

Improvement of Wood Properties by Impregnation with Macromonomeric Initiators (Macroinimers)

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SYNOPSIS

Scotch pine, eastern spruce, and eastern beech samples sawed longitudinally were impregnated with a new type of polymerization mixture (macroinimer and styrene), leading to crosslinked block copolymers of styrene and poly(ethylene glycol). Weight gains of 36.37–91.13% were obtained after polymerization for 2 h. Water uptake of the polymerized wood was found to be 35.13–72.07% after a water soak test of 144 h. While spruce gave the highest uptake (72.07%), beech showed the lowest value (35.13%). The specimens impregnated with the mixture of macroinimer and styrene showed a water-repellent effectiveness of 35.14–58.15% after a water soaking test of 144 h. The highest values of water-repellent effectiveness were found for spruce, while the lowest values were obtained for pine. A maximum antiseal efficiency (ASE) of 42.43% was obtained for spruce, followed in order by beech and pine, respectively. The ASE value increases with an increase in wt % gain. Improvements of 19.12% in longitudinal compression and 25% in bending strength were also achieved for spruce samples with low weight percent gain. IR spectroscopy was used for chemical characterization of the wood–polymer composite. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Treatment of wood to improve its physical and mechanical properties and dimensional stabilization due to moisture content and impart resistance to termites, decay, and marine organisms has been carried out via chemical modification or chemical impregnation.^{1,2} In chemical modification, compounds highly reactive to the hydroxyl groups of cellulose, hemicellulose, and lignin components of wood includes isocyanates, epoxides, anhydrides, lactones, and diols. Several liquid monomers such as styrene (St) and methyl methacrylate (MMA) were also incorporated into wood samples by means of chemical impregnation.³ Crosslinking of wood material in wood samples provides good dimensional stability to the wood–polymer composite.⁴

Macroinimers (macromonomeric initiators) reported by Hazer^{5,6} behave as macroinitiator,⁷ macromonomer,⁸ and macrocrosslinker⁹ in thermal

polymerization by themselves or copolymerization with a vinyl monomer. Macroinimers can also be prepared from the mixture of polyazoester (PAE-200), toluene diisocyanate (TDI), and hydroxyethyl methacrylate (HEMA) in the mol ratio of 1 : 2 : 2, respectively.¹⁰ This work refers to the impregnation by the mixture of PAE-200, TDI, and HEMA in St leading to the one-shot polymerization thermally. Scheme 1 shows the reaction pathways on impregnation.

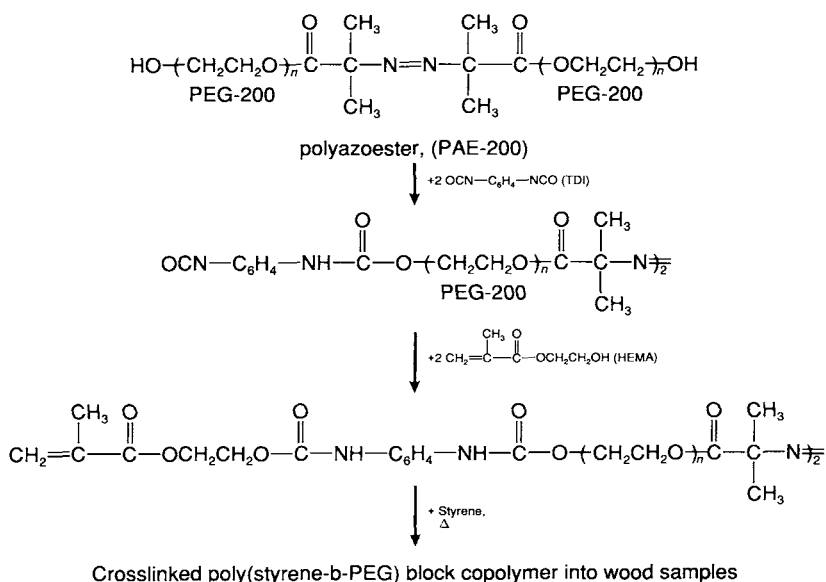
EXPERIMENTAL

Materials

TDI, stannous octoate (SO), and HEMA were supplied from Helm AG, Union Carbide, and Merck, respectively. They were also used without further purification. PAE-200 was prepared by Pinner synthesis from azobisisobutyronitrile and polyethylene glycols (PEG-200) with molecular weight 200 according to Walz et al.¹¹

The wood specimens used for testing were prepared from clear, defect-free sapwood pieces of three

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Scheme 1 Wood impregnation with one-shot polymerization of macroinimer and St solution.

wood species, namely, scotch pine (*Pinus sylvestris* L.), eastern spruce (*Picea orientalis* L.), and eastern beech (*Fagus orientalis* L.). Test specimens of each wood species were sawed in the dimension of $2.5 \times 2.5 \times 0.6$ cm longitudinally. These samples were randomly assigned to treatment. There were 10 replication for both treatment and control. All samples were oven dried at 105°C for 12 h prior to treatment.

Impregnation Process

The impregnation process was carried out by modifying published methods⁴ with a new type of polymerization mixture, leading to crosslinked block copolymer of styrene and PEG into the wood samples. All wood specimens for impregnation or testing were first oven dried at 105°C for 12 h and placed in a vacuum chamber (< 3 mm Hg) at 30°C for 30 min. The mixture, containing 140 g PAE, 80 ml TDI, 70 ml HEMA, 400 ml St, and 5 ml SO as a catalyst, was introduced into the vacuum chamber until the wood samples were covered. After 1 h of impregnation at $40\text{--}50^\circ\text{C}$, vacuum was released and the impregnation process carried out for another 30 min. Finally, wood samples were removed and wiped to remove excess monomer mixture from wood surfaces (polymerization was usually starting during the impregnation process). The wood samples were wrapped in aluminium foil and thermally polymer-

ized at 105°C for 2 h. After unwrapping, the samples were dried in a vacuum oven at 30°C overnight.

Water Uptake Test

All samples, both control and treated, were immersed in water at 18°C for various periods. After each soaking period, the samples were wiped of excess water and weighed. The water uptake was determined for 2, 4, 8, 24, 48, 72, and 144 h on the basis of oven-dry measurements.

Water-Repellent Effectiveness

The water-repellent effectiveness (WRE) test was carried out on wood samples cut in the same direction as the water uptake test. Water repellency was measured for various periods; resistance to water uptake and is expressed as WRE⁴ calculated from the following equation:

$$\text{WRE} = \frac{D_c - D_t}{D_c} \times 100 \quad (1)$$

where D_c = water uptake of control samples immersed in water for 2, 4, 8, 24, 48, 72, and 144 h and D_t = water uptake of impregnated wood samples immersed in water for the same periods as control.

Antiswell Efficiency

The dimensional stability of impregnated wood samples, cut from longitudinally, was evaluated with antiswell efficiency (ASE) values using changes in tangential, radial, and longitudinal dimensions after 7 days of soaking in water. Dimensional stability was expressed as ASE⁴ determined from eqs. (2) and (3).

$$S = \frac{V_2 - V_1}{V_1} \times 100 \quad (2)$$

where S = volumetric swelling coefficient, V_1 = volume of oven-dried sample before water-soaking test for 7 days, and V_2 = wood volume after water-soaking test for 7 days. Then

$$\text{ASE} = \frac{S_2 - S_1}{S_1} \times 100 \quad (3)$$

where ASE = volumetric antiswelling efficiency, S_1 = volumetric swelling coefficient for untreated wood, and S_2 = volumetric swelling coefficient for treated wood.

In addition, the following physical values were obtained¹²:

$$\text{wt \% gain (WPG)} = \frac{W_t - W}{W} \times 100 \quad (4)$$

$$\text{vol change} = \frac{V_t - V}{V} \times 100 \quad (5)$$

where W is the oven-dry weight of wood, W_t is the oven-dry weight of treated wood, V is the oven-dry volume of wood, and V_t is the oven-dry volume of treated wood.

IR spectra were obtained on powdered samples made into KBr pellets run on a Perkin-Elmer 177 Series spectrometer. This analysis was conducted on spruce specimens cut for control and treated samples.

Mechanical Tests

Compression strength parallel to grain was measured by a universal testing machine using samples of $2 \times 2 \times 3$ cm for spruce wood species as control and treated wood. Compression strength was performed according to the procedure of Turkish Standard (TS) 53 or DIN 52188 standard.¹² The longitudinal compression strength (σ_B) was calculated from eq.

(6) using data from the universal testing machine for this test. Five untreated and five treated wood samples were used. Values given in the tables are averages.

$$\sigma_B = \{P/F\} (\text{kg/cm}^2) \quad (6)$$

where P = maximum force (kg) and F = cross-section area (cm²).

The bending strength was also measured by a universal testing machine according to TS 53 or DIN 52188 standard¹² except the direction was radial and the length of samples was about 15 cm. For this test, spruce wood samples ($2 \times 2 \times 15$ cm) were also used. There were five replications for control and treatment. The bending strength¹³ (σ_E) was calculated from eq. (7).

$$\sigma_E = 1.5Pl/ab^2 \quad (7)$$

where P = maximum force (kg), a = width of sample (cm), b = height of samples in the direction in which the load is applied (cm), and l = distance between supports (cm).

RESULTS AND DISCUSSION

Polymerization of St by macroinimers gives cross-linked block copolymers including PEG units.^{5,6} By using such systems shown in scheme 1, wood impregnation was carried out at 30°C for 1 h under reduced pressure. Impregnated wood samples were characterized by IR spectroscopy. An increase in carbonyl peak at 1750 cm⁻¹ and appearance of a phenyl peak at 1600 cm⁻¹ in treated wood samples was characteristic compared to control peaks (Fig. 1).

The WPG, volume change (%), increase in density (%), and density of polymerized wood samples are given in Table I. WPG was determined to be 36.37–91.13% after polymerization for the used wood specimens. The highest WPG values were obtained for spruce wood samples with lower density (0.382 g/cm³). The density of the whole polymerized wood was found to be from 0.626 (for pine) to 0.745 g/cm³ (for beech). The increase in density values were found to be between 25.63% (for beech) and 65.60% (spruce). In addition, the average volume change values of samples were 2.00, 8.55, and 10.59% for pine, beech, and spruce, respectively. There is good agreement between our results obtained for WPG,

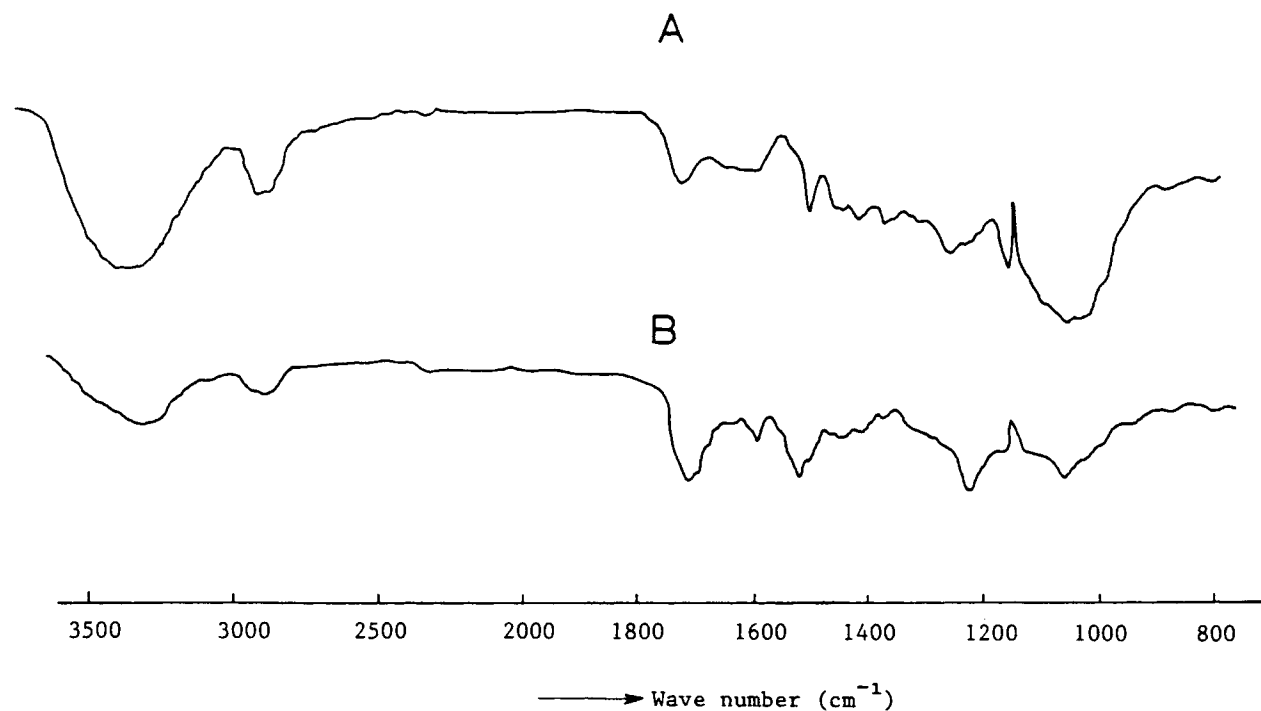


Figure 1 IR spectra of untreated wood sample (A) and impregnated wood sample (B) of spruce (in KBr disc).

increase in density, and volume change and the literature.^{4,6}

The water uptake values (%) of the wood specimens are shown in Table II. During the first 2 h of water soaking, control samples uptaked water about 54, 66, and 94% for pine, beech, and spruce wood samples cut from longitudinally, respectively, whereas samples impregnated with the mixture of macroinimer and St uptaked water about 23, 16, and 21% for the same species as mentioned above. During 144 h of water soaking, the control samples uptaked water about 112, 94, and 151% for pine, beech, and spruce specimens, respectively, whereas wood-

polymer composites uptaked water about 72, 54, and 63% for pine, beech, and spruce, respectively.

The average water uptake values of the whole polymerized wood samples immersed in water for 144 h was about 72% less, whereas those of all the control samples was about 151% less. The lowest water uptake value of treated samples compared to control was found for spruce due to its higher impregnation yield as measured by WPG after final cure and drying. For all three wood species, water uptake decreases with increasing wt % gain. It was found that there was good agreement between our results obtained for water uptake and the literature.⁴

Table I Impregnation of the Mixture of Macroinimer and St into Pine, Beech, and Spruce Wood Specimens

Wood Species	Wood Weight	Final Weight	WPG (%) ^a	Final Volume	Volume Change (%)	d_2 (g/cm ³)	d (%)
Pine	1.85	2.56	38.73	4.10	2.90	0.62	42.50
Beech	2.40	3.27	36.37	4.39	8.55	0.74	25.63
Spruce	1.54	2.95	91.13	4.66	10.59	0.63	65.60

^a Average data from 10 samples.

Table II Water Uptake of Wood Samples Impregnated with the Mixture of Macroinimer and St and Control

Wood Species	Type of Treatment	Water Uptake (%) ^a						
		Soaking Time (h)						
		2	4	8	24	48	72	144
Pine	Treated	23.49	31.23	37.42	51.28	60.02	66.54	72.07
	Control	54.29	58.47	61.06	68.37	81.19	98.27	112.58
Beech	Treated	16.28	22.88	28.16	39.90	45.86	49.80	54.29
	Control	66.66	71.50	72.50	77.04	81.16	91.25	94.08
Spruce	Treated	21.60	29.32	36.57	52.78	57.63	60.43	63.46
	Control	94.91	100.06	101.42	115.02	123.98	135.21	151.65

^a Average data from 10 samples.

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 III, WRE was significantly improved. For all samples, WRE values for a period of 2 h were between 56.72–77.23%, whereas those for a period of 144 h were between 35.14–58.15%. For the whole soaking time, the spruce wood sample impregnated with the mixture macroinimer and St gave the higher WRE values, followed in order by beech and pine, respectively. This result in general is due to the higher impregnation yield of spruce. But, the effect of impregnation yield was not shown as a main effect on WRE because of density of wood and other variables. As seen in Table III, decreases in WRE values are not linearly proportional to soaking times (2, 4, 8, 24, 48, 72, and 144 h) for all species. There is a good

agreement between our results of WRE and the literature.^{4,14}

Volumetric swelling (%) in a 1-week water-soaking test is shown in Table IV. During 1 week, control samples swelled about 10, 18, and 12% for pine, beech, and spruce, respectively, while wood-polymer composites swelled about 9, 12, and 7% for the same species range as mentioned above. Swelling values would be evaluated by means of volumetric ASE.

As seen in Table IV, the volumetric ASE values were 24.38, 32.64, and 42.43% for pine, beech, and spruce wood samples, respectively. These results showed that spruce had significantly greater ASE values than beech and pine. This may be due to the amount of WPG gain and volume change shown in Table I. But, when comparing Tables I and IV it can be seen that the main effect on the ASE of wood was volume change. Choong et al. studied dimensional stabilization of wood by impregnation with various monomers followed by irradiation.¹¹ They

Table III Water Repellent Effectiveness of Samples Impregnated with the Mixture of Macroinimer and St

Wood Species	WRE (%) ^a						
	Soaking Time (h)						
	2	4	8	24	48	72	144
Pine	56.72	46.59	38.71	24.99	25.43	32.28	35.14
Beech	75.57	68.00	61.15	48.49	43.49	45.42	42.29
Spruce	77.23	70.68	63.94	54.11	53.35	60.51	58.15

^a Average data from 10 samples.

found also that the ASE value was not depending upon WPG but also upon volume change. There is good agreement between our result of ASE and the literature.^{4,12}

As seen in Table V, the average compression strengths and bending strength of impregnated wood samples were compared with those of untreated wood. The compression strength of all samples as improved by 19.12% for spruce at about 16.80% WPG compared to untreated wood. Variations of the spruce compositions were better within the standard deviations measured. The coefficient of variation (COV, equal to SD divided by the average value) was less than 17% for the five samples measured for each composition and untreated wood. But, SD of the impregnated wood was found to be better than control.

The radial bending strength seen in Table V for wood-polymer composites showed the significant effect of the block copolymer of macromonomeric initiator and St. Bending strength of the treated spruce wood samples was improved by 25% for samples at about 20% WPG compared to untreated wood. The COV of treated wood samples was 24.00%, while that of control was 19%. For bending strength, COV and SD of control were found to be better than impregnated wood samples. Both longitudinal compression and bending strength of wood-polymer composites gave little increment due to their low WPG. That COVs of these measurements with five samples for compositions was less than 25% COVs of polystyrene-wood composite was reported for compression and bending strength by Siau et al.¹⁵

CONCLUSION

Vacuum impregnation of various wood species samples with the same dimensions, same direction, and

Table IV ASE of Wood Impregnated with the Mixture of Macroinimer and St after 7 Days of Immersion in Water at 18°C

Wood Species	Swelling (%) ^a		ASE (%)
	Control	Treated	
Pine	10.737	9.020	24.38
Beech	18.640	12.557	32.64
Spruce	12.020	6.919	42.43

^a Average data from 10 samples.

Table V Comparison of Longitudinal Compression Strengths and Bending Strength of Spruce Wood Samples Impregnated with the Mixture of Macroinime and St and Untreated Wood Samples

Treatment	Longitudinal Compression Strength	Static Bending Strength
Untreated		
Average	541.66	622.93
SD ^a	0.10	0.09
COV (%)	16.16	19.00
Treated		
Average	645.25	778.67
SD	0.06	0.10
COV (%)	16.54	24.00
WPG (%)	16.80	20.00

^a SD of five samples (+).

various bulk densities was carried out using the mixture of macromonomeric initiator and St. So, St-PEG crosslinked block copolymers were impregnated into the wood samples. The maximum impregnation yield was obtained for spruce, followed in order by pine and beech, respectively. The method brings about a considerable reduction in water uptake of wood-polymer composites. It increases significantly WRE of wood material and also improves the dimensional stabilization. The maximum WRE (58.15–77.23%) was found for spruce at 91.13% WPG. Maximum ASE (42.43%) was also obtained for spruce, while other compositions gave ASE values from 15.38–32.64%. The average improvements of 19.12% in longitudinal compression strength and 25% in bending strength for spruce were also achieved. IR spectra confirmed excellent impregnation with the mixture of macroinimer and St. This procedure can be used in the treatment of wood for some special uses.

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