

Effect of fire-retardant treatment on plywood pH and the relationship of pH to strength properties

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285

Summary This paper investigates the relationship between wood pH and the strength properties of fire-retardant-treated (FRT) plywood, as it is affected by fire-retardant (FR) formulations, processing variables, and extended high temperature exposure conditions. The objectives of this study were to (1) identify the effect of post-treatment kiln-drying temperature, followed by high temperature exposure, on wood pH; (2) identify the effect of various mixtures of FR components, followed by high temperature exposure, on wood pH; (3) determine if treatment effects on strength and pH are affected by plywood thickness; and (4) quantify the relationship between changes in wood pH and strength loss and whether pH can be used as a predictor of strength loss. Results indicate that the differences in pH resulting from the initial redry temperature became insignificant after extended periods of high temperature exposure. All FR treatments studied caused large, rapid decreases in pH, with the most rapid decreases occurring with formulations containing phosphoric acid. Additions of borate compounds, especially disodium octaborate tetrahydrate (Timbor), produced a measurable buffering effect that slowed or lessened the decreases in pH. No differences in the effect of FRT on the wood pH-strength relationship were noted between the two plywood thicknesses evaluated. A strong relationship was noted between changes in pH of the plywood and reductions in strength and energy-related properties. These findings suggest that the pH of FRT plywood is a good indicator of its current condition and may have potential as a predictor of future strength loss as the plywood is subjected to elevated in-service temperatures.

Introduction

Fire retardants are effective because they lower the temperature of pyrolysis reactions, thus increasing the amount of char and reducing the amount of volatile, combustible vapors (LeVan and Winandy 1990). Acidic-fire retardants are particularly effective at accomplishing this task (Shafizadeh 1984), and many commercial fire-retardant formulations have relied on phosphate or borate salts

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because of their ease of use and low cost. However, it appears that the same mechanism of acid dehydration that is useful in reducing flame spread can also lead to premature strength loss in treated wood in some environments.

Field problems with reduced strength in fire-retardant-treated (FRT) plywood roof sheathing have led to a continuing series of studies at the USDA Forest Service, Forest Products Laboratory (FPL), that investigated the physical, mechanical, and chemical properties of FRT wood under a variety of exposure conditions (LeVan et al. 1990; Winandy et al. 1991; Winandy 1995). To date, these studies indicate that the combination of acidic-fire retardant (FR) chemicals, high temperature, and humidity encountered in roof applications are causing acid hydrolysis of plywood and subsequent strength loss in the wood. Hemicelluloses, particularly side-chain carbohydrate constituents, are most affected by FR treatment and high temperature exposure (LeVan et al. 1990; Winandy 1995).

Past studies have shown that the amount of degrade is linked to the acidity of the original FR formulation and the cumulative temperature exposure (LeVan et al. 1990; Winandy 1995). Pasek and McIntyre (1990) calculated and included an acidity factor to quantify the kinetics of thermogravimetric/strength degrade of FR chemicals. However, the effects of treating solution pH and exposure conditions on the pH of the wood itself and the relationship between wood pH and strength properties have not been directly evaluated. A comprehensive investigation of these relationships was needed to confirm the hypothesis of thermally induced acid degradation in FRT wood.

Of equal importance is the potential for using the pH of FRT wood in service to predict current and future structural integrity. This paper reports on a study that investigated the effects of FR formulation, processing effects, and exposure conditions on the wood pH and the potential for using wood pH to predict the strength properties of FRT plywood already in service. A thorough discussion of the effects of these parameters on mechanical properties can be found in Winandy (1997).

This study had four objectives:

1. Identify the effect of post-treatment kiln-drying temperature, followed by high temperature exposure, on wood pH.
2. Identify the effect of various mixtures of FR components, followed by high temperature exposure, on wood pH.
3. Determine if treatment effects on strength and pH are affected by plywood thickness.
4. Quantify the relationship between wood pH and strength loss and whether pH can be used as a predictor of strength loss.

Materials and methods

The Southern Pine plywood samples evaluated in this study were part of a larger study that defined the effects of mixtures of FR chemical components, the temperatures used in kiln-drying FRT material after treatment, and subsequent exposure to elevated temperatures during service on the mechanical properties of plywood. Two thicknesses of plywood (12 and 16 mm) (1/2 and 5/8 in.) were evaluated to address the objectives in the study reported herein.

Specimen preparation

Twenty-four sheets of 12mm (1/2-in.) Southern Pine plywood were obtained. This material was four-ply using only 'N-grade' veneer. N-grade is a special grade

of nearly defect-free veneer that has been used in previous FPL studies to reduce variability in mechanical properties resulting from random placement of defects in interior veneers. In addition, 20 sheets of 16-mm (5/8-in.) Southern Pine plywood, constructed from five plies of similar N-grade veneer, were obtained. For both plywood thicknesses, 1.2- by 2.3-m (4- by 8-ft) sheets of plywood were cut to obtain thirty-two 150-mm (6-in.) wide by 600-mm (24-in.) long (parallel to face grain) specimens. Of the 32 specimens obtained from each sheet, one specimen from each sheet of 12-mm (1/2-in.) plywood was randomly assigned to one of 22 experimental groups, resulting in a blocked experimental design (Table 1). Similarly, one specimen from each sheet of 16-mm (5/8-in.) plywood was randomly assigned, but only to 20 experimental groups (Table 2), also resulting in a blocked experimental design.

Treatment of 12-mm (1/2-in.) specimens

As shown in Table 1, three of the 22 groups of 12-mm (1/2-in.) plywood were retained as untreated controls. These controls were not FR treated, but some were exposed to elevated temperatures. Another 11 groups of specimens were treated with monoammonium phosphate (MAP) to a target retention of 56 kg/m³ (3.5 lb/ft³). To serve as a model for a buffered inorganic FR formulation, four groups of plywood specimens were treated to 56 kg/m³ (3.5 lb/ft³), with a combination of 75% MAP and 25% Timbor (71% MAP, 29% boric acid equivalent (BAE)). To serve as a model for a highly acidic inorganic FR formulation, four groups of plywood specimens were treated with a combination of 90% MAP and 10% phosphoric acid (PA). Following treatment, groups of specimens were kiln dried at prescribed temperatures and durations, as described in Table 1. Afterward, all kiln-dried material was equilibrated to constant weight at 23 °C (74°F) and 65% relative humidity (RH). These conditions produce an approximate equilibrium moisture content of 12% in untreated lumber.

Treatment of 16-mm (5/8-in.) specimens

As described in Table 2, one group of the 16-mm (5/8-in.) plywood was retained as an untreated control. Another group was treated with water to determine

Table 1. Experimental design of study to evaluate the effects of processing parameters and exposure at elevated temperatures on FRT wood. Twenty-four replicate 12-mm (1/2-in.) plywood specimens were used for each treatment group

Treatment solution ^a	Solution PH	Schedules for kiln drying after treatment		High temperature exposure (Days at 66 °C/ 75% RH)
		(°C) ^b	(Hours to moisture content)	
None	None	None	None	
MAP	4.2	48/30	48 hours to 13%–16%	0, 160, 290
MAP	4.2	71/54	29 hours to 20%–23%	0, 60, 160, 290
MAP	4.2	88/71	23 hours to 12%–16%	0, 60, 160, 290
75% MAP/25% Timbor	5.5	71/54	29 hours to 20%–23%	0, 60, 160, 290
90% MAP/10% PA	2.8	71/54	29 hours to 20%–23%	0, 60, 160, 290

^aMAP = monoammonium phosphate; PA = phosphoric acid; Timbor = disodium octaborate tetrahydrate

^bDry-bulb temperature/wet-bulb temperature

Table 2. Experimental design study to evaluate the effects of various FR mixtures on treated wood. Twenty replicate 16-mm (5/8-in.) plywood specimens were used for each treatment group

FR mixture MAP/PA/BA ^a	Solution pH	Schedules for kiln drying after treatment		High temperature exposure (Days at 66 °C/75% RH)
		(°C) ^b	(Hours to moisture content)	
None		None	43 hours to 20%–22%	0
Water	6.5	71/54	43 hours to 20%–22%	0
100/0/0	4.2	71/54	43 hours to 20%–22%	0, 290
80/20/0	2.4	71/54	43 hours to 20%–22%	0, 160, 290
80/0/20	4.1	71/54	43 hours to 20%–22%	0, 160, 290
60/20/20	2.2	71/54	43 hours to 20%–22%	0, 160, 290
80/10/10	2.7	71/54	43 hours to 20%–22%	0, 160, 290

^aMAP = monoammonium phosphate; PA = phosphoric acid; BA = boric acid

^bDry-bulb temperature/wet-bulb temperature

uptake and allow calculation of FR solution concentration needed to achieve a target retention of 56 kg/m³ (3.5 lb/ft³) in the FRT specimens. These water-treated specimens were subsequently evaluated for strength and pH properties and used as a water-treated control. Two groups of the 16-mm (5/8-in.) plywood specimens were treated with MAP. To serve as a model for buffered inorganic FR formulations, three groups of plywood specimens were treated with a combination of 80% MAP and 20% boric acid (BA). To serve as a model for a highly acidic, inorganic FR formulation, three groups of plywood specimens were treated with a combination of 80% MAP and 20% phosphoric acid. To serve as a model for both acidified and buffered inorganic FR formulations, three groups of plywood specimens were treated with a combination of 60% MAP, 20% phosphoric acid, and 20% boric acid, and three groups of plywood specimens were treated with a combination of 80% MAP, 10% phosphoric acid, and 10% boric acid (Table 2). The strength of these acids can be compared by examining the equilibrium constants (K_a) of the chemicals; the larger the value of K_a , the stronger the acid. The K_a values of PA, MAP, and BA are 7.5×10^{-3} , 1.6×10^{-7} , and 5.8×10^{-10} , respectively (Zumdahl 1989). This indicates that PA will dissociate to its acid functional form most completely, while BA will dissociate at any condition to a lesser degree than either PA or MAP. Each plywood group, except the untreated controls, was kiln dried after treatment using a 71 °C (160°F) dry-bulb temperature and a 54 °C (130°F) wet-bulb temperature. Samples were removed after approximately 43 hours of kiln drying, with moisture content between 20% and 23%. All kiln-dried material was subsequently equilibrated to constant weight at 23 °C (74°F) and 65% RH. These conditions produce an approximate equilibrium moisture content of 12% in untreated lumber.

High temperature exposure

As detailed in Tables 1 and 2, all the FRT 12-mm (1/2-in.) plywood and 16-mm (5/8-in.) plywood specimens were placed in a controlled environment chamber and held at 66 °C (150°F) 66 °C and 75% RH for predetermined times. After the appropriate exposures, all material was re-equilibrated to constant weight at 23 °C (74°F) and 65% RH.

Mechanical testing

Each 150- by 600-mm (6- by 24-in.) plywood specimen was tested in bending using center-point loading (ASTM 1995). Load and center-span deflection were digitally recorded. Modulus of elasticity (MOE), modulus of rupture (MOR), and work to maximum load (WML) were calculated.

Determination of pH

Following mechanical testing, five specimens from each treatment group were selected so that for each plywood thickness, all specimens were originally cut from the same five pre-selected 1.2- by 2.4-m (4- by 8-ft) panels. The pH of the wood in the selected specimens was then determined in the zone immediately adjacent to where failure occurred in mechanical testing.

Initial trials were conducted to develop a method of pH determination that was reproducible yet adaptable to use in evaluation of FRT wood in service. Initially, pH was determined by grinding wood samples to pass through a 40 mesh screen, then soaking approximately 1 g of the resulting wood flour in 20-ml distilled water for various periods. These tests revealed that the pH of the water/wood flour had stabilized after 10 minutes of extraction (Fig. 1). Subsequent trials indicated that similar pH values could be obtained by simply collecting 1 g of shavings from a 12-mm- (1/2-in.-) diameter bit that was drilled into the FRT wood. Preliminary data also showed that the pH measurements were relatively insensitive to small variations in the ratio of wood to water, boding well for the applicability of this method to field use.

Based on these preliminary trials, a preferred method was developed in which a 12-mm (1/2-in.) bit was drilled to a 9-mm (3/8-in.) depth once on each side of each plywood specimen. This method produced a relatively constant volume of shavings with a weight of approximately 1 g. The shavings were then transferred to a 40-ml scintillation vial, and 20 ml of deionized water at 21 °C (70°F) was added. The vials were then capped, shaken by hand for a few seconds, and allowed to sit for 20 minutes without stirring. At the end of this extraction period, the pH

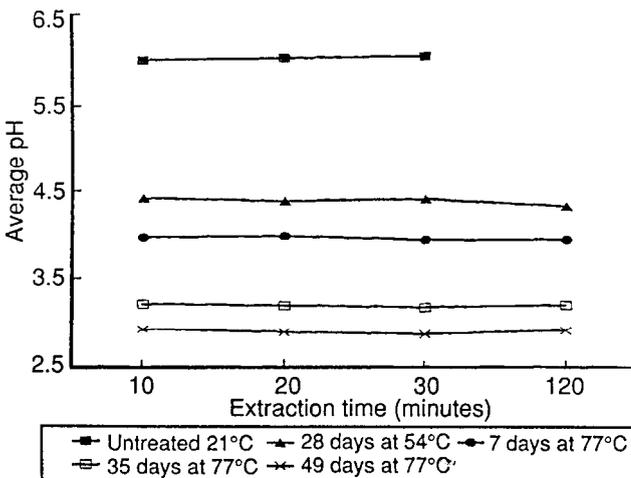


Fig. 1. Effect of extraction time on the pH of ground MAP treated wood samples allowed to soak in distilled water

of each sample was determined by inserting the probe of a Beckman 071¹ pH meter directly into the vial containing the settled wood/water mixture and allowing the pH meter reading to stabilize.

Statistical analysis

Tests for differences in the treatment groups means were conducted using the Fishers's Protected Least Significant Difference procedure (Milliken and Johnson 1992). All mean differences reported were significant at the 95% confidence level. For MOR and WML, values for all specimens in each treatment group (not just those tested for pH) were used to calculate group means.

Results and discussion

Effect of FRT on plywood pH

Regardless of FR formulation or processing parameters, the pH of all treated specimens decreased markedly after treatment, redry, and subsequent high temperature exposure (Table 3, Figs. 2 and 3). As expected with the acidic FR solutions, the pH of the FR-treated groups decreased immediately after treatment when compared with untreated groups or the group treated with water (Table 3). The exception was the 12-mm (1/2-in) group treated with a formulation containing 75% MAP and 25% Timbor, in which the pH increased above that of untreated wood immediately after treatment (Fig. 3).

Following treatment, the largest decrease in pH in all treatment groups occurred during the first 60-160 days of high temperature exposure. The pH of some groups continued to decline during subsequent exposure, but much less dramatically. Untreated specimens also began to suffer a slight, but significant, decrease in pH after 160-290 days of exposure (Fig. 3). Past research has noted that exposure of untreated wood to elevated temperatures and moisture content can eventually cause an increase in acid production (Hillis 1975).

The large decrease in pH in the 12-mm (1/2-in) FRT specimens during the first 60 days of exposure questions pH behavior during this period. To bridge this data gap, pH analyses were conducted on plywood samples from a previous study (Winandy et al. 1991). These samples had been treated with MAP, kiln dried at 71 °C (160°F), and exposed at 77 °C (170°F) for 7, 14, 35, or 49 days. As shown in Fig. 4, the pH of these samples decreased rapidly between 7 and 49 days, reaching levels below those of specimens from the current study that were exposed at 66 °C (150°F) for 60 days. The MOR of the samples also suffered large, corresponding decreases during the first 49 days of exposure. Assuming that the pH of the specimens from the previous study was similar to those of the current study immediately after treatment (pH = 5.3), it appears that the largest decrease in pH occurred during the first 7 days, with slightly smaller decreases during subsequent exposures.

Comparison of the effect of mixtures of various component ratios in FR formulations on the pH of 16-mm (5/8-in.) treated plywood indicated that although there was initially a strong pH effect, it becomes much less noticeable after high temperature exposure (Fig. 2). As expected, the formulation with the 80/20/0 MAP/PA/BA ratio had the lowest pH, and the formulation with the 80/0/20 MAP/PA/BA ratio had the highest pH after treatment but before high temperature

¹ The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Table 3. Summary of average^a pH, MOR, and WML data for all treatment groups and both plywood thicknesses

Plywood thickness (mm)	Redry (°C)	MAP/PA/BA mixture (%) ^b	Days exposed at 66 °C/75%	MOR (MPa) ^c		WML (kJ/m ³) ^c		Moisture content (%)
				RH	pH ^c			
12	None	None	0	5.4 (0.07)	71.8 (11.4)	39.9 (16.1)	9.2	
			160	5.5 (0.06)	58.3 (10.8)	34.2 (20.0)	9.9	
			290	5.4 (0.08)	55.2 (10.3)	22.4 (10.4)	9.3	
	48	100/0/0	0	5.1 (0.04)	58.9 (8.8)	29.7 (10.5)	9.1	
			160	2.7 (0.01)	28.4 (7.0)	6.8 (3.6)	9.0	
			290	2.6 (0.06)	17.4 (4.9)	2.6 (1.4)	8.9	
	71	100/0/0	0	5.3 (0.07)	57.4 (10.2)	31.6 (10.4)	9.6	
			60	3.1 (0.04)	36.3 (8.8)	11.3 (5.3)	9.7	
			160	2.8 (0.01)	25.7 (7.5)	5.2 (2.9)	8.6	
	88	100/0/0	290	2.7 (0.09)	17.1 (5.2)	2.4 (1.2)	9.6	
			0	4.8 (0.11)	51.5 (9.5)	25.0 (12.1)	9.1	
			60	3.1 (0.02)	35.5 (10.6)	10.3 (5.7)	9.2	
	71	71/0/29 ^d	160	2.7 (0.03)	23.5 (10.4)	4.5 (1.9)	10.8	
			290	2.6 (0.06)	17.0 (4.0)	2.4 (1.1)	9.4	
			0	5.9 (0.06)	59.5 (9.3)	29.2 (11.1)	9.9	
	71	90/10/0	60	3.6 (0.11)	42.4 (9.8)	14.7 (6.9)	9.6	
			160	3.1 (0.06)	34.6 (8.9)	9.9 (5.7)	9.4	
			290	3.1 (0.04)	25.8 (6.1)	5.0 (2.6)	9.2	
	16	None	None	0	4.8 (0.05)	57.5 (7.1)	28.4 (9.0)	10.1
				60	3.1 (0.02)	36.6 (9.1)	10.5 (5.4)	10.0
				160	2.7 (0.04)	26.4 (6.9)	5.5 (2.5)	10.4
290				2.7 (0.10)	17.6 (4.3)	2.7 (1.2)	9.7	
16	None	Water	0	6.1 (0.16)	67.9 (11.9)	40.5 (25.6)	10.6	
			0	6.4 (0.19)	62.7 (8.0)	34.7 (15.1)	11.7	
	71	100/0/0	0	5.2 (0.04)	55.0 (10.1)	25.7 (12.5)	13.0	
			290	2.4 (0.04)	14.6 (3.5)	2.0 (0.7)	16.3	
	71	80/20/0	0	3.8 (0.07)	53.9 (8.3)	25.0 (9.4)	13.0	
			160	2.6 (0.04)	26.1 (6.2)	5.2 (2.5)	15.0	
			290	2.4 (0.03)	16.4 (4.0)	2.3 (1.1)	16.1	
	71	80/0/20	0	5.8 (0.05)	56.2 (8.7)	23.7 (9.4)	13.6	
			160	2.8 (0.05)	27.2 (4.6)	6.1 (2.1)	14.5	
			290	2.7 (0.02)	19.0 (4.0)	3.0 (0.8)	14.8	
	71	60/20/20	0	4.8 (0.09)	54.7 (9.0)	23.2 (9.9)	13.3	
			160	2.8 (0.08)	28.4 (5.6)	7.0 (3.0)	14.5	
			290	2.6 (0.06)	21.0 (5.3)	3.4 (1.6)	15.3	
	71	80/10/10	0	5.1 (0.02)	58.5 (6.4)	29.4 (9.8)	13.3	
			160	2.7 (0.05)	27.1 (5.6)	5.7 (2.4)	14.7	
			290	2.6 (0.02)	18.9 (4.7)	3.0 (1.1)	15.3	

^aAverages for MOR and WML include all specimens in the treatment group, not just those that were evaluated for pH

^bMAP = monoammonium phosphate; PA = phosphoric acid; BA = boric acid

^cValues in parentheses are standard deviation from the mean

^dPrepared with 75% MAP, 25% Timbor

exposure. Although this difference still existed after 160 days of high temperature exposure, its magnitude was greatly diminished. Following 290 days of exposure, the pH of the wood treated with 100% MAP was nearly identical to that of the wood treated with the 80% MAP/20% PA mixture. This finding supports previous

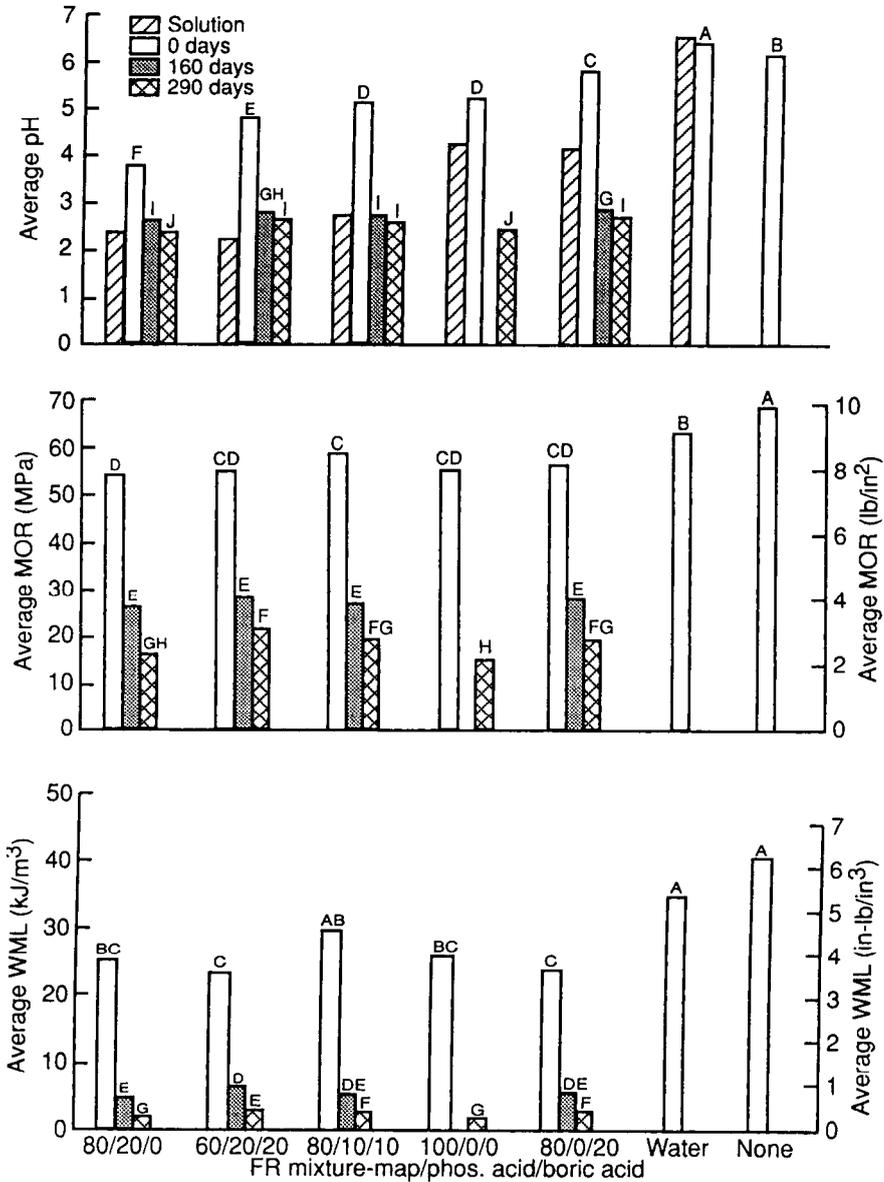


Fig. 2. Effects of various FR formulations on pH, MOR, and WML of treated 16-mm (5/8-in.) plywood specimens exposed at 66 °C (150°F) and 75% RH. Bars labeled with dissimilar letters are significantly different at the 95% confidence level. Solution pH was not included in the statistical analysis

research that suggested differences between PA-based FR chemicals are a function of the time and energy that it takes for a FR to convert to phosphoric acid (LeVan et al. 1990; Winandy 1995). During high temperature exposure, it is possible that ammonia is released from the MAP and some of the remaining phosphate is further converted to phosphoric acid. Thus, heating of MAP treated wood may increase the equilibrium ratio of PA: MAP (Winandy 1995). As a result, although

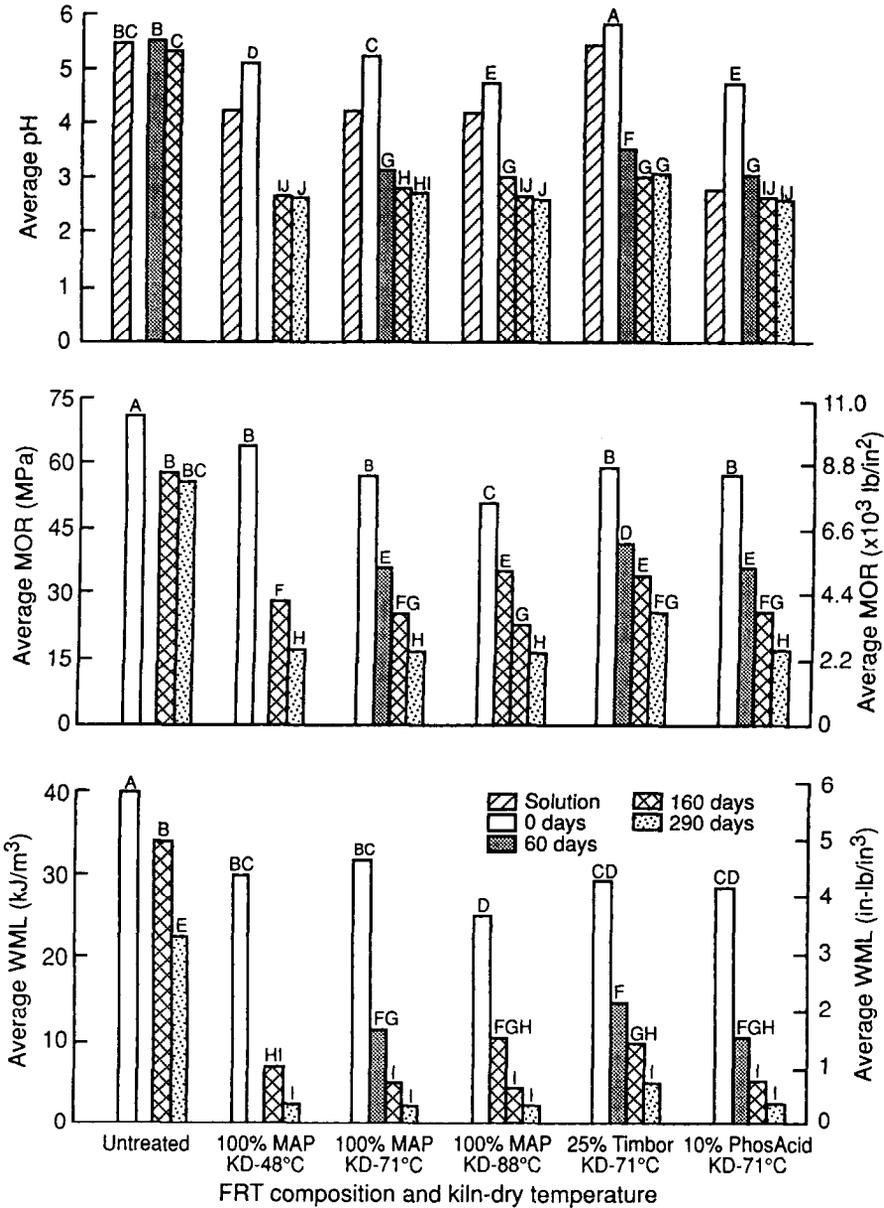


Fig. 3. Effects of various FR formulations and redry temperatures on pH, MOR, and WML of 12-mm (1/2-in.) plywood specimens exposed at 66 °C (150°F) and 75% RH. Bars with dissimilar letters are significantly different at the 95% confidence level; Table 1 defines type of processing. Solution pH was not included in the statistical analysis

specimens treated with a solution containing PA may initially have a lower pH than those treated with MAP alone, the specimens treated with MAP can potentially achieve a similar pH, depending on the MAP concentration and the availability of pH buffers.

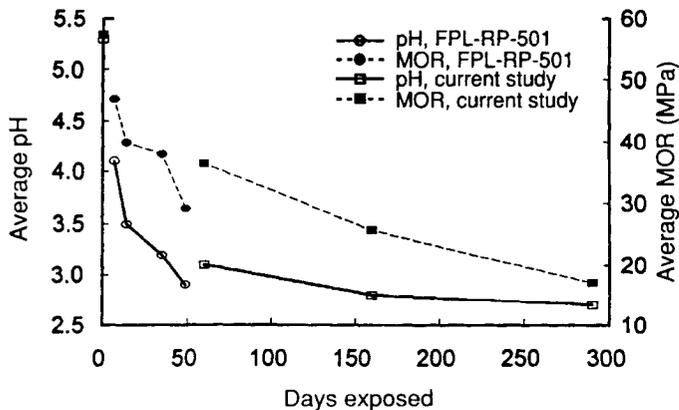


Fig. 4. Comparison of long-term exposure (up to 290 days) pH and MOR data from the current study to short-term exposure (7-49 days) data from a previous study (Winandy et al. 1991). Current study exposure was 66 °C (150°F); previous study exposure was 77 °C (170°F)

Although the pH values of some FR solutions containing boric acid were initially similar to those containing only MAP, boric acid appeared to have a buffering effect on the increase in acidity caused by the conversion or dissociation of PA and MAP to their acid forms (Fig. 2). Although this buffering effect was eventually diminished when the wood was exposed to high temperatures, after 290 days of exposure at 66 °C (150°F) the pH of the groups that were treated with formulations containing boric acid was still slightly but significantly greater than the pH of those that were not treated with boric acid. The substitution of 25% Timbor in the FR treatment of the 12-mm (1/2-in.) specimens also resulted in significantly greater pH of the treated plywood after each exposure (Fig. 3). This effect is similar to but more pronounced than that noted for the boric acid addition to the 16-mm (5/8-in.) plywood treatment. The pH of the treatment solution containing Timbor was higher than that of other solutions (Table 1).

Also similar to the effects observed with the 16-mm (5/8-in.) plywood, the addition of PA to the FR treatment caused an initial significant decrease in pH (Fig. 3), although this difference lessened after extended high temperature exposure. These findings add credibility to the theory that both MAP and PA may potentially achieve similar pH levels if sufficient energy is supplied to cause dissociation of the MAP, and that borates can act as a pH buffer to mediate the effect of the dissociation. These findings also demonstrate that the pH of the treating solution alone is not always a good predictor of wood pH, but rather it is the overall buffering potential and concentration of the components that are included in the FR formulation.

Comparison of groups re-dried at 49 °C, 71 °C, and 88 °C (120°F, 160°F, and 190°F) reveals that kiln-drying temperature had little lasting effect and no interaction with the pH of the specimens after extended high temperature exposure (Fig. 3). Although the specimens kiln dried at 88 °C (190°F) initially had a lower pH than those dried at 49 °C (120°F) or 71 °C (160°F), this difference largely disappeared after 60 to 290 days exposure at 66 °C (150°F), 75% RH. It is likely that the cumulative effects of differential temperature during a few days of kiln

drying became insignificant when compared with 60 or more days of steady-state exposure to uniformly high temperatures of 66 °C (150°F).

Relationship between pH and mechanical properties

Comparison of the plywood pH in the various treatment groups with their corresponding MOR and WML values reveals a close relationship between the FRT plywood acidity and strength loss (Table 3). Although starting and ending points often differed significantly, regression of pH against MOR for both plywood thicknesses and all treatment groups reveals that the rate of decrease in MOR with decreasing pH was similar for 8 of 10 FR treatment groups. A single correlation coefficient ($R^2 = 0.74$) was calculated for those 8 groups because there was not a significant difference in the slopes of the regression lines (Fig. 5). The two exceptions seem logical, because the group treated with the solution containing 80% MAP/20% PA lost strength at a significantly more rapid rate than did the other groups, while the group treated with a solution containing 75% MAP/25% Timbor lost strength at a significantly slower rate than did all other treatment groups. The steeper slope of the 80% MAP/20% PA line is attributable to the higher initial strength loss. At the end of the 290-day exposure, the 80% MAP/20% PA group had MOR and pH values similar to the group treated with 100% MAP (Fig. 2). There was also a poorer relationship between MOR and pH for the 75% MAP/25% Timbor treatment ($R^2 = 0.42$) than for the other treatment groups ($R^2 = 0.74$). This appears to be attributable to the generally poor relationship between pH and strength values at the higher pH levels.

A similar regression of pH against WML values reveals similar trends to that of MOR, although the differences in slopes are less significant (Fig. 6). For WML, the slope of the line for the group treated with the 80% MAP/20% PA solution was not significantly different than the slope of the other lines, and a single correlation coefficient ($R^2 = 0.68$) was calculated for these 9 groups. In addition, the difference between the 75% MAP/25% Timbor group and the other groups was only significant at the 93% confidence level. However, this is not surprising because the inherent variability of WML is significantly greater than that for MOR. As with MOR, the correlation between pH and WML was poorer for the 75% MAP/25% Timbor ($R^2 = 0.39$) group than for the other groups. There was little

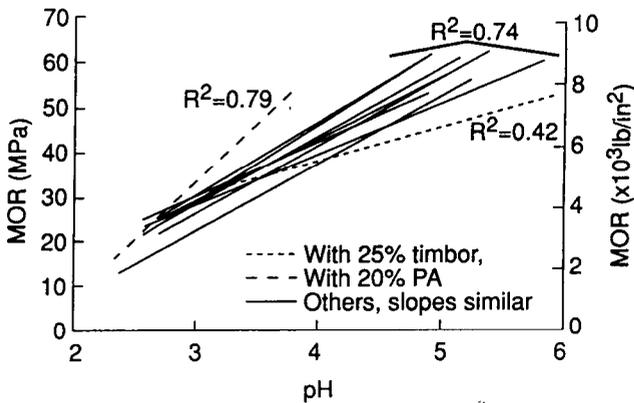


Fig. 5. Regression of pH compared with MOR across all FR treatment groups and both plywood thicknesses (control groups not shown). A single R^2 value was calculated for the eight lines with similar slopes

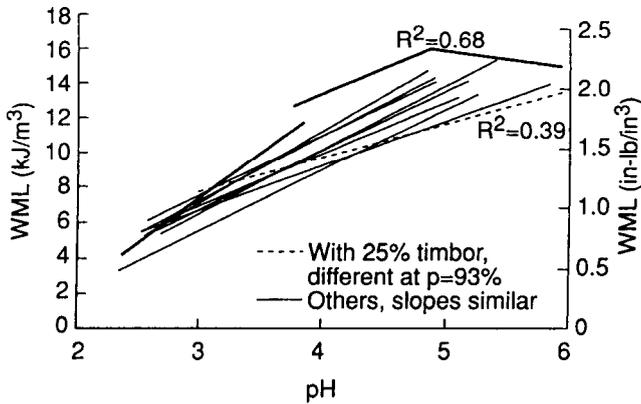


Fig. 6. Regression of pH compared with WML for all FR treatment groups and both plywood thicknesses (control groups not shown). A single R^2 value was calculated for the nine lines with similar slopes

correlation between pH and MOE of the specimens. Elastic properties are much less affected by FR degradation than are MOR or WML (Winandy et al. 1991). A detailed discussion of the relationships between FRT and MOE in this study can be found in Winandy (1997).

The similarity of the slopes of the regression lines of pH compared with WML and MOR indicates that the effects of FR treatment on strength and pH were independent of plywood thickness. Although the entire range of commercial plywood thicknesses was not evaluated, it appears likely that thickness will have little interaction with FRT effects within the range of plywood thicknesses used commercially for roof sheathing.

Although a strong overall relationship between pH and mechanical properties was noted, this was not the case immediately after treatment, because the pH of the treated wood decreased much more significantly than did either MOR or WML (Figs. 2 and 3). For example, the pH of the samples treated with the MAP/PA/BA solution ratio of 80/20/0 was significantly less than that treated with any other formulation before high temperature exposure, but neither the MOR or WML values reflected this difference (Fig. 2). These initial pH values, although substantially less than those for untreated or water-treated wood, were apparently not acidic enough to cause significant strength reductions. Wood pH also does not reflect or predict strength loss caused by the treatment process itself. For example, treatment with water alone slightly reduced the MOR of the plywood in comparison to the untreated samples, while increasing the pH of the wood (Fig. 2).

Conversely, the changes in the pH of the treatment groups closely paralleled changes in the mechanical properties of the groups after 60 to 160 days of high temperature exposure (Figs. 2 and 3). During this time, the pH of all the FR treatment groups decreased to between 2.5 and 3.5, and substantial decreases in both MOR and WML were detected. The pH decrease during this exposure apparently entered the range of acidity where damage to the wood structure began to occur. It is notable that even the formulation that contained 25% Timbor suffered substantial decreases in pH, MOR, and WML during this period. Comparison of pH and MOR values for MAP treated specimens from a previous study (Winandy 1991) indicates that closely corresponding decreases in pH and MOR occur within 7-50 days of high temperature exposure (Fig. 4).

The relationship between pH and strength properties did appear to weaken again during the final 130 days of exposure (Figs. 2 and 3). The pH of most treatment groups appeared to change relatively little after 160 days, while the MOR and WML values for the samples continued to decline. It is probable that the chemical reactions that cause a decrease in the pH reach equilibrium much more rapidly than the subsequent reactions that cause strength losses in wood. Additional extended exposure would be required to determine the final strength effects of a particular pH-temperature combination.

Thus, a low pH reading for FR plywood indicates that some strength loss has occurred and that additional strength loss is likely in the near future (given additional high temperature exposure). Using pH alone, it may be difficult to separate wood that has been severely degraded from wood that has been only moderately degraded. In contrast, it appears that a relatively high pH (4 or above) level for FRT plywood is a good indicator that the plywood has not yet suffered major strength loss. However, additional evaluations of pH and mechanical properties of plywood under in-service conditions may be necessary before pH can be used in field evaluations of FRT degrade. For example, even though the untreated 12-mm (1/2-in) plywood suffered significant reductions in MOR and WML after extended exposure at 66 °C (150°F) (Fig. 3), these strength losses were not reflected in the pH of the untreated samples. Thus, a complete understanding of how factors such as treatment and redry conditions, FRT-type, wood species, and moisture content affect the relationship between pH and mechanical properties is needed before we can simply monitor pH and predict strength loss.

Conclusions

The pH of FRT plywood is significantly affected by FR formulation and the duration of high temperature exposure. In this study, the pH of plywood treated with all FR formulations decreased dramatically during the first 60 to 160 days of exposure at 66 °C (150°F). Formulations containing PA and MAP or MAP alone eventually reached similar pH levels when subjected to lengthy high temperature exposure, lending credence to the hypothesis that the effects of the two types of formulations are similar if sufficient energy is supplied to cause conversion of the MAP to PA. Although solutions containing boric acid initially had pH values equivalent or less than those of MAP alone, these solutions appeared to lessen the decrease of pH after 290 days of high temperature exposure, perhaps by mediating the conversion of MAP to PA.

The trends in pH reduction for all the FRT groups paralleled the trends of decreasing MOR and WML. For the FRT plywood, strength loss and pH decreases attributed to thermal degradation were closely correlated during the first 160 days of high temperature exposure. During the final days of exposure, pH tended to stabilize, while strength losses continued to decline.

These findings suggest that the pH of FRT plywood is a good indicator of the potential for future strength loss if the plywood is early in its exposure to high temperatures. There is also the potential that pH combined with other evaluation techniques might be effectively used to predict the current condition of plywood. Additional research is planned in this area.

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