Improvement of White Pinewood Properties by Impregnation with Thiourea–Formaldehyde Resin and Orthophosphoric Acid

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ABSTRACT: White pinewood was impregnated with thiourea–formaldehyde (TUF) resin and orthophosphoric acid (OPA) as a crosslinking agent. The best weight gains (55–138%) were obtained after impregnation with an aqueous solution of TUF resin for 1 h and impregnation with aqueous solutions of OPA at different concentrations for 1 h. Water uptake of treated wood was found to be 23% after a water-soaking test of 168 h, and a maximum antiswell efficiency was found to be 18% for a 85% OPA solution. Compression strength of the treated wood also improved with the highest value 62 KN/m^2 for wood treated with a 70% OPA solution versus a value of 40 KN/m^2 for untreated samples. Fire retardancy of the treated wood samples was also improved based on concentration of OPA. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 390–397, 2000

INTRODUCTION

To improve the physical or mechanical properties of wood, techniques such as heat or pressure treatment, crosslamination (as in plywood), surface coating, and impregnation with reactive materials have been extensively evaluated. The most promising method for improving the specific properties of the wood cell wall material is chemical impregnation under vacuum or pressure. Compounds highly reactive to the hydroxyl groups of the cellulose, hemicellulose, and lignin components of wood include epoxides, isocyanates, anhydrides, lactones, and diols. All have been examined for the reduction of equilibrium moisture content, one of the most important factors related to dimensional stability of wood.[1] Another widely studied system is the crosslinking of wood via impregnation with formaldehyde in the presence of an acid catalyst.[2] Crosslinking of material in wood samples provides better dimensional stability to the wood–polymer composites.[3] Compounds that contain both phosphorus and nitrogen are known to be good flame-proofing agents and are used in a number of commercial finishes.[4–7]

The object of the present work was to enhance the physical and mechanical properties of white pinewood by impregnation with a thiourea–formaldehyde (TUF) resin and various concentrations of orthophosphoric (OPA) as a crosslinking agent.

EXPERIMENTAL

Materials

Thiourea, formaldehyde, orthophosphoric acid, and sodium hydroxide were supplied by Aldrich Chemical Co. They were also used without purification. The wood specimens used for testing were prepared from clear, defect-free white pinewood cut into blocks of 0.79 × 0.79 × 1.18, 0.50 × 0.50 × 1.00, and 0.50 × 0.50 × 3.00 in for measurements of compression, water-soaking, and fire retardancy tests, respectively.[8]

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Preparation of Thiourea–Formaldehyde Resin

To a 500-mL three-necked flask equipped with a stirrer and reflux condenser was charged 123.2 gm of 37% aqueous formaldehyde (1.6 mol), which was brought to a pH of about 7.5 by the addition of a 5% sodium hydroxide solution. Then 76.12 g (1.0 mol) thiourea was added and the mixture gently refluxed and stirred for 2 h. The mixture was then concentrated to 65% solid content by distillation of water under water aspirator pressure.

Impregnation Process

The wood samples were oven-dried at 105°C for 7 h, then placed in a desiccator and held under reduced pressure for 0.5 h. The desiccator was then flooded with a sufficient amount of aqueous solution of TUF resin (38.19 wt % of thiourea) from a dropping funnel to completely immerse the wood samples. The wood was allowed to soak for 1 h under reduced pressure to ensure maximum TUF resin uptake. After decantation of excess aqueous solution of TUF resin, the desiccator was flooded with sufficient aqueous solution of OPA from a dropping funnel to completely immerse wood samples; different concentrations of OPA (10, 25, 40, 55, 70, and 85%) were used in the second step of impregnation process. The impregnation process was continued for an additional 1 h under reduced pressure. Vacuum was released to ensure maximum OPA uptake. Finally, wood samples were removed and wiped to remove excess OPA, air-dried, and finally dried for 12 h at 105°C.

Water Uptake Test

Both control and treated samples were immersed in distilled water at 25°C for various periods. After each soaking period, samples were wiped of excess water and weighed. The water uptake was determined for 2, 4, 8, 24, 48, 72, 144, and 168 h on the basis of oven-dry measurements.[9]

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 different soaking periods. Resistance to water uptake is expressed as WRE[3] calculated from eq. (1),

$$\mathrm{WRE} = \{(D_c - D_t)/D_c\} \times 100 \quad (1)$$

where D_c is water uptake of control samples immersed in water for 2, 4, 8, 24, 48, 72, 144, and 168 h and D_t is water uptake of impregnated wood samples immersed in water for the same periods.

Antiswell Efficiency

The dimensional stabilities of the impregnated wood samples were evaluated with antiswell efficiency (ASE) values using changes in block dimensions after 7 days of soaking in distilled water. Dimensional stability was expressed as ASE[3] determined from eq. (2) and (3).

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

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

$$\mathrm{ASE} = \{(S_2 - S_1)/S_1\} \times 100, \quad (3)$$

where ASE is the volumetric antiswelling efficiency, S_1 is the volumetric swelling coefficient for treated wood, and S_2 is the volumetric swelling coefficient for untreated wood. In addition, the following physical values were obtained[10]:

$$\%\ \text{Wt gain (WPG)} = \{(W_t - W_o)/W_o\} \times 100 \quad (4)$$

$$\%\ \text{volume change} = \{(V_t - V_o)/V_o\} \times 100 \quad (5)$$

where W_o is the oven-dry weight of untreated wood, W_t is the oven-dry weight of treated wood, V_o is the oven-dry volume of untreated wood, and V_t is the oven-dry volume of treated wood.

Compression Strength

Compression strength parallel and perpendicular to grain was measured by a Universal Testing machine using samples of $2 \times 2 \times 3$ cm for treated and untreated wood samples. Compression strength was performed according to the Egyptian Standard procedure[11] (ES 650–1965). Samples were placed on a testing machine under a constant deformation rate = 0.0635 cm/min (accuracy in sample dimensions not 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

Table I Impregnation of White Pinewood with TUF Resin and Different Concentrations of OPA

(a) Grain in Tallest Dimension

Sample No.	Concentration of OPA (%)	Wood Weight[a] W_o	Final Weight[b] W_t	WPG[c] (%)	Wood Volume[a] V_o	Final Volume[b] V_t	Volume Change[c] (%)	Density[d] (g/cm^3)
1	85	1.80	3.00	67	4.04	4.40	9.00	0.68
2	70	1.73	2.87	66	4.12	4.44	7.77	0.65
3	55	1.86	2.85	53	4.14	4.46	7.73	0.64
4	40	1.76	2.66	51	4.15	4.36	5.00	0.61
5	25	1.88	2.41	28	4.11	4.30	4.62	0.56
6	10	1.85	2.35	27	4.12	4.29	4.13	0.55

[a] After drying at 105°C for 7 h.
[b] After complete impregnation of untreated wood samples and drying at 105°C for 12 h.
[c] Wt % gain average data from five samples.
[d] Average density of untreated wood samples: 0.4241 g/cm^3.

(b) Grain in Smallest Dimension

Sample No.	Concentration of OPA (%)	Wood Weight[a] W_o	Final Weight[b] W_t	WPG[c] (%)	Wood Volume[a] V_o	Final Volume[b] V_t	Volume Change[c] (%)	Density[d] (g/cm^3)
1	85	1.75	4.16	138	4.14	4.87	18	0.85
2	70	1.68	3.86	130	4.16	4.82	16	0.80
3	55	1.60	3.62	126	4.20	4.81	14	0.75
4	40	1.81	3.35	85	4.14	4.65	12	0.72
5	25	1.96	3.21	63	4.19	4.65	11	0.69
6	10	1.82	2.81	55	4.19	4.55	8	0.62

[a] After drying at 105°C for 7 h.
[b] After complete impregnation of untreated wood samples and drying at 105°C for 12 h.
[c] Wt % gain average data from five samples.
[d] Average density of untreated wood samples: 0.4241 g/cm^3.

external force (kg) and A the cross-sectional area of the sample (cm^2).

ASTM: E 160–50 (1965)—Crib Test for Treated Wood

This method covers a Crib fire test to evaluate the change in flammability of treated wood. The Crib test specimen was cut from the selected sample and consisted of 24 pieces 0.5 × 0.5 in in cross section and 3 in in length, with surfaces smooth-sawed to dimensions within ± 0.0794 in., and the moisture content of the specimen when tested was 7 ± 3% by weight of the dry material.

RESULTS AND DISCUSSION

The white pinewood was impregnated with TUF resin and OPA (various concentrations) as a flame-retardant and catalyst for the crosslinking reaction. Each impregnation process was carried out under reduced pressure for 1 h. Tables I(a) and (b) illustrate the WPG, volume change (%), and density of treated wood samples (grain in the tallest and smallest dimension, respectively). WPG was determined to be 27–67% and 55–138%. Volume change values of treated wood samples were found to be between 4.13–9.00% and 8–18%. In addition, the density of the whole treated wood samples was found to be 0.55–0.68 g/cm^3 and 0.62–0.85 g/cm^3 for each type of treated wood sample, respectively. There is good agreement between our results (WPG, volume change, density) and the literature.[3,12]

The water uptake values (%) of the wood specimens are shown in Table II(a) and (b) (grain in the tallest and smallest dimension, respectively). From Table II(a), during the first 2 h of water

Table II Water Uptake Values of White Pinewood Impregnated with TUF Resin and Different Concentrations of OPA

(a) Grain in Tallest Dimension

Sample No.	Concentration of OPA (%)	Water Uptake[a] % Soaking Time (h) 2	4	8	24	48	72	144	168
1	85	8	11	15	23	28	32	37	38
2	70	10	13	18	26	31	34	39	40
3	55	15	18	23	33	40	44	48	49
4	40	18	21	26	35	42	45	50	51
5	25	22	27	37	50	57	60	69	70
6	10	26	31	40	52	60	64	75	75
Untreated		64	69	75	83	90	95	103	106

(b) Grain in Smallest Dimension

Sample No.	Concentration of OPA (%)	Water Uptake[a] % Soaking Time (h) 2	4	8	24	48	72	144	168
1	85	8	8	9	11	15	18	23	23
2	70	8	10	12	15	18	20	24	25
3	55	19	18	21	24	27	29	33	33
4	40	19	21	26	31	35	37	42	43
5	25	21	23	29	35	40	42	48	49
6	10	33	38	44	53	60	62	70	72
Untreated		90	94	102	112	122	129	142	144

[a] Average data from five samples.

soaking, the control sample took up about 64% water, whereas samples impregnated with TUF resin and 85% OPA took up about 8% water. After 168 h of water soaking, the control samples gained about 106%, whereas treated wood samples gained about 38%. From Table II(b), after the first 2 h of water soaking, the control samples took up about 90% water, whereas samples impregnated with TUF resin and 85% OPA took up water about 8%. After 168 h of water soaking, the control sample took up water about 144%, whereas treated wood samples took up about 23% water.

It may be seen from Figures 1(a) and (b) that water uptake values (%) decrease with an increasing concentration of OPA. It is clear that water uptake values (%) of treated wood that has the grain in the direction of the smallest dimension are lower than the water uptake values of treated wood samples with the grain in the direction of the tallest dimension. For all wood species there is an inverse relationship between water uptake (%) and WPG (%). Our results for water uptake are in good agreement with those listed in the literature.[3]

Dimensional stability and water repellency were measured using a simple water-soaking test. This test estimated not only dimensional stability (from data obtained for various periods) but also water repellency (from data obtained for long-term water soaking), as shown in Table III(a) and (b) for treated wood samples (grain in the direction of tallest and smallest dimensions, respectively). From Table III(a), WRE values for periods of 2 h were 40–81%, whereas those for a period of 144 h were 6–45%. Also, in Table III(b), WRE values for a period of 2 h were 38–83%, whereas those for a period of 144 h were 18–63%. For the entire soaking time, the white pinewood samples impregnated with the 85% OPA solution

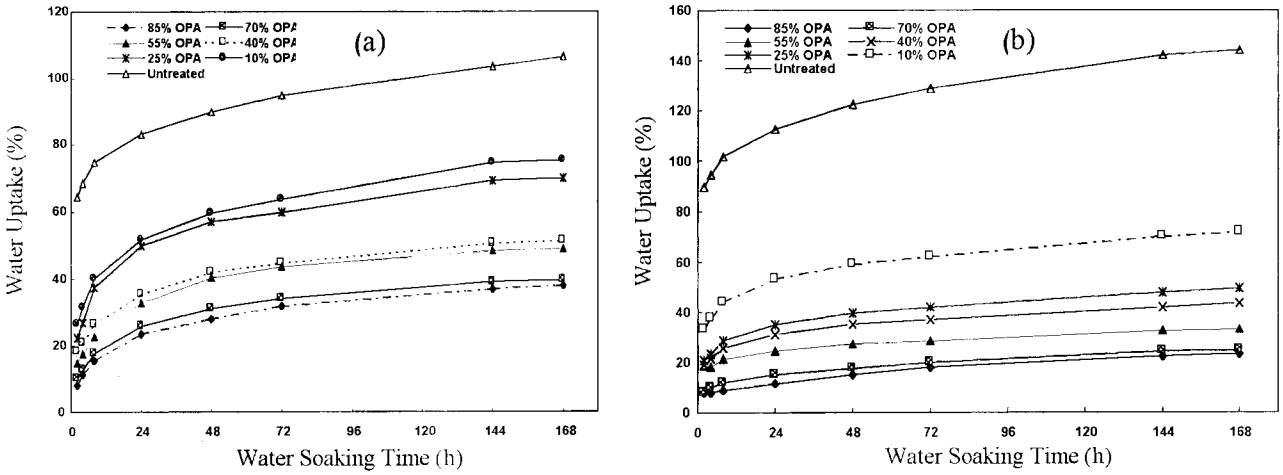

Figure 1 Effect of soaking time on percent of water uptake of treated and untreated wood samples: (a) grain in the tallest dimension, (b) grain in the smallest dimension.

gave the higher WRE values. As seen in Table III(a) and (b), decreases in WRE values are proportional to soaking times (2, 4, 8, 24, 48, 72, and 144 h) for all species. There is a good agreement between our WRE results and those in the literature.[3,13]

Table III Water Repellent Effectiveness of White Pinewood Samples Impregnated with TUF Resin and Different Concentrations of OPA

(a) Grain in Tallest Dimension

Sample No.	Concentration of OPA (%)	WRE[a] Soaking Time (h) 2	4	8	24	48	72	144	168
1	85	81	75	69	53	48	46	45	43
2	70	75	70	63	55	51	47	43	29
3	55	66	62	52	42	34	32	31	33
4	40	58	55	49	37	31	31	28	29
5	25	55	50	37	23	18	19	14	16
6	10	40	40	32	14	13	13	6	9

(b) Grain in Smallest Dimension

Sample No.	Concentration of OPA (%)	WRE[a] Soaking Time (h) 2	4	8	24	48	72	144	168
1	85	83	81	80	77	72	69	63	64
2	70	40	76	72	69	66	64	61	61
3	55	60	59	56	53	52	51	51	52
4	40	58	55	51	45	42	41	41	43
5	25	50	44	40	37	37	36	35	36
6	10	38	33	27	20	18	18	18	20

[a] Average data from five samples.

Table IV ASE of White Pinewood Impregnated with TUF Resin and Different Concentrations of OPA, After 7 Days' Immersion in Distilled Water at 25°C

(a) Grain in Tallest Dimension

Sample No.	Concentration of OPA (%)	S (%)	ASE[a] (%)
Untreated		19.16	—
1	85	16.64	15
2	70	17.26	11
3	55	17.76	8
4	40	18.06	6
5	25	18.51	3.5
6	10	18.62	3

(b) Grain in Smallest Dimension

Sample no.	Concentration of OPA (%)	S (%)	ASE[a] (%)
Untrated		16.75	—
1	85	141.19	18
2	70	14.84	13
3	55	15.46	8
4	40	15.57	6
5	25	16.09	4
6	10	16.14	3.7

[a] Average data from five samples.

Volumetric swelling (%) in a 1-week water-soaking test is shown in Tables IV(a) and (b) (grain in the tallest and smallest dimension, respectively). It is clear that during 1 week treated wood samples had ASE values between 3 and 15% for 10 and 85% OPA solutions, respectively, for wood samples that had grain in the tallest dimension. These results showed that 85% OPA solution had a greater ASE value than other solutions. The same behavior was obtained for grain in the direction of the smallest dimension as shown in Table III(b). This may result from the amount of (%) WPG.

Compressive Strength

Compression Parallel to Grain

Data averages of three runs for compressive strength parallel to the grain of treated wood compared to untreated controls (grain in the smallest dimension) are illustrated in Figure 2(a). The highest values were observed for wood samples impregnated with TUF resin and 70% OPA solution.

Compression Perpendicular to Grain

Data for compressive strength perpendicular to the grain of treated wood samples compared to untreated controls (grain in the smallest dimension) are illustrated in Figure 2(b). The highest

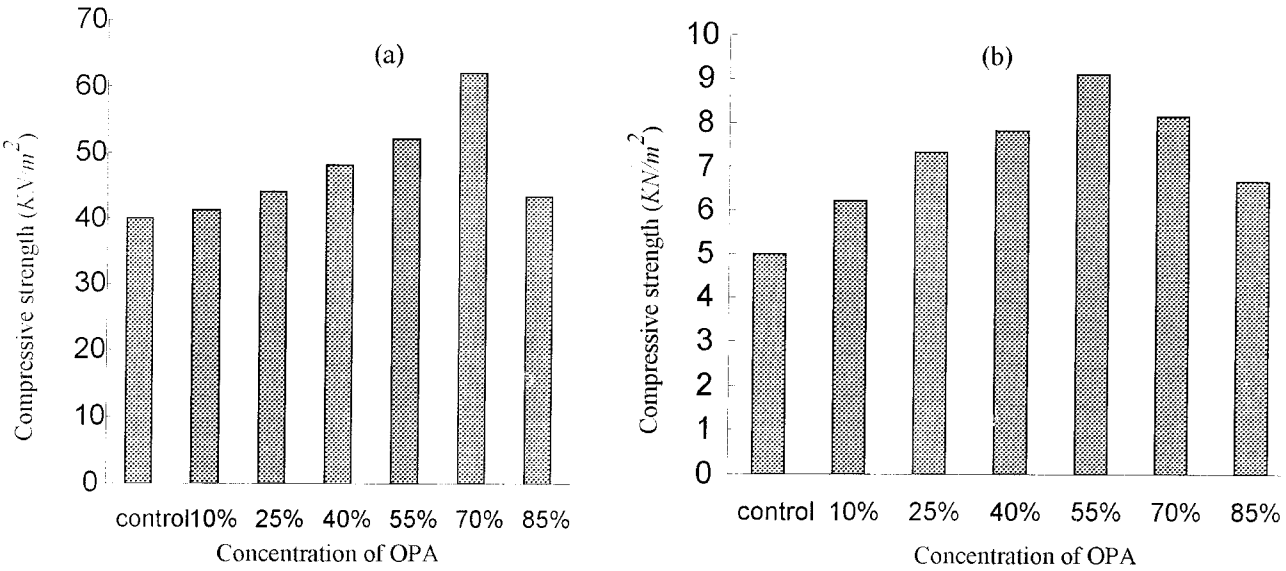

Figure 2 Compression strength of treated and untreated white pinewood based on an average of three samples, Where (a) is compression strength parallel to grain and (b) is compression strength perpendicular to grain.

Table V ASTM [E160–50 (1965)] Results for White Pinewood Impregnated with TUF Resin and OPA at Different Concentrations

(a) Grain in Tallest Dimension

Sample No.	Concentration of OPA (%)	w_o[a]	w[b]	% wt Loss	Observations: Flaming Time (min)	Observations: Glowing Time (min)
Untreated		130	2	98	14–16	9–10
1	85	189	116	38	5–6	0.85–1
2	70	170	113	33	5–6	1–2
3	55	157	79	52	7–8.5	8–9
4	40	160	85	47	6–7.5	5–6
5	25	156	73	53	7–8	7–8
6	10	154	86	44	6–7	5–6

(b) Grain in Smallest Dimension

Sample No.	Concentration of OPA (%)	w_o[a]	w[b]	% wt Loss	Observations: Flaming Time (min)	Observations: Glowing Time (min)
Untreated		136	4	97	9–10	8–9
1	85	253	242	4	–	–
2	70	257	244	5	–	–
3	55	244	230	6	–	–
4	40	243	227	6	1.5–2	0.166
5	25	222	201	9	2–3	0.5–0.7
6	10	205	178	13	2–3	0.85–1

[a] Weight of wood samples after drying at 105°C for 12 h and before applying the igniting flame.
[b] Weight of wood samples after the removal of igniting flame and after all flaming and glowing has ceased.

values were observed for wood samples impregnated with TUF resin and 55% OPA solution. This may be because of the nonisotropic properties of the wood material (fibers of the wood are not parallel across the cross-sectional area), which give rise to experimental error for the perpendicular direction. In addition, the more solid crosslinked polymer was obtained for 70% OPA. So the highest value of compression strength was obtained for 70% OPA in both directions.

Fire Retarding Property of Treated Wood

White pinewood was impregnated with TUF resin, followed by another impregnation with an OPA solution at various concentrations. The original and final weights and glowing and flaming times are listed in Table 5(a) and (b). The loss in weight is expressed as a percentage of the original weight of the specimen. From Table 5(a) and (b) (grain in the tallest and smallest dimension, respectively) it is clear that all treated wood samples had fire retardant properties compared with untreated wood samples. In the case of treated wood samples with grain in the direction of the smallest dimension, maximum and minimum weight losses were found to be 13% and 4%, respectively. On the other hand, the treated wood samples with grain in the direction of the tallest dimension showed maximum and minimum weight loss of 52% and 33%, respectively. The treated wood samples with grain in the direction of the smallest dimension were found to possess excellent flame-retardant properties.

A possible explanation for this phenomenon is the greater percentage of WPG for the treated wood samples with grain in the smallest dimension than for samples with grain in the tallest dimension because more wood cells are open and

exposed to the impregnated solution in wood samples with grain in the smallest dimension.

CONCLUSIONS

Two successive vacuum impregnation processes on white pinewood samples with grain in the tallest and smallest dimensions were carried out using thiourea–formaldehyde (TUF) resin and orthophosphoric acid (OPA) at different concentrations. TUF–OPA crosslinked polymers were formed *in situ* to give wood polymer composites with good physical and mechanical properties, especially for treated wood samples with grain in the smallest dimension due to the greater cell wall number filling and adhesion. Water-repellent effectiveness (WRE) and antiswelling efficiency (ASE) values of wood polymer composites were greatly improved for all treated wood samples, especially for wood samples treated with 85% OPA, followed in order by a decreasing concentration of OPA. Compression strength in both directions was carried out, and there is no a parallel relation between results obtained in both directions due to the nonisotropic properties of wood. Maximum values of compression strength in both directions were obtained for treated wood by 70% OPA. Fire retardancy for all treated wood samples was greatly improved from the better fire retarding properties of OPA. This procedure can be used in the treatment of wood for some special uses.

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