31, and 21% for impregnated samples with PE/St mixture of bromine concentration of 5.3, 7.8, and 10.6 wt %, respectively. This result in general is attributed to the higher impregnation yield of treated wood samples. However, the effect of impregnation yield was not shown as a main effect on WRE because of the density of wood and other variables. As seen in Table IV, decreases in WRE values are not linearly proportional to soaking times (2, 4, 8, 24, 48, 72, 144, and 168 h) for all species. There is good agreement between our results and those in the literature.[16]

Volumetric swelling (%) in a 1-week water-soaking test is shown in Table V. The ASE values for impregnated wood–polymer composites with PE/St mixtures with various concentrations of bromine varied proportionally with increasing bromine concentration in PE/St mixtures. Most samples showed significant gain in antiswell efficiency, indicating improved resistance to swelling. On long-term exposure to water, where the highest value of ASE (48.497) is obtained for the

Table VI Compression Strength Parallel and Perpendicular to Grain of WPC Compared to That of Untreated Control

Sample Number[a]	Bromine Content (wt %)	Compression Strength	
		Parallel to Grain (kN/m^2)	Perpendicular to Grain (kN/m^2)
Control	—	40	5
1	0.0	66	15
2	5.3	59	12
3	7.8	56	11
4	10.6	47	9

[a] Average data from three samples.

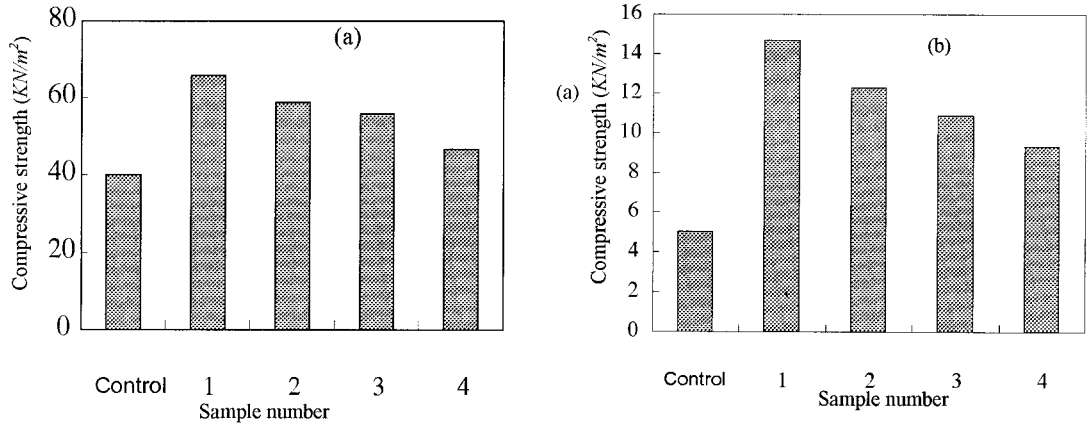

Figure 2 Compression strength of treated and untreated white pine wood average of three samples: (a) parallel to grain; (b) perpendicular to grain.

impregnated wood of samples by PE/St mixture with 10.6 wt % bromine, but the lowest value (13) is obtained for the wood samples impregnated with PE/St mixture without bromine content.

The compressive strength of impregnated wood samples is compared to that of untreated wood, as shown in Table VI. The compressive strength (in both directions, parallel and perpendicular to grain) of all samples was improved compared to that of untreated wood samples. The highest values for compressive strength were 66 and 15 kN/m^2 in the parallel and perpendicular direction, respectively, which were obtained for impregnated wood samples with PE/St mixture without bromine content. But the compressive strength for WPC in the case of 10.6 wt % bromine was found to be 47 and 9 kN/m^2, whereas untreated wood samples had 40 and 5 kN/m^2 in both directions, respectively. See Figure 2(a) and (b).

Fire Retardancy

ASTM D635-68T (1956)

The specimen without bromine content continues to burn after the first ignition and was classified as a burning substance, with a burning rate $(180/t)$ = 81.08 in./min. However, the other three samples containing bromine were classified as self-extinguishing, in which the flame dose did not reach to the 4-in. mark after the second ignition and the extent of burning had its highest value (0.40 in.) for the polymer sample with higher bromine content, as illustrated in Table VII.

ASTM E160-50 (1965)

The original and final weights, and glowing and flaming time were determined. The loss in weight after all flaming and glowing shall be expressed as a percentage of the original weight of the specimen. It is obvious that all treated wood samples have little fire retardancy as a result of the shrinking of polymer into the bulk of the wood specimens, further resulting in the higher flaming and glowing time and subsequently higher weight loss (95–90%) after all flaming and glowing has ceased for wood samples treated with PE/St resins of 0.0, 5.3, 7.8, and 10.6 wt % bromine, respectively.

Table VII Relative Flammability of the Rigid Prepared Plastics of Various Bromine Weight Percentages by ASTM D635-56T (1956)

Sample Number[a]	Bromine Content (wt %)	Extent of Burning (in.)	Burning Rate (in./min)	Classification of Samples
1	0	—	81.08	Burning
2	5.3	0.63	—	Self-extinguishing
3	7.8	0.45	—	Self-extinguishing
4	10.6	0.40	—	Self-extinguishing

[a] Number of specimens tested, 10; thickness of specimens, 0.792 in.

Table VIII Flame-Spread Test of White Pine Wood Sheets Coated by PE/St Resins

Sample Number[a]	Bromine Content (wt %)	Extent of Burning (in.)	Burning Rate (in./min)	Classification of Samples
Control	—	—	265	Burning
1	0.0	—	160	Burning
2	5.3	1.538	—	Self-extinguishing
3	7.8	1.136	—	Self-extinguishing
4	10.6	0.575	—	Self-extinguishing

[a] Data obtained were averaged from 10 samples for each PE/St resin.

Flame-Spread Test for Coated Wood Samples

On the basis of ASTM D635-68 we obtain the data included in Table VIII, which shows an inverse relation between bromine wt % and the distance burned by the flame from the free end. This relation has its highest value for wood sheets coated by PE/St resin without bromine content, to give a burning rate of 180 in./min, and the smallest burned distance for wood sheets coated by PE/St resin with the highest wt % of bromine, to give an extent of burning of 0.575 in. On the other hand, the burning rate of uncoated wood sheets was found to be 265 in./min, which classified them as a burning substance.

CONCLUSIONS

White pine wood samples were impregnated and coated by PE/St resins with various bromine contents after which curing and polymerization were affected by Bz_2O_2–heat technique, resulting in a wood plastic combination (WPC) with generally enhanced physical properties. The maximum percentage of retention, wood polymer gain, crosslinking, water uptake, and highest value of compression strength were obtained for wood samples impregnated by PE/St resin without bromine content. The highest value of WRE was obtained for wood samples impregnated by PE/St resin containing the lowest wt % of bromine. The maximum ASE percentage was obtained for wood samples impregnated by PE/St resin with the highest wt % bromine; and coated wood sheets impregnated by PE/St resin had the lowest extent of burning and classified as self-extinguishing. Molded polymers containing bromine were classified as self-extinguishing samples, whereas the free-bromine molded plastics were classified as burning substances. Thus coated wood had a better fire retardancy than that of impregnated wood samples. This procedure can be used in the treatment of wood for some special uses.

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