

IRREVERSIBLE PROPERTY CHANGES OF SMALL LOBLOLLY PINE SPECIMENS HEATED IN AIR, NITROGEN, OR OXYGEN

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ABSTRACT

The objective of this research was to characterize the roles played by atmospheric oxygen and wood moisture in the thermal degradation of loblolly pine as measured by selected physical and mechanical properties. These two factors relate, respectively, to the oxidation and hydrolysis reactions that comprise the total degradation reaction.

Small clear specimens were individually heated at 150 C from 1 to 16 hours in airtight cylinders, which were flushed with oxygen, nitrogen, or air prior to being sealed. Measured properties were reflectance, specific gravity, hygroscopicity, and the moduli of rupture and elasticity in bending.

Property values generally exhibited a decrease with increasing exposure time. The properties can be ranked from most-to-least degraded as follows: reflectance, modulus of rupture, hygroscopicity, modulus of elasticity, and specific gravity. The degradation of these properties was not adequately described by first-order reaction kinetics. Instead, a nonlinear equation was used, which accurately described the data and still reflected a rate controlled process.

The rate of property loss was accelerated by the presence of wood moisture, with the exception of residual hygroscopicity. The greatest decrease in property due to the presence of wood moisture occurred with reflectance. The degradation of modulus of rupture and modulus of elasticity was directly related to the amount of wood moisture present.

The apparent role of oxygen in total thermal degradation depended on specimen moisture content. The influence of oxygen on the degradation process was apparent for specimens heated in the oven-dry condition. When moist specimens were heated, however, losses caused by hydrolysis overshadowed oxygen-dependent degradation. Oxygen-dependent degradation was most visible for moduli of rupture and elasticity, and, to a lesser degree for reflectivity. No effect due to the presence of oxygen could be discerned for residual specific gravity and hygroscopicity.

Keywords: *Pinus taeda*, heating, thermal degradation, strength loss, stiffness loss, hygroscopicity, hydrolysis, oxidation.

INTRODUCTION

The strength and stiffness of wood decrease when it is heated and increase when it is cooled. When wood is heated for short durations, the temperature effect is immediate and reversible. Permanent (irreversible) reductions in strength and stiffness can result if wood is exposed to elevated temperatures for an extended time. These irreversible changes in the mechanical and physical properties of wood are generally attributed to the thermal degradation of the wood substance.

The thermal degradation of dry wood has been characterized as a first-order kinetic reaction, although the actual chemical reaction is very complex and is probably several simultaneous reactions (Millett and Gerhards 1972; Stamm 1956). For a first-order reaction, the plot of the logarithm of the residual property versus

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heating time is linear for a given temperature, and the slope of that line is the reaction rate constant. According to the integrated form of the first-order reaction equation:

$$K = -\ln[(a - x)/a]/t \quad (1)$$

where K is the rate constant, a is the value of the property prior to treatment, and x is the loss in property at time t . The rate at which wood degrades and the magnitude of the loss depend upon temperature, exposure duration, species, moisture content, and heating medium or atmosphere.

The rate at which wood degrades is highly sensitive to the exposure temperature (Millett and Gerhards 1972; Stamm 1956). For example, the degradation rate of bending strength is five times as great at 150 C as at 130 C for dry wood samples heated in an oven (Millett and Gerhards 1972).

To a lesser extent, species influences the rate of degradation. In general, hardwoods degrade faster than do softwoods, possibly due to the greater number of acetyl groups in the former (Hillis 1975; MacLean 1951, 1953; Millett and Gerhards 1972).

Wood degrades much faster when heated in either steam or water than when heated in the dry condition (MacLean 1951, 1953; Stamm 1956). Heating wood in the presence of water or steam causes the formation of organic acids, mainly acetic acid, which catalyzes the hydrolysis of the hemicelluloses to soluble sugars, thus speeding the degradation process (Hillis 1975; McGinnis et al. 1984). The degradation of moist wood, however, does not exhibit the linear relationship described by Eq. (1) and hence is not a first-order kinetic reaction (Skaar 1976; Stamm 1956).

The rate of thermal degradation is also dependent on the surrounding atmosphere, especially regarding the presence or absence of oxygen. Stamm (1956) demonstrated that the thermal degradation of wood heated in the presence of oxygen is more rapid than that of wood heated in an oxygen-free atmosphere. The presence of oxygen during hydrolysis results in a process known as wet oxidation. The initial reaction during wet oxidation is the formation of acids. As these acids increase in concentration, hydrolytic reactions become favorable. The rate of hydrolysis is increased not only for the hemicellulose, but for the cellulose component as well (McGinnis et al. 1984). Thus the combined processes of hydrolysis and oxidation contribute to the thermal degradation of wood.

The thermal degradation of wood may occur either in the production process, or in the service life of the wood member. Of particular concern is the potential for thermal degradation during the lumber drying process, resulting in physical and mechanical property changes. Impact and bending strengths are the wood properties most degraded by thermal degradation; bending stiffness and weight are affected the least (MacLean 1951, 1953, 1954, 1955; Millett and Gerhards 1972). The thermal degradation of wood also results in permanent reductions of hygroscopicity and a noticeable darkening of the wood (MacLean 1951; Stamm et al. 1955). The widespread industry practice of drying dimension southern pine lumber at 118 C has been shown to have no deleterious effects on strength (Koch 1971, 1976; Price and Koch 1980; Yao and Taylor 1979). The desire to dry lumber at even higher temperatures must be moderated with the knowledge that elevated temperatures may be deleterious to wood strength. For example, it has

been suggested that drying at 132 C for longer than 9 hours may cause a significant reduction in bending strength (Price and Koch 1980).

The objective of this work was to provide information on the permanent property changes that occur when small, clear loblolly pine specimens of various moisture contents are heated at 150 C (but prevented from drying) in oxygen, nitrogen, or air atmospheres. From these data, comparative reaction rates for the different heating conditions can be established. Properties evaluated and reported here are modulus of rupture (MOR), modulus of elasticity (MOE), hygroscopicity, specific gravity (SG), and reflectance.

MATERIALS AND METHODS

Fresh, green loblolly pine was obtained and sawn into specimens measuring $1.5 \times 2 \times 28$ cm long. Specimens were sorted into nine treatment groups of 50 specimens each and one control group of 30 specimens. Each of the nine groups was randomly assigned to one of the nine treatment conditions. These treatment conditions consisted of combinations of the three specimen moisture contents (MC) (0%, 12%, or green) and the three heating environments (oxygen, nitrogen, or air). Conditioning to 12% MC was done at 21 C and 65% relative humidity (RH); 0% MC content was attained by drying in a convection oven at 102 C.

Upon reaching moisture equilibrium, each group of 50 specimens was further divided into five groups of ten specimens. Each of these smaller groups was heated at 150 C for either 1, 2, 4, 8, or 16 hours in airtight cylinders only large enough (160 cm^3) to contain one specimen. The remaining group of 30 specimens was not heated, but was conditioned at 12% equilibrium moisture content (EMC) (21 C, 65% RH) and served as a control group for comparison.

Following heat treatment, all specimens were stored in a conditioning room maintained at 12% EMC until constant weights were obtained. Specimens were then remachined to final dimensions of $1 \times 1.5 \times 28$ cm long.

For each group of ten specimens that had been heat treated at the same condition, surface reflectivity was measured using a Gardner Reflectometer. The reflectivity of control specimens was also measured and served as a basis for comparison.

Static bending tests (to failure) were performed on specimens representing all treatments. Prior to the test, the dimensions were measured to the nearest 0.001 inch, and their weights were recorded to the nearest 0.01 gram. Static bending was performed using centerpoint loading over a 23-cm span with the load applied in the tangential direction, resulting in a span to depth ratio of 23. Crosshead speed was fixed at 0.05 inch per minute. The load-deflection curves plotted for each test were used to determine MOR and MOE. Following static bending tests, a 10-cm piece was cut from one end of each specimen for moisture content and specific gravity determination. Green specific gravity was determined using the green volume of the coupon and its oven-dry weight.

Moisture content adjustments were made on the treated values of MOR and MOE using the compound interest formulae:

$$\text{MOR}_a = \text{MOR}_u(1.04)^{\Delta\text{MC}} \quad (2)$$

$$\text{MOE}_a = \text{MOE}_u(1.02)^{\Delta\text{MC}} \quad (3)$$

where the a and u subscripts indicate the adjusted and unadjusted values, re-

spectively, and ΔMC is the difference in MC between the control group and treated specimen.

Samples from two of the static bending specimens were analyzed using a Nicolet DX-20 Fourier transform infrared spectrometer (FT-IR), employing a resolution of 4 cm^{-1} . One sample was from a specimen that had undergone thermal degradation; the other was from a control specimen. The spectrum of each was obtained using pellets made from ground wood and potassium bromide.²

RESULTS AND DISCUSSION

The results tabulated in Tables 1–5 are expressed in terms of the mean percent residual property, defined as the ratio of the thermally treated property to that of the control property, expressed as a percentage. The residual values for MOR and MOE are based on property values adjusted to the MC of the control group.

It is quite obvious from Tables 1–5 that the time of exposure at 150 C and the specimen MC influenced the residual property. Reflectance, MOR, and MC (residual hygroscopicity) were most affected by thermal treatment, while MOE and SG were least affected. Only residual MC appeared to be largely unaffected by specimen MC at time of thermal treatment.

The relationship between the residual property and time was sufficiently curvilinear that a first-order kinetic relationship did not fit the data. The curves suggested by the data were best fit using nonlinear regression equations of the form:

$$RP = B2 - B0[1 - e^{-[B1T]}] \quad (4)$$

where RP = percent residual property
 T = time of exposure (hours)
 B2, B0, B1 = parameters.

Equation (4) was fitted by a nonlinear least squares method using Statistical Analysis System (SAS) AOSVS Version (SAS Institute Inc. 1985). The nonlinear least squares procedure provided estimates of B0, B1, and B2.

Figures 1 and 2 illustrate the fit obtained by Eq. (4) with representative MOR and MC data. The function described by Eq. (4) was chosen not only on the basis of the form suggested by the data but also because the treatments reflect a reaction rate type of process. The model indicates that with increasing exposure time, the residual property will asymptotically approach a constant value of $B2 - B0$, where B2 is the untreated, or control value. The magnitude of the property loss due to thermal treatment is given by B0. By differentiating Eq. (4), the parameter B1 is shown to be a measure of the rate of loss, as shown in Eq. (5):

$$dRP/dT = -B1[RP - (B2 - B0)] \quad (5)$$

A large value of B1 indicates a rapid change to the final value.

Equation (5) was used to evaluate rates for all properties with the exception of SG. The slow rate of SG degradation (Table 1) resulted in inconsistent trends, and hence the data did not suggest a good fit with Eq. (4). Model parameters and

² Gratitude is expressed to Dr. Tor P. Schultz, Mississippi Forest Products Lab, for conducting the FT-IR analysis and interpreting the results.

TABLE 1. Average percent residual specific gravity (green volume basis) of coupons removed from static bending specimens.^{1,2}

		Oxygen		Nitrogen		Air	
		Mean	C.V. ³	Mean	C.V. ³	Mean	C.V. ³
0%	1	101.2	12.6	101.4	10.9	106.5	9.2
	2	102.5	9.7	104.1	7.1	102.7	13.0
	4	104.5	13.3	103.2	11.9	102.8	12.1
	8	101.9	13.1	102.9	13.4	98.6	13.9
	16	101.5	13.4	102.3	14.6	101.6	11.8
12%	1	105.6	9.9	106.6	12.9	103.7	11.1
	2	105.7	15.1	106.2	12.3	105.1	11.6
	4	105.4	9.9	104.9	14.6	104.2	9.9
	8	106.8	11.6	101.7	11.9	104.6	11.9
	16	103.7	12.2	103.9	12.5	104.1	10.8
Green	1	105.0	7.0	102.4	10.4	103.8	12.1
	2	100.6	11.7	97.8	12.0	100.4	10.9
	4	97.0	13.3	98.3	11.3	102.2	15.9
	8	96.0	13.1	95.6	12.3	97.4	13.2
	16	99.3	12.5	96.8	12.4	95.6	15.8

¹ Values are relative to the control group average specific gravity of 0.48.² Each mean is based on ten specimens.³ C.V. = Coefficient of variation (percent).

the rate of loss for the other properties are presented in Table 6. The mean rate of loss represents the average of hourly losses from 0 to 16 hours as calculated by Eq. (5). Also shown are the initial rate of loss (0 hours) and the rate of loss at 16 hours. The difference, B2 - B0, is an indicator of the magnitude of the degradation, and is also listed in Table 6.

Evidence found in the literature that the thermal degradation mechanism involves acid hydrolysis was collaborated by FT-IR analysis. The spectrum of the thermally treated specimen exhibited a decrease in the carbonyl peak when com-

TABLE 2. Average percent residual moisture content of specimens at time of static bending tests.^{1,2}

		Oxygen		Nitrogen		Air	
		Mean	C.V. ³	Mean	C.V. ³	Mean	C.V. ³
0%	1	82.4	1.8	82.3	3.3	83.5	2.1
	2	79.4	4.1	80.4	4.6	83.3	2.5
	4	78.7	2.5	79.7	4.5	79.6	2.9
	8	76.5	2.3	78.8	1.9	78.4	4.0
	16	72.7	6.0	76.1	3.8	76.0	3.2
12%	1	84.8	3.6	87.3	1.5	87.7	4.0
	2	81.9	2.7	81.8	2.3	81.7	3.6
	4	77.0	3.6	78.0	4.0	79.1	2.1
	8	74.6	3.3	73.4	3.9	72.6	3.7
	16	69.1	2.8	68.9	4.5	70.1	4.1
Green	1	97.4	3.3	95.4	4.0	95.6	3.2
	2	88.1	2.7	88.3	3.3	87.5	3.6
	4	79.9	4.0	79.8	4.3	80.8	3.5
	8	75.5	3.0	76.5	4.4	75.0	3.0
	16	72.8	3.9	73.7	3.3	73.4	2.6

¹ Values are relative to the control group average moisture content of 12.2 percent.² Each mean is based on ten specimens.³ C.V. = Coefficient of variation (percent).

TABLE 3. Percent residual reflectance measured on each treatment group prior to static bending test.¹

		Oxygen	Nitrogen	Air
0%	1	98.6	95.8	100.5
	2	102.4	95.8	96.7
	4	92.5	94.3	85.8
	8	77.8	86.3	89.2
	16	73.6	80.2	77.4
12%	1	75.5	85.8	77.4
	2	55.7	64.6	67.9
	4	44.3	43.9	47.6
	8	29.2	35.4	30.2
	16	22.2	24.1	25.5
Green	1	82.1	84.4	71.2
	2	48.6	48.6	51.9
	4	42.9	40.1	38.7
	8	28.8	29.2	29.7
	16	18.4	16.5	19.8

¹ Values are relative to the reflectance of the control group.

pared to the spectrum of the control sample. This decrease in the carbonyl peak can be associated with the hydrolysis of acetyl and uronic groups from hemicelluloses to form acidic compounds.

Residual moisture content

The nonlinear curves generated by fitting the residual MC data with Eq. (4) are shown in Fig. 3. In conjunction with the data presented in Table 6, it is apparent that the loss in hygroscopicity occurs quickly with all treatment conditions applied in this study. This is shown by the rapid approach to the asymptotic values (B2 – B0, Table 6) and the very small rate of loss after 16 hours of treatment.

A higher specimen MC at the time of treatment resulted in a slight decrease in

TABLE 4. Average percent residual modulus of rupture of thermally treated specimens.^{1,2}

		Oxygen		Nitrogen		Air	
		Mean	C.V. ³	Mean	C.V. ³	Mean	C.V. ³
0%	1	102.9	16.2	98.4	18.0	104.7	15.0
	2	99.9	17.3	100.7	14.1	97.5	19.0
	4	95.5	17.4	100.3	17.5	101.3	19.5
	8	90.6	19.9	96.2	16.9	98.3	16.7
	16	83.6	24.8	99.0	18.5	99.4	13.9
12%	1	95.8	15.4	102.1	15.4	101.1	15.3
	2	97.1	20.8	98.3	18.6	90.7	21.4
	4	83.7	29.1	89.9	19.8	85.0	22.2
	8	82.0	15.9	84.0	24.2	81.9	12.1
	16	80.9	16.0	76.5	20.7	78.3	17.3
Green	1	100.5	13.7	96.4	16.5	99.0	18.1
	2	86.4	12.6	85.2	18.5	84.1	16.6
	4	69.8	17.1	70.7	19.7	77.5	19.6
	8	63.2	26.6	65.6	21.9	65.0	16.5
	16	62.0	28.5	64.6	16.6	60.8	23.2

¹ Values are relative to the mean modulus of rupture of the control group of 15,300 psi.

² Each mean is based on ten specimens.

³ C.V. = Coefficient of variation (percent).

TABLE 5. Average percent residual modulus of elasticity of thermally treated specimens.^{1,2}

		Oxygen		Nitrogen		Air	
		Mean	C.V. ³	Mean	C.V. ³	Mean	C.V. ³
0%	1	105.9	18.9	98.8	21.8	105.6	20.3
	2	105.0	20.5	102.2	19.4	96.1	21.1
	4	101.4	21.1	101.6	18.6	101.1	24.4
	8	89.6	21.5	100.3	20.3	101.7	18.0
	16	83.4	31.9	105.9	19.1	105.8	15.7
12%	1	95.2	16.9	100.6	16.2	102.0	15.1
	2	100.7	28.5	102.3	20.3	93.9	25.2
	4	99.1	28.3	101.6	25.3	97.3	23.8
	8	97.3	16.4	93.8	29.0	101.4	15.3
	16	97.4	14.1	91.9	22.1	98.3	16.9
Green	1	106.2	17.7	98.8	20.6	103.6	21.2
	2	91.8	18.4	100.5	22.5	91.5	22.3
	4	83.1	21.8	86.1	22.8	95.0	21.9
	8	81.5	27.7	83.7	23.7	80.1	25.1
	16	83.1	24.7	80.0	18.2	76.9	22.8

¹ Values are relative to the mean modulus of elasticity of the control group of 1.91×10^6 psi.

² Each mean is based on ten specimens.

³ C.V. = Coefficient of variation (percent).

the mean rate of loss. The reduction of the initial rate of loss with increasing moisture content was more pronounced, however. In spite of the higher initial rate of hygroscopic loss for oven-dry specimens, their asymptotic values were higher than specimens that were either green or at 12% MC.

The residual MC was affected by the presence of oxygen only slightly. As seen

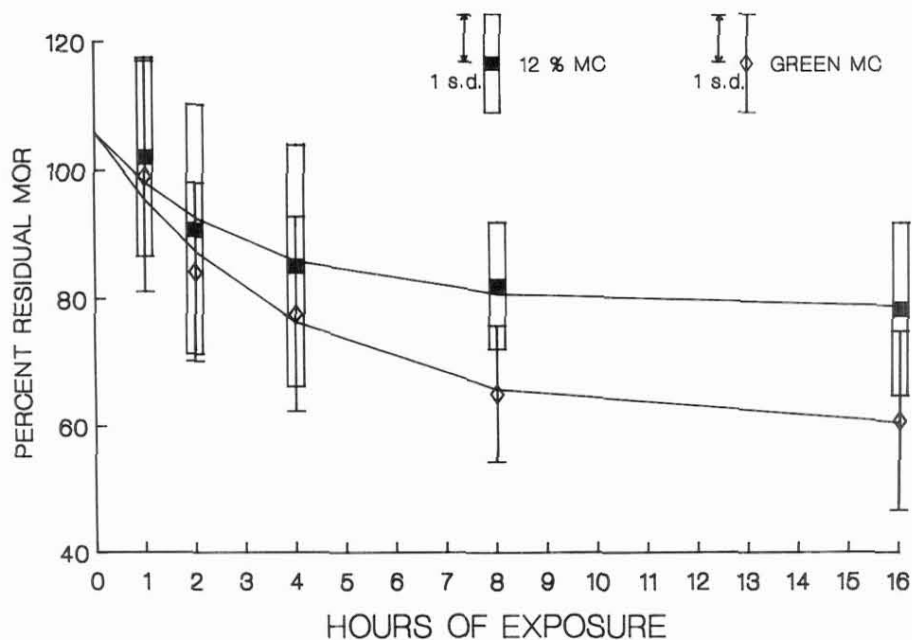


FIG. 1. Relationship between exposure period and percent residual MOR for specimens with moisture contents of 12% and green when heated in air. The results of Eq. (4) are represented by the solid lines.

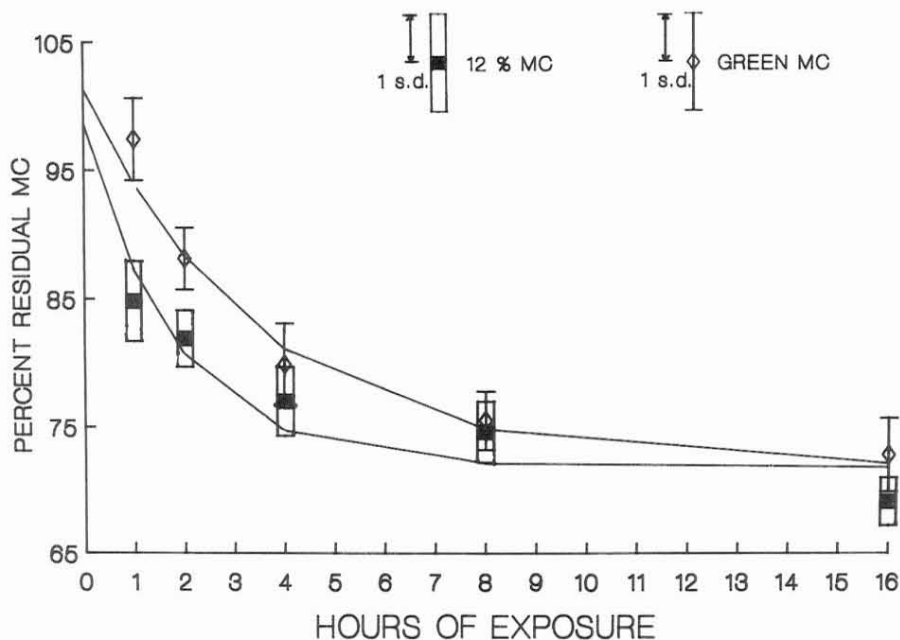


FIG. 2. Relationship between exposure period and percent residual MC for specimens with moisture contents of 12% and green when heated in oxygen. The results of Eq. (4) are represented by the solid lines.

in Fig. 3 and exhibited by the slightly lower constant residual MC approached, heat treatment at 0% MC in the presence of oxygen resulted in a greater reduction in hygroscopicity compared to heating in air or nitrogen.

Residual reflectance

Figure 4 presents a graphical depiction of the curves resulting when residual reflectance data are fitted with Eq. (4). It is obvious in both Fig. 4 and Table 6 that the presence or absence of moisture greatly affected the residual reflectivity of the wood. Differences in the mean, initial, and 16-hour rates show that the presence of moisture greatly accelerates the loss in reflectivity. In addition, the final level of reflectivity approached was much higher for specimens that contained no moisture. For specimens that contained moisture, the amount of water present affected the total loss in reflectivity only slightly. Although the loss in reflectivity was much greater for moist specimens than for oven-dry specimens, the former approached the asymptotic value during the 16-hour heating period, while the latter did not.

Considering Fig. 4 and Table 6, the presence of oxygen for specimens heated in the oven-dry condition accelerated the loss in reflectivity. Acceleration due to the presence of oxygen was not obvious for wood heated at 12% or green moisture contents. For oven-dry specimens, however, heating in an oxygen environment resulted in an initial rate of loss nearly twice that of heating in a nitrogen environment. Heating in the presence of air resulted in an approximately 50% increase in the initial rate over that of dry specimens heated in nitrogen. For oven-dry specimens, a lower final value resulted when heating was done in an oxygen compared to either an air or a nitrogen environment.

TABLE 6. Model parameters (Equation 4), mean rate of loss (Equation 5) and rate of loss at 0 and 16 hours for each treatment condition for residual moisture content, reflectivity, modulus of rupture, and modulus of elasticity.

Exposure conditions	B0	B1	B2	Mean rate	0 hr rate	16 hr rate	B2 - B0
Residual moisture content							
Oxygen							
0%	23.86	1.1501	99.48	-2.36	-27.44	0.00	75.6
12%	26.84	0.5514	98.61	-2.05	-14.80	0.00	71.8
Green	29.41	0.2894	101.27	-1.98	-8.51	-0.08	71.9
Nitrogen							
0%	22.52	1.6693	100.61	-2.72	-37.59	0.00	78.1
12%	28.63	0.4793	99.67	-2.12	-13.72	-0.01	71.0
Green	28.14	0.3264	101.42	-1.93	-9.18	-0.05	73.3
Air							
0%	20.16	0.9960	97.89	-1.87	-20.07	0.00	77.7
12%	26.60	0.3962	97.33	-1.89	-10.54	-0.02	70.7
Green	27.23	0.2833	99.46	-1.82	-7.71	-0.08	72.2
Residual reflectance							
Oxygen							
0%	41.26	0.0861	103.02	-1.95	-3.55	-0.90	61.8
12%	74.92	0.3751	99.00	-5.28	-28.10	-0.07	24.1
Green	79.27	0.3826	100.85	-5.60	-30.33	-0.07	21.6
Nitrogen							
0%	31.17	0.0601	99.25	-1.21	-1.87	-0.72	68.1
12%	76.65	0.3102	101.75	-5.22	-23.78	-0.17	25.1
Green	81.63	0.3774	101.74	-5.76	-30.81	-0.07	20.1
Air							
0%	28.03	0.1018	100.82	-1.43	-2.85	-0.56	72.8
12%	74.92	0.2950	99.18	-5.06	-22.10	-0.20	24.3
Green	75.29	0.4510	99.12	-5.50	-33.96	-0.02	23.8
Residual modulus of rupture							
Oxygen							
0%	36.49	0.0454	102.24	-1.18	-1.66	-0.80	65.8
12%	21.52	0.2614	101.23	-1.42	-5.63	-0.09	79.7
Green	44.88	0.2787	104.44	-3.00	-12.51	-0.14	59.6
Nitrogen							
0%	0.0012	-3.3E-6	101.71	11.00	0.00	0.00	101.7
12%	32.06	0.1304	104.53	-1.79	-4.18	-0.52	72.5
Green	42.03	0.3429	105.21	-2.91	-14.41	-0.06	63.2
Air							
0%	6.19	0.6594	105.29	-0.50	-4.08	0.00	99.1
12%	27.09	0.3335	105.79	-1.87	-9.03	-0.04	78.7
Green	46.16	0.2569	105.92	-3.04	-11.86	-0.19	59.8
Residual modulus of elasticity							
Oxygen							
0%	101.22	0.0159	105.32	-1.42	-1.61	-1.25	4.1
12%	2.21	0.1529	99.33	-0.13	-0.34	-0.03	97.1
Green	24.23	0.3393	105.00	-1.68	-8.22	-0.04	80.8

TABLE 6. Continued.

Exposure conditions	B0	B1	B2	Mean rate	0 hr rate	16 hr rate	B2 - B0
Nitrogen							
0%	*	*	*	*	*	*	*
12%	26.21	0.0350	102.58	-0.70	-0.92	-0.52	76.4
Green	25.02	0.1913	103.30	-1.55	-4.79	-0.22	78.3
Air							
0%	1.21	1.2821	103.03	-0.13	-1.55	0.00	101.8
12%	*	*	*	*	*	*	*
Green	31.22	0.1389	103.87	-1.78	-4.34	-0.47	72.7

* Equation 4 did not fit the data.

Residual modulus of rupture

The loss in MOR as described by the nonlinear relationship of Eq. (4) is shown in Fig. 5. The amount of water present when the wood was heated affected both the rate of MOR loss and the degree of MOR loss (Table 6). For each of the three environmental conditions, an increase in specimen moisture content increased the mean and initial rates of loss. Compared to oven-dry specimens heated in air, the mean rate of MOR loss was 6 and 4 times as great for specimens heated

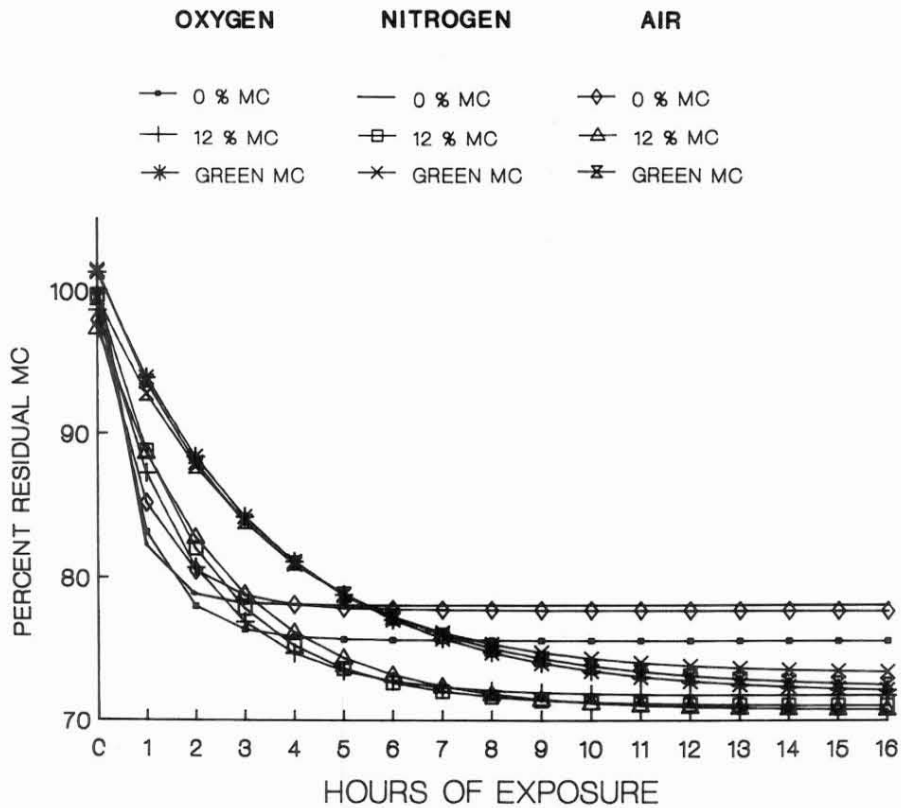


FIG. 3. Nonlinear relationship between exposure time and the percent residual MC as described by Eq. (4) for each of the nine treatment conditions.

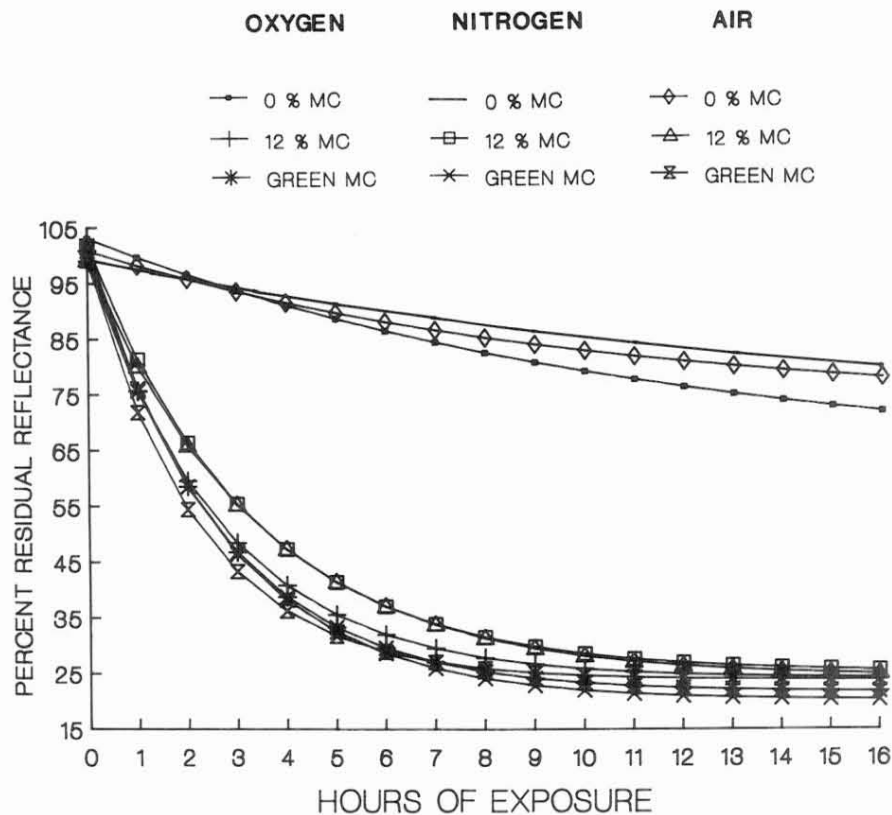


FIG. 4. Nonlinear relationship between exposure time and the percent residual reflectance as described by Eq. (4) for each of the nine treatment conditions.

green and at 12% MC, respectively. When oven-dry specimens were heated in nitrogen or air, the maximum MOR loss (B2-B0) was negligible, while heating 12% MC specimens resulted in a 22 to 28% loss in MOR, and heating green specimens caused a maximum loss of 37 to 40%.

The presence or absence of oxygen greatly affected MOR loss for specimens that were heated in the oven-dry condition. Heating oven-dry specimens in an oxygen environment resulted in a much greater mean rate of loss and a lower final value than heating in either nitrogen or air environments. As seen in Fig. 5, the rate of decrease in MOR of oven-dry specimens heated in nitrogen was nearly zero and the loss for specimens heated in air was only slightly greater. The curve depicting MOR decrease for specimens heated in oxygen has a much steeper slope. As mentioned above, the maximum loss in MOR when heating oven-dry wood in nitrogen or air was negligible; however, the maximum loss when heated in oxygen was 34%.

The effect of oxygen on MOR degradation for specimens that were either green or at 12% MC was not discernable. Apparently the presence of moisture in the wood catalyzed the hydrolysis and thereby increased the reaction rate to such a degree that any obvious effects attributable to the presence or absence of oxygen were masked.

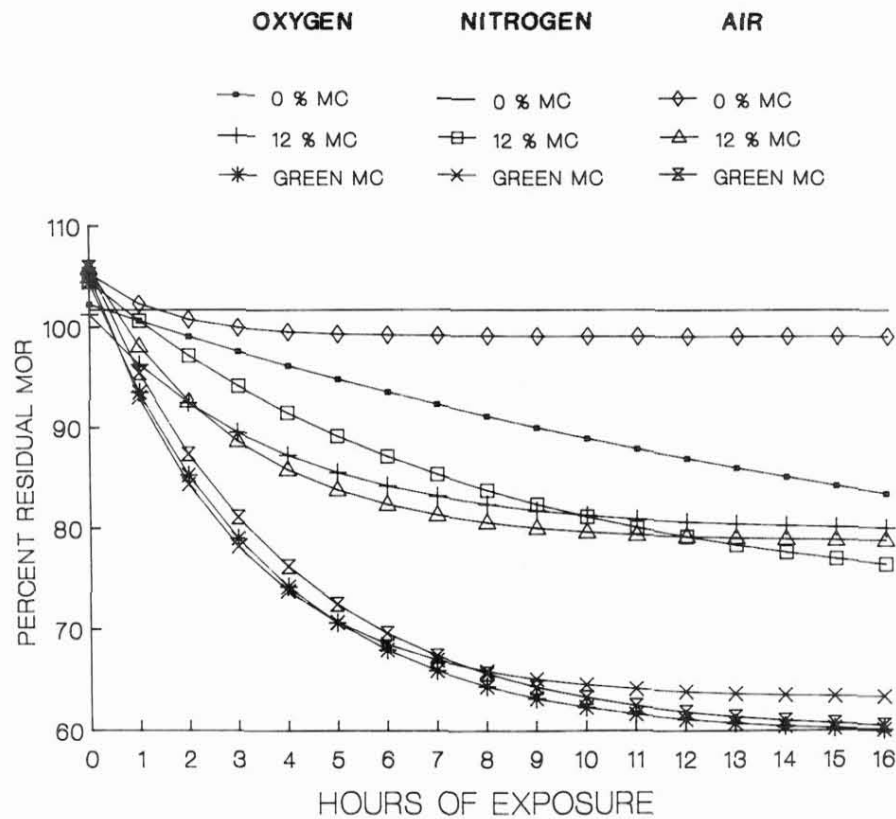


FIG. 5. Nonlinear relationship between exposure time and the percent residual modulus of rupture as described by Eq. (4) for each of the nine treatment conditions.

Modulus of elasticity

The loss in MOE exhibited an irregular decrease with increasing treatment period (Table 5). Regardless, the data were generally fit by Eq. (4), although data from two of the nine heat treatment groups were not, and are approximated by linear regression curves in Fig. 6.

Green specimens incurred an MOE loss much faster than did oven-dry specimens. When heated in air, the mean rate of MOE loss was nearly 14 times greater for green than for dry specimens. Equation (4) predicted a total loss of 27% for green specimens, while the loss for oven-dry specimens was negligible.

The effect caused by the presence of oxygen is readily apparent for specimens heated in the oven-dry condition. The magnitude of loss (Table 5) and the mean rate of loss (Table 6) are nearly as great as for specimens heated green. The extremely low final value predicted by Eq. (4) for dry specimens heated in oxygen Table (6) is probably an anomaly caused by variability of the MOE data.

The role of moisture

With the exception of residual hygroscopicity, an increase in specimen MC increased the mean rate of property loss. Obviously, any loss in property in the absence of moisture results from moisture independent reactions. This is best

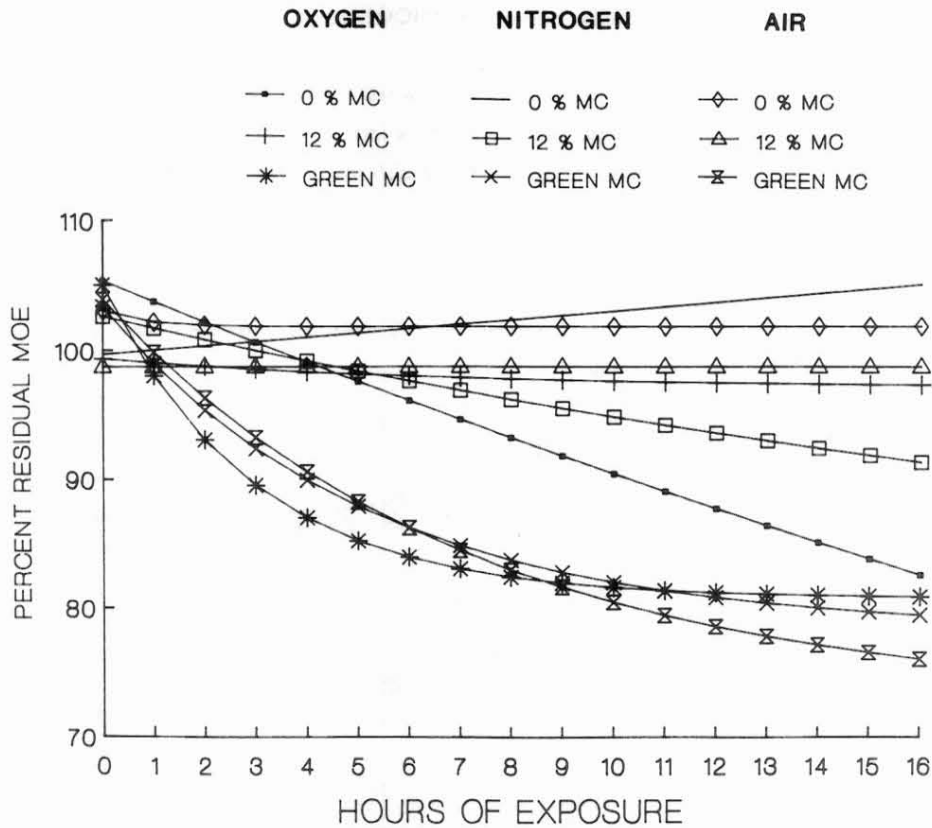


FIG. 6. Nonlinear relationship between exposure time and the percent residual modulus of elasticity as described by Eq. (4) for each of the nine treatment conditions, with the exception of two treatment conditions, nitrogen-0% MC, and air-12% MC which were described using a linear equation (R -squares = 0.65 and 0.00, respectively).

seen for specimens heated in the presence of nitrogen without the confounding influence of oxygen. A relative rate of degradation can be used to express the dependence of the degradation reaction on the presence of moisture. Such a relative rate of degradation was obtained by calculating a rate ratio, using the rate for green specimens as the basis.

For reflectance, the relative mean rates for specimens heated (in nitrogen) at 0%, 12% and green moisture contents were 0.21, 0.91, and 1.0, respectively. This implies that 21% of the loss in reflectance in nitrogen is from moisture-independent processes. The presence of a moderate amount of hygroscopic moisture triggered a significantly greater response in the reaction that decreased reflectivity. Additional moisture, however, did not affect the reaction very much.

Within the limits of exposure periods used in this study, the absence of moisture essentially halted the reaction causing MOR loss, indicating the reaction to be highly dependent on the presence or absence of water. The rate at which MOR was lost was dependent on the amount of water present, as evidenced by the fact that the rate for specimens heated at 12% MC was only 62% of the rate for specimens heated green.

The effect of wood moisture on the degradation rate of MOE was similar to

the effect on MOR. As with MOR the absence of any wood moisture essentially prevented degradation from occurring in the maximum exposure period employed in this study. In the presence of hygroscopic moisture (12% MC), the rate was 45% of the rate for green specimens.

The role of oxygen

In general, the presence of oxygen increased both the rate and the final amount of property loss. The exception was hygroscopicity, whose mean rate did not accelerate in the presence of oxygen, though the final value approached was slightly less than the final value for heating in air or nitrogen. The effect of oxygen was most noticeable for specimens heated in the oven-dry condition, which avoided the greater effect caused by the presence of wood moisture.

The rate of loss is the sum of the rate of oxygen-independent reactions (hydrolysis) and the rate of oxygen-dependent reactions. Losses that occur in the presence of nitrogen can be considered to be the result of oxygen-independent reactions. (Actually, even if the surrounding environment was comprised totally of nitrogen, approximately 9% of the total gas was oxygen due to entrapped cell air.) Relative rates were calculated as described in the previous section, except that the degradation rate obtained when heating specimens in the presence of oxygen was used as the basis.

Of the properties whose rate of degradation was accelerated by the presence of oxygen, reflectance was affected the least. The relative mean rate of oven-dry specimens heated in nitrogen was 62% that of specimens heated in oxygen, indicating that most of the reaction causing loss in reflectance was oxygen-independent.

The degradation of MOR in oven-dry specimens was totally an oxygen-dependent phenomenon. During the 16-hour heat treatment period, no loss in MOR resulted when heating was done in nitrogen. The rate of MOR loss when specimens were heated in air was 42% of the rate for specimens heated in oxygen. The large role of oxygen in MOR loss for specimens heated in the oven-dry condition is apparent in Fig. 5.

The loss in MOE was also highly oxygen-dependent. When specimens were heated in nitrogen, no loss in MOE occurred. The mean rate of MOE loss for dry specimens heated in air was only 9% of the rate of specimens that were heated in an oxygen environment.

SUMMARY AND CONCLUSIONS

Small clear loblolly pine specimens of different moisture contents were heated at 150 C for short exposure periods to study the oxidative and hydrolytic degradation of physical and mechanical properties. Specimens were heated individually in airtight cylinders that were flushed either with oxygen or nitrogen and then sealed, or simply sealed in an air environment. Heating periods varied from 1 to 16 hours. Reflectance, specific gravity, hygroscopicity, and the moduli of rupture and elasticity in bending were determined for all specimens.

The rate of degradation as measured by these properties did not follow first-order reaction kinetics, as indicated by the poor fit that resulted when first-order kinetic relationships were applied. Instead, an alternative nonlinear equation was used, which better described the data, yet still reflected a reaction rate type of

process. The nonlinear equation describes a degradation limit that is asymptotically approached with increasing exposure time. Although this form of equation describes the degradation process very well for the relatively short exposure periods used in this study, extrapolation to longer periods may result in inaccurate predictions and hence is not recommended.

Property values generally exhibited a decrease with increasing exposure period. A list ranking the properties from most-to-least degraded follows: reflectance, modulus of rupture, hygroscopicity, modulus of elasticity, and specific gravity.

Increasing specimen MC increased the loss in property for any given exposure period, with the exception of hygroscopicity. In terms of magnitude of loss, reflectance exhibited the greatest sensitivity to the presence of wood moisture. The degradation processes for the moduli of rupture and elasticity were highly dependent on whether moisture was present, and, if present, on the amount. Oven-dry specimens heated in nitrogen exhibited no loss in these moduli during 16 hours of exposure, and hence had a loss rate of zero. (Extrapolation beyond 16 hours should be avoided, as heating for longer periods will likely result in moduli losses.)

The apparent role of oxygen in total degradation depended on specimen MC. For specimens heated in the oven-dry condition, oxidative effects were apparent; however, when moist specimens were heated (those either green or at about 12% MC), losses caused by hydrolysis overshadowed oxygen-dependent degradation. The dependence of degradation on the presence of oxygen was most visible for moduli of rupture and elasticity, less obvious for reflectance, and not apparent for hygroscopicity and specific gravity.

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