

Treatment-Processing Effects Model for WBP-Treated Lumber

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Abstract

A rationally based procedure has long been needed for assigning design adjustments to Southern Pine lumber treated with waterborne preservative. This paper attempts to develop such a procedure by evaluating a series of models to predict the short-term effects of waterborne preservative treatments on the strength of U.S. Southern Pine lumber. Input data consisted of non-parametric treated to untreated strength ratios normalized from data of seven recent reports. Input variables included material quality factors, such as grade and size, and treatment processing factors, such as preservative retention and redrying temperature. For the best models evaluated, the loss in bending strength from preservative treatment was significantly related to the differential between the pH of the treating solution and that of the untreated wood, post-treatment redrying temperature, and initial material quality. Mechanistic-based models were found to fit the compiled data set as well as or better than the best empirical models. Both mechanistic and empirical models provided a reasonable level of predictive capability, but neither was flawless. When used with the recently developed short-term load-duration adjustment model for waterborne-preservative-treated lumber, this accumulated treatment-processing effects model can result in a rationally based procedure for assigning design adjustments to waterborne-preservative-treated Southern Pine lumber.

Keywords: Preservative, treatment, modeling, strength, allowable stress design values

Introduction

Recognizing that waterborne preservative (WBP) treatments can sometimes reduce mechanical properties, a number of studies were conducted over the last 15 years to quantify WBP-treatment effects. As a result, U.S. Treating Standards were revised in 1987 to include process limitations for a maximum dry-bulb temperature in the redrying process of 88°C (190°F), then further limited to 74°C (165°F) in 1990 (AWPA 1995). However, there is a practical need for a rational basis for assigning adjustments to allowable stress design values based on a systematic analysis of these recently developed data

Most of the treatment effects data for lumber are for Southern Pine (*Pinus* spp.). As such, the treatment effects models developed herein pertain only to WBP-treated Southern Pine lumber. In addition, the vast majority of the Southern Pine data pertains to chromated copper arsenate (CCA) preservatives, so the application of this model to ammoniacal preservative systems such as ammoniacal copper quats (ACQ), ammoniacal copper zinc arsenate (ACZA), and ammoniacal copper arsenate (ACA) should be done judiciously.

A rational basis is needed to compare candidate predictive models of strength loss induced by preservative treatment. The models developed herein use data from several independent studies that reported mechanical tests of full-size dimension lumber. Two criteria were used to select the lumber studies for this systematic analysis: (1) each study had a representative sampling plan and (2) the experimental design provided enough replicates per experimental cell to yield sufficient statistical power to reliably estimate the effect of treatment variables throughout the lower tails of the strength distribution for treated lumber. These criteria were critical because using experimental groups with less than 60 specimens inhibits both the accuracy and the reliability of ensuing models developed to

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predict lower tail strength properties (Green and Evans 1988). (Note: Accuracy is defined here as the ability to predict strength loss precisely, without over- or underpredicting. Reliability is defined as the ability to be accurate or at least conservative in predicting strength loss without underpredicting.)

Background

The two basic modeling approaches are empirical approaches and mechanistic or theoretical approaches. The purely empirical approach establishes a statistical/mathematical fit to the data, which provides optimum fit with respect to the available input parameters. Mechanistic modeling assumes that some inherent physical characteristic or characteristics control the modeled relationship. Use of mechanistic-based models requires basic knowledge of the physical properties or principles controlling the process. Mechanistic models provide good fit, but they often do not quite approach the level of fit of the empirical approach. Nevertheless, mechanistic models generally have a wider range of application because the predicted outcome is dictated by the physical characteristics of the modeled material or process.

The literature on treatments effects was recently reviewed (Winandy 1995a). Many of these studies were evaluated as potential candidates for the modeling program described in this report. After careful evaluation, only seven studies contained sufficiently comprehensive and accessible data: work on the effects of WBP treatment and post-treatment redrying (Barnes and Mitchell 1984, Barnes and others 1993, Winandy and Boone 1988, Winandy 1989), the relationship between duration of load and effects of CCA treatment (Soltis and Winandy 1989), the impact of initial kiln drying temperature on subsequent CCA effects on bending (Barnes and others 1990), and the relationship between rate of load application (e.g., time to failure) and moisture content at time of test on CCA effects (Winandy 1995b). For complete details, the reader is referred to the original publications.

Data on individual bending strength (modulus of rupture, MOR) properties for each study-group combination of the seven selected studies were obtained from the authors. These data were then used to nonparametrically estimate the treatment effect on MOR between the 5th through 95th percentiles in 5-percentile increments. Because the predictive treatment effects model or models will be primarily used to adjust design values, primary emphasis was placed at predicting treatment effects at the median value and

below. Accordingly, only treated-to-untreated (**t/u**) ratios below the 60th percentile were used. Selection of the ≤ 55 th percentile was arbitrary; however, using truncated t/u ratios at or below the 55th percentile was desirable because it generated more powerful confidence bounds in the lower tails of the nonparametrically predicted strength distributions.

Development and Description of Models

In practice, a design engineer uses a short-term design modification factor (C_p) to adjust allowable bending stress design values for the effect (t/u) of WBP treatments on strength where $C_p \approx t/u$. Based on an understanding of the physical principles driving the strength loss potential of treatment processing and material quality factors, four candidate model forms were developed for intensive evaluation. Each model initially contained terms for either pH or relative change in pH, initial kiln-drying temperature, either redrying temperature or phase-change potential (tx), grade, and size (width, section modulus, moment of inertia, or some combination thereof). Whereas one model used a pre-model in a sequential two-step approach, the other models used a single-step approach. Throughout the development of the four candidate models, terms that did not significantly ($\alpha \leq 0.10$) improve the fit of the model were systematically removed. The resulting descriptions of each model will include only terms found to enhance fit significantly.

Material quality factors have a major role in determining both anticipated strength and the magnitude of the strength effect. The one set of input variables for the developed models included quality-related variables that relate to strength. The effect of WBP treatments on strength also appears to be dated to specimen size. As width, thickness, volume, section modulus, or moment of inertia increase, t/u and C_p decrease. To explore these size-related effects, width, volume and moment of inertia were evaluated as model components.

The effect of CCA retention is related to the pH of the treating solution. Thus, two possible input parameters were evaluated, pH and the relative change in wood pH (dpH), which was defined as absolute value $15.0 - \text{pH}$ where 4.7-5.2 is the average pH for Southern Pine. Although merely using pH would work well for strictly acidic solutions, the use of the relative change in pH factor would be more appropriate for modeling both acidic solutions, such as CCA, or basic solutions, such as ACQ, ACA, or ACZA. Thus, because of its more mechanistic character, the latter input form was

selected for further evaluation. Each candidate model had a characteristic set of assumptions, problems, and advantages associated with its use as a predictive tool. One major practice used for all models (which is henceforth not discussed) was that the predicted value (C_{pi}) is unitless, so the units of each fitted parameter estimate are merely the inverse of that of its appropriate variable. Effectively, this practice immediately canceled any units in the model building process.

Model B/A

The first two-stage model (Model B/A) is empirical in nature. While Model B/A attempts to account for mechanistic relationships, final model components were solely selected to achieve maximum fit. The general form of Model A of Model B/A is

$$C_{pA} = \epsilon + \beta * MOR \quad (1)$$

where

$$C_{pA} = \text{predicted residual strength ratio}$$

$$\epsilon = b_0 + b_1 * \text{redry temperature} + b_2 * \text{grade} + b_3 * \text{width} + b_{23} * \text{grade} * \text{width} \quad (2)$$

$$\beta = b_0 + b_1 * \text{dpH} + b_2 * \text{redry} + b_3 * \text{grade} + b_4 * \text{width} + b_{34} * \text{grade} * \text{width} \quad (3)$$

$$MORK = MOR \text{ (MPa)}$$

From this we derive Model B/A as

$$C_{pB} = b_{B1} * C_{pA} + b_{B2} * ROL + b_{B3} * EMC + b_{B4} * AC \quad (4)$$

where

$$ROL = \text{Log}_{10}(ROL) \text{ as specified in ASTM D 198 (ASTM 1995)}^2$$

$$EMC = P_1/P_2 \text{ as specified from Eq. 3 of ASTM D 2915 (1995)}^3$$

$$AC = 1 \text{ if treating solution pH} > 7.0 \text{ and } 0 \text{ if solution pH} \leq 7.0$$

²Loading rate (ROL) where ASTM D 198 rate of 5 mm/min is defined as 1x and other evaluated rates are 10x = 50 mm/min and 100x = 500 mm/min.

³The ASTM D 2915 moisture content (MC) factor was selected over the Green and Evans' Quadratic Surface (Green and Evans 1989) and the ASTM D 1990 (ASTM 1995) MC adjustment models because Model B/A assumes independence between C_{p1} and equilibrium moisture content (EMC), which would be violated if either of the latter two MC adjustment models were used.

Model B/A is a sequential two-step method because it uses a pre-model (Model A) to develop fitted-input parameters for the second-step model (Model B). In this pre-model approach, a least-squares fit was used to predict the magnitude (ϵ) and rate of change (β) in the distribution of t/u ratios. These ϵ and β criteria could then be used to predict actual strength loss as a function of expected untreated strength. Six fitted-input model forms were considered: constant, linear, quadratic, square root, reduced exponential, and full exponential. The constant and linear procedures were selected as yielding the best fits (Winandy 1993). When the slope (β) of the linear form was significant ($\alpha < 0.10$), both the linear y-intercept (ϵ) and β -term were chosen. When the β -term was not significant, it was set equal to zero and the ϵ -term from the constant-model form was chosen for use as the fitted-input variable.

Material quality factors, such as grade and width, and treatment processing factors, such as dpH and redrying temperature, are the variables that drive Model B/A. In a simpler form without material quality factors, Models A and B are each extensions of a quadratic response-surface model based on a chemical preservative retention and redrying temperature model developed previously (Winandy and others 1985).

Model A was developed using data from five studies: Barnes and Mitchell (1984), Barnes and others (1990), Soltis and Winandy (1989), Winandy and Boone (1988), and Winandy (1989). In each study, data were obtained at nearly equal loading rates and tested under similar 12-percent equilibrium moisture content (EMC) conditions. These studies permitted evaluation of a fairly comprehensive set of complex second-order interactions. Model B was an expansion of Model A to account for loading rate (ROL) and EMC, using data of Winandy (1995b), and differential characteristics between ammoniacal treatments and acidic solutions, using data of Barnes and others (1993).

Model B/A requires the most complex set of input variables to predict t/u . It also has several explicit assumptions. The user assumes that the ROL and EMC effects on t/u are applicable to all other studies. Thus, the implicit assumption is that no interaction exists between ROL and EMC with respect to pH, redrying, grade, and size effects. Another implicit assumption is that the redrying temperature, retention, and grade effects are the same for all studies, so that no interaction exists between ammoniacal copper and pH, redrying, grade, and size effects.

The primary advantage of Model B/A is that despite its cumbersome nature, it works well. Because not all data are used, the user tends to have less than complete confidence in the predicted results. Finally, by its rather complex nature, Model B/A is prone to excessive over-fitting, which might be a serious potential error in a composite modeling technique such as employed here.

Model C

Model C is a simplified linear model that is considered empirical. It is very similar in form to Model A except that it is a single-step model that relates to and was fit using all seven available data sets. Like both the earlier models, Model C generates separate estimates of the magnitude (b_0) and rate of change (b_1) in t/u ratios, then combines them in a simple first-order linear format. The general form of Model C is

$$C_{pC} = b_{c0} + b_{c1} * \text{MORK} \quad (5)$$

where

C_{pC} = predicted residual strength ratio from Model C

$$b_{c0} = b_0 + b_1 * \text{dpH} + b_2 * \text{tx} + b_3 * \text{grade} + b_4 * \text{width} + b_{34} * \text{grade} * \text{width} \quad (6)$$

$$b_{c1} = b_0 + b_1 * \text{dpH} + b_2 * \text{tx} + b_3 * \text{grade} + b_4 * \text{width} + b_{34} * \text{grade} * \text{width} \quad (7)$$

$$\text{dpH} = | 5 - \text{pH} | \quad (8)$$

$$\text{tx} = (\text{redry temperature} - 273 \text{ K}) / 273 \text{ K} \quad (9)$$

MORK = MOR (MPa), grade and width (mm) as specified by PS20-94 (USDC 1994)

The primary input variables that drive Model C are the material variables of grade and width and the grade-width interaction along with anticipated untreated strength (MORK) and the mechanistic variables dpH and redrying temperature thermal potential ratio (tx). Use of the thermal potential ratio recognizes that the potential for strength loss is related more to the relative temperature change from ambient than to the temperature itself. In the respect that Model C is driven by temperature and retention, it is even more closely related to the quadratic response-surface model (Winandy and others 1985) than is Model B/A. In that Model C involves the global data set, it implicitly assumes that ROL and EMC are not differentially affected and that they are accounted for by other means.

Model C requires the same complex set of input variables to predict t/u as does Model B/A. However, because Model C analyzes the global data set, it has a different set of explicit assumptions. The primary advantage of Model C is that its global one-step

approach makes it slightly less complex to use and comprehend. Model C excelled when compared to any model using both the global data set and the fitted-input variables for predicting the effect of both main factors and second-order interactions.

Model D

Model D is a mechanistic model transformed to a linear mode using natural logarithms. The general form of Model D is

$$-\ln(C_{pD}) = b_{D0} + b_{D1} * \text{dpH} + b_{D2} * \text{tx} + b_{D3} * (1/\text{MORK}) \quad (10)$$

In a general sense, Model D is a transformed linear hybrid of Winandy and others (1985). The primary input variables that drive Model D are the material quality variable of anticipated untreated strength (MORK) and the mechanistic treatment variables dpH and tx . Model D implicitly assumes that ROL and EMC are not interactive with dpH and tx . It also assumes that any effects of ROL and EMC are accounted for by other means in the design process.

Model D assumes that no interaction exists between pH and redrying temperature and that grade-related effects can be ignored when using MORK as a de facto material quality input variable. Model D initially contained terms for both grade and width. Both added to the fit of the model, but to a lesser degree than did differential wood solution pH , strength level, or redrying temperature-related thermal potential ratio (tx) in that neither were significant ($\alpha \leq 0.10$) parameters in the mechanistic Model D. The primary advantages of Model D are its mechanistic nature and simplicity, which enhance the user's ability to comprehend how and why the model predicts as it does. Accordingly, Model D is easy to use although Model E also has some advantages in that regard.

Model E

Model E is another mechanistic model without log transformation. The general form is

$$C_{pE} = 1 - b_{E1} * (\gamma) \quad (11)$$

$$\text{where } \gamma = \text{dpH} * \text{tx} * \text{MORK} \quad (12)$$

Model E is quite similar to Model D except that it assumes a multiplicative relationship between the primary input variables of anticipated untreated strength (MORK) and treatment variables dpH and tx rather than the additive relationship of Model D. Like Models C

and D, Model E explicitly assumes that ROL and EMC are accounted for elsewhere in the design process.

Model E assumes that no interaction exists between pH and redrying temperature. It also assumes that grade-related effects are accounted for by expected strength and that the width effect for treated material is similar to that exhibited by untreated material. The primary advantage of Model E is its simplified mechanistic nature. Of the four candidate models, Model E is the easiest to use because it requires the use of only one least-squares fit term.

Comparison of Models

A systematic comparison of predictive capability of the four candidate models indicated that Models B/A and D did a slightly better job than did Models C and E (Winandy 1993). While Model B/A did a better job of accurately predicting strength loss more often than did Model D, Model B/A also tended to underpredict strength loss more often than did Model D. The number of times this occurred was computed by comparing relative positions of the predictions of Model B/A to those of Model D at the 25th percentile or below. The results show that Model D was more conservative 12 of 31 times, Model B/A was more conservative 8 of 31 times, and the models were roughly equivalent 12 of 31 times. Thus, Model D was 50 percent more conservative than Model B/A throughout the lower 25th percentile of the bending strength distribution.

The accuracy and reliability of the predictive capability of the four candidate models could not be evaluated by comparing common statistics like root mean square error (RMSE) or correlation coefficient (r^2) because these comparative criteria are of limited application when comparing dissimilar model forms. To overcome this problem, a comparable factor that judges “fit” through an empirically derived estimate was needed. This factor could then be used to test the hypothesis that the predicted values from each candidate model could accurately predict the observed values. To accomplish this, the differential predictive value (dpv) statistic was developed where

$$dpv = \sqrt{\left[\sum_{i=1}^i \sum_{j=1}^j \sum_{k=1}^k ((p-r)^2 / n) \right]} \quad (13)$$

where

- p = predicted t/u-ratio
- r = observed t/u-ratio
- i = number of studies
- j = number of groups in each study
- k = number of observations (percentiles) in each study-group
- n = total number of study-group combinations

The dpv statistic is simply a nonparametric estimate of the standard error associated with the relation between each predicted value and the actual observed value it predicts. It is quite analogous to standard deviation, which assumes normality. The reader is again referred to Winandy (1993) for complete details on the calculated dpv statistic and calculated standard error associated with each prediction.

A comparative evaluation based on a graphical analysis of predicted versus observed values indicated that in many cases the four models were very conservative in that they overpredicted strength loss. A comparison of the reliability of the calculated dpv statistic to conservatively predict strength loss for each study-group-model combination is given in Table 1 using a t-test with a ≤ 0.05 and in Table 2 using an arbitrarily selected practical limit of ± 2.5 percent. Models B/A and D were shown to accurately predict strength loss at nearly equivalent rates (Winandy 1993). However, if additional points were awarded for being conservative (i.e., overpredicting the t/u ratio) and points were subtracted for underpredicting the actual t/u ratio, then Model D did a slightly better job overall compared to Models B/A, C, and E (Table 1). Further, note that in this comparison, both mechanistic-type models—Models D and E—did best. When a much more restrictive limit of ± 2.5 percent was used to compare accuracy and reliability, Model B/A did best with no difference between Models D or E, which, in turn, both did better than Model C (Table 2). If this practical limit were to be further opened to ± 5 percent, the relative performance in accuracy and reliability would be closer to that shown in Table 1 because the nonparametrically calculated standard error derived from the dpv statistic averaged from 0.04 to 0.06.

When comparing the observed C_p values of the individual global data sets to the predicted values of the two best models, Model D seems more realistic. This conclusion is based on the excessively low treated-to-untreated ratios predicted by Model B/A for lower strength material in the No. 1 and Better grade and for the higher strength material in the No. 2 grade. These

Table 1—Comparison of accuracy and reliability of 10 consecutive predictions from the 5-to-50th percentile in 5% increments for each candidate model using a t-test at $p \leq 0.05^a$

Study and group number	Model B/A			Model C			Model D			Model E		
	>	=	<	>	=	<	>	=	<	>	=	<
Winandy (1989)												
1		6	4		7	3		8	2		8	2
2		5	5		5	5		5	5		5	5
3	6	4		5	4	1	3	5	2	7	3	
4	2	5	3		6	4		7	3		6	4
Winandy & Boone (1988)												
1	2	5	3	5	5		5	5		4	6	
2	2	6	2	3	7		3	7		3	7	
3	4	6		6	4		6	4		5	5	
4	1	6	3	2	8		2	8		1	6	3
5		6	4	2	6	2	1	6	3	3	4	3
8	2	5	3	2	6	2	2	6	2	2	5	3
Barnes & Mitchell (1984)												
1	2	6	2	4	6			6	4	3	7	
2	1	7	2	3	7		2	8		4	6	
Barnes & others (1993)												
A	2	6	2		2	8	1	5	4		4	6
B	3	5	2		3	7		6	4		6	4
C	2	8		2	8		5	5		6	4	
Barnes & others (1990)												
3		8	2	1	6	3	1	6	3		7	3
4		5	5		6	4		6	4		5	5
5	5	5		5	5		6	4		4	6	
8		6	4		6	4		6	4		6	4
9	3	7		2	8		2	8		2	8	
10	1	6	3		8	2		7	3		7	3
Soltis & Winandy (1989)												
5	4	6		1	5	4	1	6	3	4	4	2
Winandy (1995b)												
P	1	6	3	1	9		1	7	2	1	9	
Z	3	7		6	4		5	5		6	4	
Q	1	7	2	3	5	2	3	5	2	3	5	2
U	3	6	1	7	3		6	4		5	5	
T	4	6		4	6		5	5		6	4	
X	2	4	4	2	3	5	2	3	5	2	4	4
N	3	6	1	5	5		4	6		7	3	
S		7	3		6	4		9	1		9	1
L	3	7		3	6	1	3	6	1	3	6	1
Count of >=,<	62	185	63	74	175	61	69	184	57	81	174	55
Points from >=,<	62	370	-63	74	350	-61	69	368	-57	81	348	-55
Total points			369			363			380			374

^aTwo points were awarded for accurately predicting (=) strength loss within the $p \leq 0.05$ confidence interval, one point awarded for conservatively overpredicting (>) strength loss, and one point subtracted for underpredicting (<) strength loss

Table 2—Comparison of accuracy and reliability of 10 consecutive predictions from the 5–to–50th percentile in 5% increments for each candidate model using an arbitrarily selected limit of +2.5 percent^a

Study and group number	Model B/A			Model C			Model D			Model E		
	>	=	<	>	=	<	>	=	<	>	=	<
Winandy (1989)												
1		7	3		7	3		7	3		7	3
2		1	9			10		2	8	7		10
3	10			6	3	1	3	5	2		3	
4	1	6	3		3	7		3	7		3	7
Winandy & Boone (1988)												
1	4	3	3	6	3	1	7	2	1	6	2	2
2	3	2	5	4	4	2	4	4	2	5	4	1
3	7	2	1	9	1		9	1		8	2	
4	2	4	4	3	5	2	2	8		3	3	4
5	1	5	4	3	5	2	3	3	4	5	2	3
8	3	4	3	5	1	4	3	4	3	2	5	3
Barnes & Mitchell (1984)												
1	2	6	2	5	5			7	3	3	7	
2	1	8	1	5	5		2	8		5	5	
Barnes & others (1993)												
A	2	6	2			10	1	4	5		1	9
B	3	5	2			10			10			10
C	4	6		4	4	2	10			10		
Barnes & others (1990)												
3		5	5	2	4	4	2	4	4	1	4	5
4		3	7		2	8		2	8		2	8
5	8	2		9	1		8	2		4	5	1
8		4	6	1	5	4	1	5	4		6	4
9	8	1	1	8		2	8		2	6	2	2
10	6	1	3	6		4	6	1	3		6	4
Soltis & Winandy (1989)												
5	4	6		1	5	4	1	5	4	4	3	3
Winandy (1995b)												
P	1	5	4	1	8	1	1	7	2	2	8	
Z	2	8		6	4		5	5		7	3	
Q	2	6	2	5	3	2	3	5	2	5	3	2
U	1	8	1	8	2		7	2	1	7	3	
T	7	3		10			8	2		9	1	
X	4	1	5	4	1	5	4		6	4		6
N	2	8		9	1		8	2		9	1	
S			10		2	8			10		4	6
L	3	7		3	6	1	3	5	2	3	6	1
Count of >,<	91	133	86	123	90	97	109	105	96	115	101	94
Points from >,<	91	266	-86	123	180	-97	109	210	-96	115	202	-94
Total points			271			206			223			223

^aTwo points were awarded for accurately predicting (=) strength loss, one point awarded for conservatively overpredicting (>) strength loss, and one point subtracted for underpredicting (<) strength loss.

unrealistic results for C_p when using Model B/A relate to an excessive grade-strength interaction exhibited by Model B/A (Winandy 1993). Although several earlier researchers had noted a grade-related effect (Winandy and Boone 1988, Winandy 1989), the magnitude of the grade-related interaction with C_p in Model B/A seems unreasonable because grade is an arbitrary value defined through Standards and Code authorities and not a physical characteristic.

In summary, given the relative performance of the four candidate models, the empirically derived Model B/A and the mechanistic Model D appear to better predict strength loss when compared to Models C and E. When individually compared to Model B/A, Model D appears to better predict treatment-induced strength loss based on its more conservative predictive nature and its enhanced ease of use. The predicted least-squares fit parameters for Model D are given in Table 3. Figure 1

Table 3—Final predicted least-squares fit parameters associated with Model D*

Term (b _i)	Description	Parameter estimate
b ₀	Intercept	-0.341
b ₁	MORK ⁻¹	-0.042
b ₂	tx	0.327
b ₃	dpH	0.143
	RMSE	0.0647
	r ²	0.382

*The terms b₀, b₂, and b₃ are unitless; b₁ is expressed in MPa.⁻¹

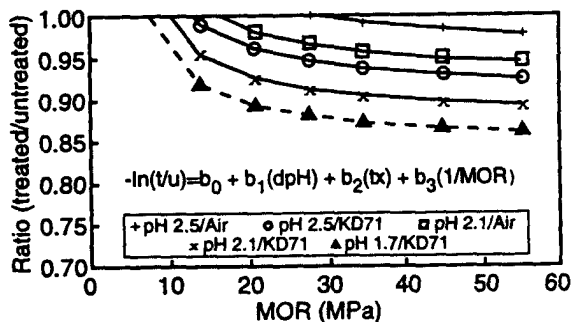


Figure 1. Predicted treated to untreated bending strength ratio for hypothetical example having three pH levels (1.7, 2.1, and 2.5) and two redrying temperature levels (air-dry and 71°C (160°F)) using mechanistic Model D.

shows a hypothetical set of predictions of C_p for various combinations of treatment, redrying, and grade for Model D.

Conclusions

The best mechanistic-based model did as well as or better than the best empirical model. Both mechanistic and empirical models provided an acceptable level of predictive capability, but neither was flawless. In some cases, the models fit poorly. However, these cases seemed to be characterized by extremely variable t/u ratios, which might indicate lack of uniformity or matching in the data rather than a direct lack of fit for the models.

A mechanistic transformed-additive effects model (Model D) was selected as best:

$$-\ln(C_p) = b_{D0} + b_{D1} * dpH + b_{D2} * tx + b_{D3} * (1/MORK) \quad (10)$$

where

$$dpH = |5 - pH| \quad (8)$$

$$tx = (\text{redry temperature} - 273 \text{ K}) / 273 \text{ K} \quad (9)$$

$$MORK = MOR (\times 10^3 \text{ lb/in}^2)$$

b_{D0} , b_{D1} , b_{D2} , and b_{D3} = least square fit parameters (Table 3)

The decision to select Model D was based on the nearly equivalent accuracy and slightly better reliability of Model D when compared to the best empirical Model B/A. It was also based on Model D's generally conservative predictive nature, ease of use, and ease in conceptualizing predictive results.

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