VERIFICATION OF A KINETICS-BASED MODEL FOR LONG-TERM EFFECTS OF FIRE RETARDANTS ON BENDING STRENGTH AT ELEVATED TEMPERATURES

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ABSTRACT

This study verifies a single-stage reaction-rate model for the long-term effects of various fire retardants. The adequacy of predictions from our previously reported models was tested using data from fire-retardant-treated wood exposed at 66°C (150°F) and 75% relative humidity for 3 or 4 years. Our analysis showed that if the treated wood experienced significant thermal degradation early during exposure to high temperature, then the previously reported model parameters adequately predicted thermal degradation for up to 4 years of steady-state exposure. However, if the treated wood did not experience significant thermal degradation early during high-temperature exposure, then the previous parameter estimates tended to underpredict degrade. Modified parameter estimates are presented where appropriate. This report also describes the practical implications of running the verified models for up to 10 annual iterations of an actual year of measured roof sheathing temperatures derived from structures exposed in the field. Our results predict that monoammonium phosphate, a generic fire-retardant formulation, can be expected to cause an additional 15% loss in original strength capacity in 10 years if used for roof sheathing under similar conditions.

Keywords: Fire retardant, treatment, thermal degradation, modeling, kinetics, serviceability.

INTRODUCTION

Over the last few years, some fire-retardant (FR)-treated plywood roof sheathing and roof truss lumber have failed in-service upon extended exposure to elevated roof-attic temperatures (APA 1989; NAHB 1990). To understand this phenomenon, several kinetics-based models have been evaluated to predict strength loss in FR-treated and untreated wood as a function of cumulative thermal exposure. New standardized test methods have been developed to generate strength-loss data at elevated temperatures (ASTM 1997a, b). Recently, another new standard (ASTM 1998) was approved that develops design adjustments from application of kinetic-based models to these strength-loss data. Previous studies had suggested that thermal degradation of FR-treated wood might be modeled using a classic two-stage kinetic theory (Woo 1981; Pasek and McIntyre 1990; Winandy et al. 1991). Our

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subsequent analysis of alternative models led us to support instead the use of a nontraditional, single-stage "full" modeling approach because of its reduced residual error, more random error structure, and improved statistical properties under certain assumptions. In a previous report (Winandy and Lebow 1996), we discussed the advantages and disadvantages of using a two-stage approach to predict strength loss over time of exposure. We showed that "full" models were superior to the best alternative two-stage models, due to their maximized fit and more random error structure. Comparison of the two-stage models showed that the most appropriate choice is the model that uses a nonlinear first step with additive error at each temperature, followed by a second step using a weighted regression across temperatures. This weighted-regression approach offsets problems arising from excessive variability in measuring thermal degradation at lower temperatures (≤54°C (≤130°F)). The traditional two-stage model and alternative single-stage (full) model are described in detail in the Appendix.

We found that when modeling the reaction rate (i.e., rate of strength loss over time) of wood treated with inorganic phosphates, the essential difference between the full model and the nonlinear-weighted two-stage approach was that the reaction rates predicted with the full model were greater (i.e., faster) at higher temperatures (≥66°C (≥150°F)) and less (i.e., slower) at lower temperatures (Winandy and Lebow 1996). Such a finding partially explained the difference between laboratory degradation and excessive field degradation (Winandy et al. 1991). The inherent variability in assessing degradation in the mechanical properties of wood had made it difficult for early attempts at modeling thermal degrade to obtain stable rate estimates for thermal degradation at lower temperatures (≤54°C (≤130°F)). Accordingly, we showed that the decision of the "best" model form was essential in addressing the critical question of whether thermal degradation of FR-treated wood in roof systems is more, less, or equally influenced by a limited number of roof exposure hours at higher temperatures (≥66°C (≥150°F)) or by many more hours of exposure at lower temperatures (Winandy and Lebow 1996).

The practical implications of the divergent kinetic parameter estimates between the full and two-stage models were significant. They implied that wood treated with inorganic phosphate (phosphoric acid or monoammonium phosphate) underwent a measurably greater strength loss than did untreated wood or even wood treated with organic phosphates, like guanylurea phosphate/boric acid, for every hour of exposure when exposed at higher temperatures (≥54°C (≥130°F)). This characteristic was of interest because it partially explained the poor in-service performance of some inorganic phosphate based FR-treatments used on plywood roof sheathing (APA 1989; NAHB 1990).

The objective of this report is to present verification for a mechanistic, single-stage (full) reaction-rate model using 3- and 4-year exposure data obtained at 66°C (150°F) and 75% relative humidity (RH). The 14 groups of specimens used in this study were a subset of 161 groups of specimens matched for modulus of elasticity and density; the remaining groups were primarily used in shorter-term exposure tests (LeVan et al. 1990; Winandy 1995). The full model can be used to identify FR chemicals that are most susceptible to accelerating thermal degradation and the critical temperature levels above which accelerated degradation occurs.

EXPERIMENTAL METHODS

Small, clear 16-mm (5/8-inch) tangential by 35-mm (13/8-inch) radial by 305-mm (12-inch) long test specimens were cut from 19-mm-(nominal l-inch-) thick vertical grain southern pine lumber. Each specimen was nondestructively evaluated using stress-wave timer and density to measure modulus of elasticity (MOE). This MOE value was then used as a sorting criterion to assign the 4,830 individual

TABLE 1. *Fire-retardant treatments.*

Chemical	Average retention (kg/m^3 (lb/ft^3))	Concentration (% wt)	pH Pre-treatment	pH Post-treatment	Dissociation constant[a] (Ka)
Phosphoric acid (PA)	58.2 (3.64)	8.38	1.43	1.3	7.5×10^{-3}
Monoammonium phosphate (MAP)	55.5 (3.47)	8.14	4.27	4.21	1.6×10^{-7}
Guanylurea phosphate/boric acid (GUP/B)	55.5 (3.47)	8.19	3.10	3.13	7.9×10^{-8}
Dicyandiamide-phosphoric acid-formaldehyde (DPF)	56.8 (3.55)	8.24	3.75	3.75	—
Diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate (OPE)	55.4 (3.46)	8.14	6.58	5.46	—
Borax/boric acid (BBA)	56.3 (3.52)	8.14	7.96	8.06	5.8×10^{-10}
Untreated (UNT)	—	—	—	—	—

[a] Zumdahl 1989.

specimens into 161 E-matched groups of 30 specimens each (25 for strength measurements and 5 for treatment retention measurements). Each density/E-matched group had nearly equal proportions of high, medium, and low density/E-rated specimens.

Eighty-four (84) matched groups of FR-treated specimens and controls were exposed at 27°C (80°F)/30% RH, 54°C (130°F)/73% RH, or 82°C (180°F)/50% RH for up to 5 months. The specimens were mechanically tested in flexure as simply supported flat-wise beams with center-point loading over a 229-mm (9-in.) span. These results were reported previously (LeVan et al. 1990), as were the results of tests on an additional set of 42 matched groups exposed at 66°C (150°F)/75% RH for up to 18 months (Winandy 1995). In the current report, mechanical test results for yet another set of 14 matched groups (1 untreated and 6 FR-treated groups × two exposure periods) after 3- and 4-year exposures at 66°C (150°F)/75% RH are reported. The remaining 21 matched groups were tested after 2, 4, and 6 years of exposure at 27°C (80°F); these results were unchanged from those reported for the 3- and 160-day exposures (LeVan et al. 1990).

TABLE 2. *Specific gravity and moisture content of FR-treated wood after 3 or 4 years of exposure at 66°C (150°F) and 75% relative humidity.*

FR treatment[a]	Exposure (years)	Sample size	Moisture content (%)	Specific gravity Mean	Specific gravity SD[b]
PA[c]	3	—	—	—	—
	4	—	—	—	—
MAP	3	25	12.9	0.47	0.04
	4	13[d]	11.2[e]	0.39[e]	—
GUP/B	3	25	11.2	0.53	0.05
	4	25	11.4	0.50	0.05
DPF	3	25	11.1	0.54	0.04
	4	25	11.8	0.53	0.05
OPE	3	25	11.2	0.54	0.04
	4	25	11.8	0.51	0.04
BBA	3	25	12.5	0.53	0.05
	4	25	10.8	0.50	0.05
UNT	3	25	12.1	0.52	0.04
	4	23	11.5	0.51	0.04

[a] See Table 1 for definition of treatment abbreviations. UNT is untreated.

[b] Standard deviation.

[c] All PA-treated specimens were too degraded to mechanically test or evaluate

[d] Twelve of 25 MAP-treated specimens were too degraded to test or evaluate.

[c] Median of 25 specimens (13 tested, 12 untested with assumed specific gravity less than tested specific gravity).

The acronyms for the FR formulations and formulation characteristics are given in Table 1. The experimental design, specimens (preparation, sorting, and evaluation), FR treatments, exposure conditions, and mechanical testing were described in detail previously (LeVan et al. 1990; Winandy 1995).

RESULTS

Physical and mechanical property data for FR-treated wood exposed for 3 and 4 years at 66°C (150°F)/75% RH are shown in Tables 2 and 3. Specimens treated with phosphoric acid (PA) completely disintegrated within the course of the initial 18-month exposure period

TABLE 3. *Flexural properties of FR-treated wood after 3 or 4 years of exposure at 66°C (150°F) and 75% relative humidity.*[a]

FR treatment	Exposure (years)	Sample Size	MOE (GPa)		MOR (MPa)		WML (kJ/m^3)	
			Mean	SD	Mean	SD	Mean	SD
MAP	3	25	7.6	1.9	18.8	6.3	2.6	1.4
	4	13	2.2[b]	—	5.8[b]	—	0.6[b]	—
GUP/B	3	25	11.6	1.7	38.5	9.2	7.6	3.0
	4	25	8.0	1.8	17.9	6.4	3.3	3.0
DPF	3	25	13.8	1.5	55.8	13.5	16.3	8.3
	4	25	8.4	1.9	22.1	8.1	5.3	5.5
OPE	3	25	14.1	1.0	72.3	13.8	28.4	10.8
	4	25	9.1	1.4	33.6	9.8	7.8	4.1
BBA	3	25	12.8	1.3	73.5	13.6	32.3	12.6
	4	25	11.7	2.5	50.3	18.4	16.2	9.2
UNT	3	25	14.6	1.4	81.3	10.8	32.7	11.4
	4	23	11.2	2.0	42.5	15.4	10.8	5.9

*MOE is modulus of elasticity; MOR, modulus of rupture; and WML, work to maximum load. For MOE, 1 GPa = 1.45 × 10^5 lb/in.^{2}; for MOR, 1 MPa = 145 lb/in^2; for WML, 1 kJ/m^3 = 0.145 in.·lbf/in.^{3}.

[b] Median values of 25 specimens (13 tested, 12 untested with assumed strength properties less than that of tested).

(Winandy 1995). Similarly, 12 of 25 specimens treated with monoammonium phosphate (MAP) experienced severe thermal degradation during the 4-year exposure and were damaged beyond testing capability. These 12 specimens resembled wood charcoal and were so severely degraded that they broke on handling. Still those specimens had not broken at zero load, and imputing zero strength into the models would have been inappropriate. Thus, for the purpose of subsequent modeling, we estimated the load imposed during normal handling and assumed an ultimate failing load of less than 44 N (10 lbf) for these specimens. In reporting this single group, we chose to use the median of all 25 specimens in that group as opposed to the mean because it provided the most reasonable estimate of the central tendency of properties for this group if the underlying distribution is symmetric (Tables 2 and 3).

Two untreated specimens in the 4-year exposure group were inadvertently not tested and were therefore treated as data missing completely at random. Considering that these data were not lost as a result of specimen degradation, property estimates based on the remaining 23 untreated specimens were considered representative of the entire group.

The new data for the 3- and 4-year exposures at 66°C (150°F) were compared with previously reported matched data (LeVan et al. 1990; Winandy 1995) using previously reported models (Winandy and Lebow 1996). Figure 1 shows extrapolation to 3 and 4 years for the nonlinear "full" model (Appendix, Eq. (6)) and the nonlinear-weighted and nonlinear-linear two-stage models. The dashes on the vertical lines indicate the minimum, mean, and maximum strength response observed for each group, with the exception of the 4-year MAP-treated group (Fig. lb). For this group, the top and bottom dashes are the maximum and median strength response, and the star represents the group of 12 severely degraded specimens that broke on handling.

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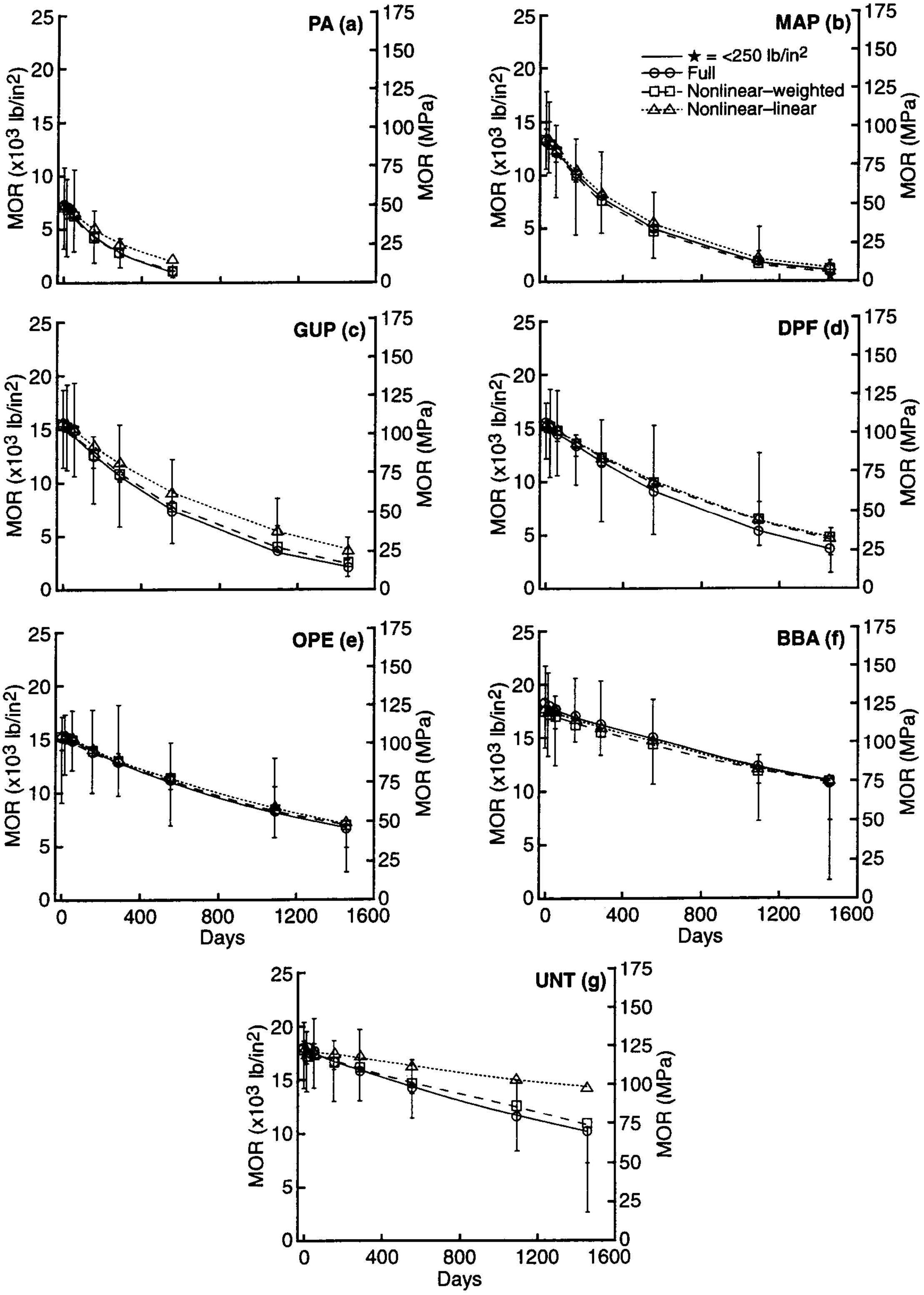
Fig. 1. Predicted strength for single-stage "full" nonlinear model and two-stage nonlinear-weighted and nonlinear-linear models using old model parameter estimates for data from long-term (3 to 4 years) exposure of untreated and FR-treated wood at 66°C (150°F). For PA, MAP (3-year), GUP/B, DPF, OPE, BBA, and UNT, dashes on vertical lines indicate minimum, mean, and maximum strength response. For MAP (4-year), top and bottom dashes indicate maximum and median strength response; the star represents the 12 severely degraded specimens.


PA (a)
MAP (b)
GUP (c)
DPF (d)
OPE (e)
BBA (f)
UNT (g)
★ = <250 lb/in²
Full
Nonlinear–weighted
Nonlinear–linear
MOR (x10³ lb/in²)
MOR (MPa)
Days
0
5
10
15
20
25
0
25
50
75
100
125
150
175
0
400
800
1200
1600

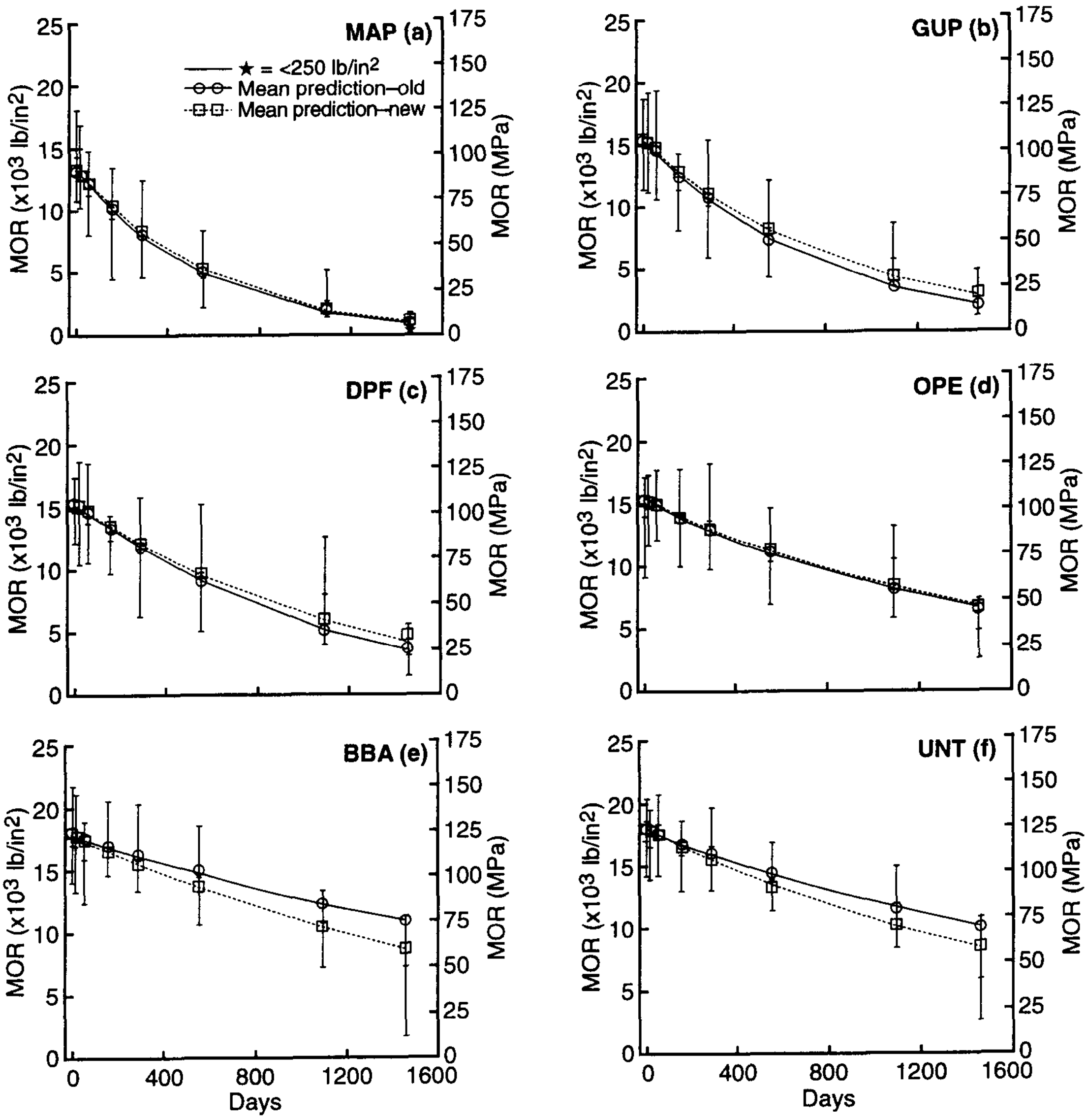


Fig. 2. Predicted strength for "full" model using old and new model parameter estimates for data from long-term exposure of untreated and FR-treated wood at 66°C (150°F).

Figure 2 compares the predicted mean strength response based on the full model (Winandy and Lebow 1996) to that of the full model modified to include the 3- and 4-year data in parameter estimates.

DISCUSSION

Two comparisons were used to evaluate the validity of the model forms and parameter estimates proposed in our earlier work (Winandy and Lebow 1996).

First, we expected the predicted estimates obtained via extrapolation for each FR treatment and untreated material to coincide with measured values after 3 and 4 years of exposure at 66°C (150°F) (Fig. 1). The differences between the nonlinear-weighted and nonlinear-linear models for dicyandiamide-phosphoric

TABLE 4. *Root mean square error for 3- and 4-year exposures based on published parameter estimates.*[a]

FR treatment	Root mean square error (MPa)								
	3 year			4 year			3 and 4 year		
	Nonlinear linear	Nonlinear weighted	Full	Nonlinear linear	Nonlinear weighted	Full	Nonlinear linear	Nonlinear weighted	Full
MAP	6.98	9.54	8.69	1.87[b]	3.39[b]	2.77[b]	5.76[b]	7.99[b]	7.23[b]
GUP/B	9.09	14.65	16.78	10.22	6.34	7.01	9.67	11.29	12.86
DPF	17.75	17.99	22.52	13.29	13.08	9.10	15.68	15.72	17.18
OPE	19.60	19.83	20.74	17.23	17.02	15.80	18.46	18.48	18.44
BBA	17.01	16.28	17.41	30.23	29.38	30.45	24.53	23.75	24.80
UNT	24.63	11.24	10.64	57.71	36.35	31.46	43.73	26.44	23.09

[a] Winandy and Lebow 1996.

[b] Root mean square error based on observed values only; broken specimens not included in calculation

acid-formaldehyde (DPF), diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate (OPE), and borax/boric acid (BBA) (Fig. 1d-f) are the result of differences in estimates of their initial strength.

Second, we expected the root mean square error from this analysis to be similar to that reported previously. For this analysis, we used root mean square error as a measure for goodness of fit (Tables 4 and 6). A direct comparison of parameter estimates and the percentage of change in mean square error due to updating the estimates (Table 5) shows that the Winandy and Lebow (1996) models adequately fit the new 3- and 4-year data for acidic phosphate-based FR-treated specimens. These acidic FR-formulations (i.e., specimens treated with MAP, guanylurea phosphate/boric acid (GUP/B), DPF, and OPE) showed significant strength loss from thermal degradation during

TABLE 5. *Regression coefficients for two-stage and single-stage model forms*

Model type	FR treatment	Old parameters[a]		New parameters		Change in parameters (%)		MSE[e] (% reduction)
		Ln(A) (day^{-1})	E_a ($kJ \cdot mole^{-1} \cdot day^{-1}$)	Ln(A) (day^{-1})	E_a ($kJ \cdot mole^{-1} \cdot day^{-1}$)	Ln(a) (day^{-1})	E_a ($kJ \cdot mole^{-1} \cdot day^{-1}$)	
Nonlinear-weighted[b]	MAP[c]	21.2	77.6	22.3	81.0	5.2	4.4	0.8
	GUP/B	23.9	86.5	26.6	94.4	11.3	9.1	–0.2
	DPF	30.1	105.0	31.1	108.0	3.3	2.9	–0.7
	OPE	20.6	79.5	20.3	78.7	–1.5	–1.0	–0.3
	BBA	–8.6	–1.3	–22.0	–40.2	155.8	2992.3	6.8
	UNT	24.9	93.1	15.9	66.6	–36.1	–28.5	15.2
Nonlinear-linear[b]	MAP[c]	25.7	90.8	25.8	91.0	0.4	0.2	–0.6
	GUP/B	31.5	108.5	31.6	109.0	0.3	0.5	–1.5
	DPF	30.1	105.0	31.1	108.0	3.3	2.9	–0.8
	OPE	20.6	79.5	20.3	78.7	–1.5	–1.0	0.2
	BBA	–8.6	–1.3	–22.0	–40.2	155.8	2992.3	7.4
	UNT	48.5	161.8	48.1	160.3	–0.8	–0.9	3.7
Full model[d]	MAP[c]	28.2	97.4	28.8	99.3	2.1	2.0	0.1
	GUP/B	20.8	77.5	23.1	84.3	11.1	8.8	2.3
	DPF	23.4	85.9	25.6	92.2	9.4	7.3	1.6
	OPE	12.5	56.6	13.0	58.0	4.0	2.5	0.0
	BBA	–3.2	–13.8	–11.2	–9.8	250.0	–29.0	9.0
	UNT	16.8	69.9	13.1	58.5	–22.0	–16.3	7.7

[a] Winandy and Lebow 1996. 1 kJ/mole·day = 8.85 × 10^3 in.·lbf/mole·day.

[b] Two-stage model (fire stage–second stage).

[c] New estimates based on using substitution methods for 12 broken specimens (see text).

[d] Single-stage model.

[e] Mean square error.

the first 18 months of exposure. In Table 4, extreme deviances from previously reported values (Winandy and Lebow 1996) are an indication of improper fit at these extrapolated regions. An example of such can be seen in Fig. 1, for untreated specimens using the two-stage, nonlinear-linear model. For that model the predicted values were not within the range of those 4-year untreated data, and the resulting change in mean square error is moderate (Table 5). Recall that since the PA-treated specimens completely disintegrated within the initial 18-month exposure period, we were unable to obtain independent 3- and 4-year data with which to verify model fit and parameter estimates. Specimens treated with the other FR formulations (MPA, GUP/B, DPF, OPE) that were similar to PA in their chemistry, but less acidic, also experienced significant thermal degradation and their corresponding models had minimal parameter estimate changes. Therefore, we assumed that the previously reported model parameter estimates for PA were appropriate.

Compared to previously published model parameter estimates, the updated estimates were practically unchanged for FR-treated specimens that experienced significant strength loss from thermal degradation during the first 18 months of exposure (Table 5, MAP, GUP/B, DPF, and OPE). However, significant parameter changes were needed for untreated specimens and specimens treated with BBA. These untreated specimens and the specimen treated with alkali-based FR-formulations each seemed to experience inconsistent thermal degradation early in the exposure period. This phenomenon was previously noted where the inherent variability in strength limits analysis due to the small magnitude of the treatment-thermal degrade effect and/or precision of test instrumentation. Specifically, these problems limited our ability to measure strength degradation during the first 2 to 3 months of exposure at 66°C (150°F) (Winandy 1995) or at any time at temperatures lower than 54°C (130°F) (LeVan et al. 1990). Because the MAP, GUP/B, DPF, and OPE treatments initially ranged from quite to slightly acidic, they overcame the natural pH-buffering capacity of untreated wood more quickly than did BBA or no treatment. Untreated wood would have retained all of its original pH-buffering capacity, and BBA-treatments would have imparted additional pH-buffering capacity when compared to the untreated wood. This pH buffering might explain why both experienced increased resistance to thermal degradation or increased variability in the rate of acid-mediated thermal-induced degradation.

As seen in Fig. 1, the 3- and 4-year exposure data for untreated (Fig. 1g) and BBA-treated (Fig. 1f) specimens show that the initial parameter estimates were influenced by the lack of consistent thermal degradation during the first 2 to 3 months of exposure at 66°C (150°F). However, based on the consistency in strength loss experienced after the first 2 to 3 months through 4 years of exposure, it would clearly seem that the revised model parameters are appropriate for all the FR treatments and the untreated material (Tables 5 and 6). Graphical analysis also showed that the new models maintained reasonable fits at the other temperatures (54°C (130°F) and 82°C (180°F)).

The variability in the 3-year data appeared consistent with previously reported data, but for several treatment groups, the 4-year strength values tended to be less variable than those for the other exposure groups. This reduced variability for MAP, GUP/B, and DPF (Fig. 1) was related to the data approaching the zero strength boundary. These fitted models do not take this into account. Also, the updated MAP parameter estimates were obtained by replacing the 12 broken specimens with the value of 0.86 MPa (125 lb/in.^{2}), which represented the midpoint between no load and the estimated 44-N (10-lbf) maximum “failure by hand” load that induced a stress of 1.72 MPa (250 lb/in.^{2}). This resulted in estimates similar to those obtained through more complicated procedures that take censoring into account (±0.3%) and substitution methods that use one set of extremes (0 or 1.72 MPa (250 lb/in.^{2})) (±0.2%). In general, such estimates are not

TABLE 6. *Updated regression coefficients with standard errors for various model forms.*

Model type	FR treatment	Ln(A) (day-‘)	SE (day^{-1})	E_a ($kJ \cdot mole^{-1} day^{-1}$)	SE ($kJ \cdot mol^{-1} \cdot day^{-1}$)	RMSE (MPa)
Nonlinear-weighted	MAP[a]	22.3	2.43	81.0	6.88	14.42
	GUP/B	26.6	2.27	94.4	6.45	14.18
	DPF	31.1	2.47	108.0	6.99	14.96
	OPE	20.3	4.08	78.7	11.62	14.92
	BBA	–22.0	28.59	–40.2	81.86	17.92
	UNT	15.9	4.44	66.6	12.54	14.08
Nonlinear-linear	MAP[a]	25.8	5.38	91.0	15.60	14.36
	GUP/B	31.6	8.82	109.0	25.67	14.72
	DPF	31.1	2.47	108.0	6.99	14.92
	OPE	20.3	4.08	78.7	11.62	14.89
	BBA	–22.0	28.59	–40.2	81.86	17.74
	UNT	48.1	147.60	160.3	429.83	19.26
Full model	MAP[a]	28.8	1.65	99.3	4.71	14.16
	GUP/B	23.1	1.75	84.3	4.97	14.09
	DPF	25.6	2.08	92.2	5.89	14.78
	OPE	13.0	4.25	58.0	11.98	14.80
	BBA	–11.2	7.62	–9.8	21.45	17.50
	UNT	13.1	3.71	58.5	10.45	14.06

[a] New estmutes based on using substitution methods for 12 broken specimens (see text)

desirable since substitution methods introduce bias.

The comparison of old and new parameter estimates using all available data through the 4-year exposure at 66°C (150°F) (Table 5) is shown in Fig. 2. The new, verified kinetic-based model parameters can now be used to identify FR chemicals that are more or less susceptible to accelerated thermal degradation. Use of these new models might also provide guidance on identifying the temperature thresholds at which that acceleration might occur. These kinetics-based models can be used as a tool to project serviceability assessments for partially degraded material and for establishing qualification limits for new FR formulations intended for use in high-temperature environments.

To address field serviceability concerns from laboratory data, we need to make some assumptions. Many of these assumptions in applying laboratory data and resultant kinetic models to field serviceability issues were discussed in more detail by Winandy (1994). A few of the more important ones will be reviewed here. The first assumption is that reaction rate data derived from clear wood are indicative of plywood response. A comparison of recent work on the thermal degrade of plywood and clear wood shows that rate of plywood degrade for MAP-treated plywood (Winandy et al. 1991) exposed at 66°C (150°F) was nearly equivalent based on a time-at-temperature comparison to that reported for MAP-treated clear wood (Winandy 1995). Another assumption is that derived degradation rate estimates are applicable across a wide range of wood quality levels. To address this, recent work by S. T. Lebow and Winandy (1998) found no significant (or even noticeable) differences in rate of thermal degrade between the highest to lowest plywood grade or quality levels. Further, questions exist on the interactive effects of wood moisture content on thermal degradation rates. Winandy et al. (1991) compared plywood exposed at about 6% versus 12% moisture content and found no significant differences in rate of degrade at elevated temperatures for the two tested wood moisture conditions. The final assumption is that rate of degrade is a direct response to the accumulative time-temperature history of the exposure regardless of whether it is from long-term/steady-state exposure or seasonal-cyclic/

TABLE 7. *Accumulated hours of exposure at various temperatures for FR-treated plywood roof sheathing.*[a]

Exceedence temperature		Accumulated exposure time	
(°C)	(°F)	Hours	Days
37.8	100	303	12.63
43.3	110	246	10.25
48.9	120	218	9.08
54.4	130	148	6.17
60.0	140	60	2.50
65.6	150	13	0.54
71.1	160	2	0.08

[a] Simulated attic roof structures had black shingles and no ventilation. Measurements taken on top of sheathing between 1 Oct. 1993 and 30 Sept. 1994 (Winandy and Beaumont 1995).

diurnal exposures. LeVan et al. (1996) found that rates of thermal degrade when based on the cumulative time-temperature exposure of the air in the surrounding environment were not directly comparable. But these researchers monitored only fluctuations in chamber air temperature and not actual wood temperatures. Recalling that wood is an efficient thermal insulator, LeVan et al. (1996) pointed out that the cumulative wood temperature exposure was not the same as the surrounding air temperature. When such a comparison of thermal degrade/reaction rates for plywood is adjusted and based on cumulative time-temperature exposures of the wood, degradation rates for long-term/steady-state exposure and cyclic exposures were similar.

IMPLICATIONS

To evaluate the practical implications of the various damage-accumulation models on serviceability, we ran the two "best" models (the single-stage full model and the two-stage model with a nonlinear first stage and weighted-regression second stage) for up to 10 annual iterations of one actual year of measured thermal roof sheathing exposures. Results from the actual thermal exposure of FR-treated plywood roof sheathing for 1 year (1 October 1993 through 30 September 1994) were reported by Winandy and Beaumont (1995) and are given in Table 7. The thermal load data for the top surface of the plywood roof sheathing were obtained via thermocouples attached to the sheathing and located between the roofing felt and the top surface of the sheathing. The thermal load data were obtained from 4.88-m (16-ft) by 3.66-m (12-ft) nonventilated simulated attic roof-structures with a 3 in 12 roof slope. The attic roof-structures were located and monitored at the Forest Products Laboratory Valley View test site, which is located 12.9 km (8 mi) southwest of Madison, WI. The roofing shingles were black.

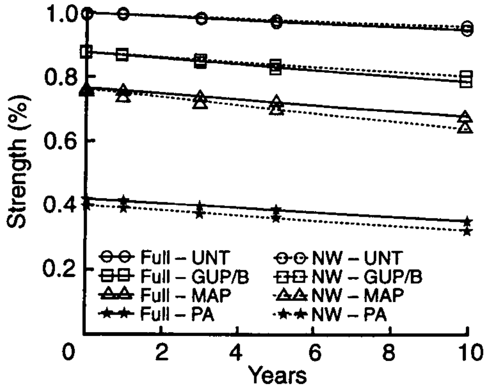


Fig. 3. Expected change in strength of FR-treated roof sheathing over projected 10-year exposure.

Figure 3 shows the expected change in strength as expressed by strength ratio (strength of treated and exposed specimens to strength of untreated and unexposed specimens) when both the full and two-stage models were run for as many as 10 annual iterations. The loss in strength projected over a 10-year period suggests that either model could be used without great differences in predicted effects. The generic FR formulation with the poorest performance was PA, for which strength was reduced from approximately 43% of the strength of untreated, unexposed material to less than 32%. This represented a 25% relative loss or an additional 11% loss in original in-service capacity in 10 years. For MAP, the strength ratio was reduced from approximately 80% of initial untreated strength to almost 65% (19% relative loss or 15% original in-service capacity loss) and for GUP/B, from approximately 90% of initial untreated strength to about 80% (11% relative loss or 10% original in-service capacity loss). The untreated material, which started the degradation cycle with more than twice the initial strength of PA-treated material, experienced a 4% loss in original in-service capacity over 10 years.

The similarity in performance between MAP-treated and GUP/B-treated specimens implies that MAP-treated material that had not been damaged in treatment and post-treatment processing might be expected to have field performance similar to that of GUP/B-treated material, which has been successfully used for more than 15 years without known thermal degradation-related in-service failures. Based on these results and those of a recent related report on pH-buffers (Winandy 1997), the predicted performance of MAP-treated material would be significantly diminished if the MAP formulation were combined with or contaminated by significant quantities of PA. Similarly, the predicted performance of MAP-treated material would be expected to be significantly improved if pH-buffered with borates.

Recalling the divergence in predicted reaction rates between the full and two-stage models, especially at higher temperatures, the predicted difference in field serviceability would have been greater when using the single-stage full model if roof sheathing temperature data from a warmer, sunnier climate than Madison, WI had been used.

Further work is now needed to go beyond point estimates and to account for environmental variability as well as model variability.

CONCLUSIONS

New data for 3- and 4-year exposures at 66°C (150°F)/75 % relative humidity were used to verify previously reported models. Previously reported model parameters were practically unchanged for four of five fire-retardant (FR) formulations that showed significant strength loss from thermal degradation during the first 18 months of exposure (MAP, GUP/B, DPF, and OPE). Although the previously reported model form seemed appropriate, significant parameter estimate updates were nevertheless needed for untreated wood and BBA-treated wood, which did not experience consistent thermal degradation during the first 2 to 3 months of exposure at 66°C (150°F).

Applying the full model to actual roof sheathing temperature data to make field serviceability projections showed that PA, the generic FR formulation that caused the greatest initial strength loss, would experience more than 10% loss in original in-service capacity in 10 years if used as roof sheathing in Madison, WI. Based on time-temperature superposition, this loss in capacity would be greater in warmer, sunnier climates. For MAP, GUP/B, and untreated material, which start the degradation cycle with nearly twice the initial strength of PA-treated material, the loss in original in-service capacity over 10 years might amount to an additional 15%, 10%, and 4%, respectively.

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APPENDIX

Two modeling approaches were considered in this research program, the traditional two-stage Arrhenius approach and a single-stage (i.e., "full") approach based on time-temperature superposition. When considering the two-stage approach, three initial model forms were considered in the first stage to obtain estimates of the rate of strength loss at each exposure temperature.

TRADITIONAL MODELS

A two-stage Arrhenius-based modeling approach has often been used in modeling fire-retardant (FR) reaction rates (i.e., rate of strength loss over time) (Woo 1981; Pasek and McIntyre 1990; Winandy et al. 1991). In this approach, the same functional form is used at each temperature, and the model parameters are estimated using the appropriate temperature data set. In the first stage of a traditional two-stage approach, the dependent variable, in our case strength, or a suitable transformation is defined as a function of time at several temperatures:

linear approach

$$Y_{ij} = b_{ij} + (-k_{ij}X) \tag{1}$$

nonlinear approach

$$Y_{ij} = b_{ij}\exp(-k_{ij}X) \tag{2}$$

transformed linear approach

$$\ln Y_{ij} = b_{ij} + (-k_{ij}X) \tag{3}$$

where

i = index of temperature of exposure (e.g., T_1 = 328 K (54°C), T_2 = 339 K (66°C), ...),

j = index of FR chemical (e.g., F_1 = PA, F_2 = MAP,...),

Y_{ij} = bending strength (MPa) at temperature T_i for FR F_j,

X = time (days) at temperature T_i for FR F_j, and

b_{ij}, k_{ij} are fitted parameters at temperature T_i and FR F_j.

It is often reasonable to assume that the initial mean strength will be the same at different temperatures. This can be done by forcing b_{ij} to be equal at each temperature, which adds another stage to modeling. The choice of functional form is dependent on the assumption of how deviations arise.

Based on kinetic theory, it could be expected that the rates of strength loss over time are dependent on temperature via the Arrhenius theory:

$$k'_j = A_j\exp(-E_{aj}/RT) \tag{4}$$

where

k'_j = rate constant (adjusted to a common relative humidity) for FR F_j,

A_j = pre-exponential factor,

E_{aj} = activation energy,

R = gas constant (J/K·mole), and

T = temperature (K).

Thus, in the second stage of the two-stage approach, the fitted model parameters (k_{ij}) that were derived in the first stage for each temperature are fit to Eq. (4) after humidity adjustment (i.e., the Arrhenius equation is used to determine the fire retardant's characteristic rate constant of strength loss over the range of temperatures studied). When Eq. (4) is constrained to include only positive strength loss estimates, it can be expressed in terms of natural logarithms as

$$k_j^* = \ln(k'_j) = \ln(A_j) + (-E_{aj}/RT) \quad (5)$$

As listed, the first-stage models are the linear (1) transformably linear (3) and nonlinear (2) models. Once estimated in the first stage, these isothermal rate constants (k_{ij}) are considered as independent observations of the dependent variable, which are applied in the second stage using an Arrhenius-type approach to model rate of strength loss as a function of thermal exposure. Hence, the estimated parameters of the second stage are functions of the first-stage parameter estimates. If the second-stage estimates for the parameters of Eq. (5) are obtained using simple linear regression, then this stage is called linear. These estimates may also be obtained by a weighted linear regression to take into account variability of the first-stage estimates; this second stage is then called weighted.

After concluding that the nonlinear model best described the 66°C (150°F) data, the 82°C (180°F) data (reported in LeVan et al. 1990) were modeled with similar results in that the nonlinear model fit the data better than did the linear or transformed linear models, However, the 54°C (130°F) data fit only slightly better, which was probably related to the general lack of strength loss at 54°C (130°F). Since the specimens exposed at 27°C (80°F) showed no strength loss over their test period of 6 years, these data were not included in further model development. In our overall opinion, results (both parameter estimates and standard errors) from the weighted regression technique seem more appropriate than those obtained from a simple linear regression, especially given that the estimates were obtained from different experiments over different lengths of time with different sample sizes,

FULL MODELS

A single-stage approach quantitatively based on time-temperature superposition was also feasible for use in modeling reaction rates. Thus, we also considered one-stage (commonly termed "full") models that, in just one step, relate strength loss to time, temperature, and relative humidity. Based on the results of the two-stage model-building process just outlined, back substitution of Eq. (4) into (2) yields

$$Y_{ij} = b_j \exp(-XA_j(H_i/H_0)\exp(E_{aj}/RT_i)) \quad (6)$$

where

i = index of exposure temperature,

j = index of FR chemical,

Y_{ij} = bending strength (MPa) at temperature T_i for FR F_j,

X = time (days) at temperature T_i for FR F_j,

b_j = initial bending strength (MPa) at time $X = 0$,

H_i = relative humidity at test for temperature T_i,

H_0 = normalized relative humidity, 67% RH, per ASTM D5516 (1996),

A_j = pre-exponential factor,

$E_{a\,j}$ = activation energy,

R = gas constant (J/K·mole), and

T_i = temperature (K).

The "full" model appeared to fit the combined data set (54°C (130°F), 66°C (150°F), and 82°C (180°F)) as well as or slightly better than did the nonlinear-weighted two-stage approach based on a graphical comparison.