

DEGRADATIVE EFFECTS OF ULTRAVIOLET LIGHT AND ACID RAIN ON WOOD SURFACE QUALITY

David N.-S. Hon

Professor
Department of Forest Resources
Wood Chemistry Laboratory
Clemson University
Clemson, SC 29634-1003

(Received July 1993)

ABSTRACT

Wood surface quality deteriorated when wood was exposed to ultraviolet light, acid rain, and the combination of these two elements. When wood surfaces were exposed to ultraviolet light, carbonyl group content increased and lignin content decreased simultaneously. These changes were accelerated when they were also exposed to a dilute sulfuric acid solution—a laboratory simulation of acid rain—especially at 65 C and 65% relative humidity. Experimental results showed that ultraviolet light changed the surface quality by generating oxidized products, and the sulfuric acid contributed to the deterioration of tensile strength.

Keywords: Acid precipitation, cellulose, lignin, carbonyl group, infrared spectrophotometer, degradation, tensile strength.

INTRODUCTION

Acid precipitation, commonly called “acid rain,” has been called “an unseen plague of the industrial age,” and has been a rallying cry of the “environmentalists” over the past three decades. A powerful political, scientific, and popular interest has developed around the problem. Acid rain is generally regarded as one of the most serious environmental problems in developed countries. During the past thirty-five years in Europe and twenty years in North America, scientific evidence has accumulated suggesting that air pollution resulting from emissions of oxides of sulfur and nitrogen may have significant adverse effects on ecosystems. Recent technical reports have highlighted growing concern about the acid precipitation problem (Brezonki et al. 1980). Measurements have been made on the pH of rainwater in Florida during a recent year, where isolated measurements ranging from a low of 3.76 to a high of 5.8 have been recorded. Single incidents of precipitation with pHs as low as 2.1 have also been recorded recently in Los Angeles (Ember 1981; Likens and Borman 1974). At these ranges of low pH, acid rain will dis-

solve many natural and synthetic polymers such as cotton and nylon, as women in a Florida city who wore blouses and stockings made of nylon discovered to their dismay.

The deleterious effects of acid rain on lakes, aquatic ecosystems, vegetation, forests, buildings, and artifacts have come to the fore in the past two decades and are the subjects of continuing investigation (Paparozzi 1986). Wood materials offer an impressive range of attractive properties and in many of their applications they are exposed to the outdoor environment. Hence, they are subject to sunlight, weathering, and acid precipitation. Although ultraviolet light is a major element in degrading wood polymers (Hon 1991), it is to be expected that for lignocellulosic biopolymers, where hydrolytic breakdown can be an important mode of deterioration (Goldstein 1981), acid rain will have a catalytic effect.

Despite the importance of acid effects on wood surface quality, little research information was available in the literature. Hovland et al. (1980) exposed cellulose sheets and aspen wood (*Populus tremula*) to artificial acid “rain” to determine its effect on decomposition. These

materials were placed on the leaf litter in three coniferous forest sites. The only result was that application of pH 2.5 water reduced the decomposition rate of cellulose at one of the sites. Banks and Evan (1985), using thin and thick sections of pine (*Pinus sylvestris*) and linden (*Tilia vulgaris*), found significant strength losses when 100 μm longitudinal sections were exposed to dilute acid solutions, particularly sulfurous acid solutions. Using larger, transverse sections, significant loss in mechanical properties occurred only to a depth of about 0.5 mm. Thus, the wood surface may be modified and this could influence the susceptibility of surfaces to oxidation.

Previously, we have found that wood readily absorbs sulfur dioxide, one of the principal elements in acid rain, to trigger a whole series of free radical reactions, especially in the presence of ultraviolet light. These reactions ultimately lead to discoloration and loss of surface integrity (Hon and Chao 1989; Hon and Feist 1993). In this paper, the effect of acid rain on wood surface quality is demonstrated. The synergistic effects of acid, heat, ultraviolet light, and humidity were investigated; and the effects on chemical components of wood and tensile strength were assessed.

MATERIALS AND METHODS

Materials

Earlywood of southern yellow pine (*Pinus* spp.) was used for this study. Wood specimens (earlywood) were microtomed into a thin section with dimensions of 12 mm \times 45 mm \times 10 μm . In order to avoid complicated reactions from extractives, they were removed by extracting wood with the co-solvents benzene and methanol (2:1) in Soxhlet extractors for 8 h. The wood was air-dried after extraction.

Acid treatments

Since sulfuric acid is considered to be the major contributor to acid rain, it was selected for this study. The wood specimens were sprayed with a mist of a total of 4 ml of 0, 0.002, 0.009, and 0.074% (volume percent) of

sulfuric acid solution, which corresponded to pH values of 7, 4.4, 3.0, and 2.0, respectively. These values were determined by a pH meter (Fischer Scientific). These values also represent the range of pH levels of acid precipitation in the United States east of the Mississippi River.

Exposure to heat, ultraviolet light, and moisture

The control and acid-sprayed specimens were exposed either to darkness or to a UV light for a specific period of time in a chamber in which the temperature and humidity were accurately controlled. While certain specimens were exposed at ambient temperature, other specimens were exposed at 65 C and 65% relative humidity, with or without ultraviolet irradiation. A high pressure quartz mercury-vapor lamp with a lowest wavelength of 223 nm was used as the ultraviolet source (ACE-Hanovia, lamp type 6531-12, 200 W).

Evaluation

The changes in the amounts of carbonyl group and lignin of treated specimens were examined using a Fourier transform infrared (FTIR) spectrophotometer (Nicolet 20 DX; 2 cm^{-1} resolution) equipped with a Harrick diffuse reflectance accessory (Hon and Feist 1992). Water-soluble degradation products were obtained by soaking the wood specimens that were exposed to sulfuric acid for 12 h in distilled water for 3 h. The solution was characterized by an ultraviolet-visible spectrophotometer (Perkin Elmer Lambda 3). The tensile strength of treated specimens, which were air-dried at room temperature after acid treatments, was tested using an Instron tester (Model 4204). Testing was conducted at room temperature. An average of ten readings was made for each set of specimens.

RESULTS AND DISCUSSION

Effect of acid at ambient temperature

It is known that holocellulose of wood, e.g., cellulose and hemicelluloses, is readily hydro-

lyzed by concentrated acid at ambient temperature and by diluted acid at high temperature (Goldstein 1981). Lignin is more resistant to acid degradation. After wood specimens were treated with sulfuric acid in a concentration range from 0.002 to 0.074% at ambient temperature for 12 h and soaked in distilled water for 3 h, the soluble degradation products in water were examined by a UV spectrophotometer. The absorption spectra revealed that the water-soluble products from acid-treated wood did not exhibit significant UV absorption differences when compared to the untreated (control) wood. The FTIR spectra of treated wood also exhibited no change in absorption peaks at $1,725\text{ cm}^{-1}$ and $1,510\text{ cm}^{-1}$, which correspond to the absorption characteristics of the carbonyl group and the aromaticity of lignin in wood, respectively. These results suggest that wood chemical components are quite resistant to dilute acid aqueous solutions at ambient temperature.

Changes in carbonyl group and lignin contents

In previous studies, the author found that wood is susceptible to ultraviolet degradation (Hon 1991). An increase in carbonyl groups, based on the calculation using the FTIR relative absorption peak ratio of $1,735\text{ cm}^{-1}/895\text{ cm}^{-1}$, was observed when wood specimens were irradiated with UV light (without acid) at ambient temperature, as shown in Table 1. This demonstrated that carbonyl groups were generated at the wood surface, which could be derived either from cellulose, hemicelluloses, or lignin. As also shown in Table 1, in the presence of acid, the rate of increase in carbonyl groups was further enhanced. In short, the higher the concentration, the more carbonyl groups were detected. This phenomenon implies that photo-oxidative reactions were accelerated by acid. Although cellulose and hemicelluloses are more susceptible to acid reaction than lignin, the formation of carbonyl groups is not necessarily limited to these two; it can also be generated from lignin, as will be discussed in a subsequent section. Since acid

TABLE 1. *Effect of acid rain on carbonyl group content of wood at ambient temperature in the presence of UV light.*

Exposure time (h)	Acid concentration (%)			
	0	0.002	0.009	0.074
0	3.7*	3.7	3.7	3.7
6	6.5	8.1	10.0	11.4
12	8.6	11.3	11.3	12.3
24	12.7	12.1	13.4	13.9
36	15.4	14.0	14.2	14.5
48	15.6	17.5	16.7	17.0

* FTIR absorption peak ratio: $1,735\text{ cm}^{-1}/895\text{ cm}^{-1}$.

itself does not generate any significant amount of water-soluble products or carbonyl groups, the oxidation of wood is evidently due to the interaction between light and the wood components. Acid may function as a mild catalyst to promote hydrolytic oxidation. The presence of water-soluble products was confirmed by UV differential spectra from the wood irradiated with UV light in the presence of acid.

Although lignin is relatively resistant to acid, it is sensitive to light. It is degraded readily by light (Hon 1992). FTIR studies revealed a reduction of lignin content on wood surfaces. Table 2 showed that the wood surface lost 39% of its lignin concentration after 48 h of UV irradiation without acid. The UV spectra of water-soluble products from UV irradiated wood specimens exhibited absorptions at 195, 227, 275, and 310 nm. These are the characteristic absorption peaks of lignin or polyphenolic compounds (Hon and Chang 1984). The addition of sodium hydroxide into such a solution resulting in the shift of UV peaks further supported the presence of phenolic compounds in the solution (Hon and Chang 1984). In the presence of acid, the degradation of lignin appeared to be slower than that without acid between 6 and 12 h of irradiation. However, after 36 h of photoirradiation, the degradation rate was accelerated. The amount of water-soluble degradation products with absorption at 275 nm, a typical absorption of lignin, is shown in Table 3. It can be seen that ultraviolet light played the major role in degrading lignin. The effect of concentration of acid on the rate of degradation of wood, especially lignin, was negligible.

TABLE 2. *Effect of acid rain on lignin in wood at ambient temperature in the presence of UV light.*

Exposure time (h)	Acid concentration (%)			
	0	0.002	0.009	0.074
0	4.4*	4.4	4.4	4.4
6	2.8	3.3	3.0	4.2
12	2.9	3.0	2.9	4.1
24	2.8	2.6	2.7	3.9
36	2.7	2.5	2.5	2.3
48	2.7	2.3	2.5	2.2

* FTIR absorption peak ratio: 1,507 cm⁻¹/895 cm⁻¹.

When wood was exposed to an elevated temperature, i.e., at 65 C and 65% relative humidity, its chemical components did not show a noticeable degradation. The carbonyl content of untreated wood remained almost constant as the exposure time increased. The same is true for lignin content. In the presence of acid under such conditions, the carbonyl groups did increase slightly as a function of acid concentration (Table 4). No significant change in lignin was observed (Table 5).

The effect of acid and UV light at 65 C and at 65% relative humidity on carbonyl groups and lignin content was significant (Table 6). When wood was exposed to UV light in the absence of acid at such conditions, it was noticed that carbonyl group content increased almost six-fold after 48 h of irradiation. About 80% loss of lignin content was observed (Table 7). The rate of degradation was further enhanced in the presence of acid. The higher the acid concentration, the more carbonyl groups

TABLE 3. *Change of UV absorbance at 275 nm due to water-soluble degradation products from wood treated with acid rain at ambient temperature in the presence of UV light.*

Exposure time (h)	Acid concentration (%)			
	0	0.002	0.009	0.074
0	0	0	0	0
10	0.3	0.3	0.4	0.4
15	0.5	0.4	0.4	0.5
24	0.5	0.5	0.5	0.6
36	0.7	0.5	0.5	0.7
48	0.7	0.6	0.7	0.7
	(0.8)*	(0.7)	(0.7)	(0.9)

* Values in parentheses were obtained from specimens treated at 65 C.

TABLE 4. *Effect of acid rain on carbonyl group content in wood at 65 C and 65% relative humidity in the absence of UV light.*

Exposure time (h)	Acid concentration (%)			
	0	0.002	0.009	0.074
0	3.7*	3.7	3.8	3.8
6	3.8	4.1	4.5	5.1
12	3.9	4.1	4.2	5.6
24	3.9	4.2	3.9	5.7
36	—	—	—	—
48	3.9	4.2	3.8	5.1

* FTIR absorption peak ratio: 1,735 cm⁻¹/895 cm⁻¹.

were found. Although lignin is resistant to acid attack, under such conditions significant reduction of lignin content was observed.

Effect of acid rain and UV irradiation on tensile strength

The increase in carbonyl group content and reduction of lignin content at wood surfaces being exposed to acid and UV light at ambient and at high temperature and high humidity, signaled that chemical reactions took place in the polymeric components of wood, i.e., cellulose, hemicelluloses, and lignin. Since holo-cellulose is sensitive to acid hydrolysis, there is little doubt that the strength of wood will be reduced due to the chain scission reaction. The change in color of wood from pale yellow to dark brown and the embrittlement of wood specimens clearly indicated severe degradation of wood quality. The change of tensile strength of wood under the studied conditions was investigated. When wood was exposed to acid at ambient temperature and at 65 C, changes in tensile strength were clearly ob-

TABLE 5. *Effect of acid rain on lignin in wood at 65 C and 65% relative humidity in the absence of UV light.*

Exposure time (h)	Acid concentration (%)			
	0	0.002	0.009	0.074
0	4.4*	4.4	4.4	4.5
6	4.3	3.8	3.6	5.2
12	4.2	3.8	3.8	5.5
24	4.1	3.8	3.9	5.8
36	—	—	—	—
48	4.1	3.8	3.7	5.0

* FTIR absorption peak ratio: 1,507 cm⁻¹/895 cm⁻¹.

TABLE 6. Effect of acid rain on carbonyl group content in wood at 65 C and 65% relative humidity in the presence of UV light.

Exposure time (h)	Acid concentration (%)			
	0	0.002	0.009	0.074
0	3.7*	3.7	3.7	3.7
6	8.2	9.8	11.7	11.9
12	15.1	16.0	16.5	19.2
24	18.7	19.0	20.4	22.8
36	20.0	19.3	21.3	24.4
48	21.5	23.0	23.7	25.4

* FTIR absorption peak ratio: 1,735 cm⁻¹/895 cm⁻¹.

served. Wood itself at ambient temperature did not suffer any loss of tensile strength during the period of study. When it was exposed to 65 C, a slight reduction of tensile strength was observed, as shown in Fig. 1. In the presence of acid, the reduction of tensile strength was significant. At 0.074% acid concentration, the tensile strength of wood was reduced more than 60% at ambient temperature. More loss was observed at the same acid concentration at 65 C. A similar loss of tensile strength was observed when acid-treated wood was exposed to UV irradiation at ambient temperature (Fig. 2). At 65 C, in the presence of UV light, the rate of reduction of tensile strength was slightly increased (Fig. 3). Based on these observations, it is evident that when wood is exposed to outdoor conditions, oxidative degradation of its surface is initiated by UV irradiation, resulting in generation of carbonyl groups and loss of lignin at its surface. Photo-oxidation by itself appeared not to be a contributor to the loss of tensile strength. Acid rain appeared to be the major culprit contributing to the loss of strength.

TABLE 7. Effect of acid rain on lignin in wood at 65 C and 65% relative humidity in the presence of UV light.

Exposure time (h)	Acid concentration (%)			
	0	0.002	0.009	0.074
0	4.4*	4.4	4.4	4.5
6	1.8	2.1	2.0	2.5
12	1.7	1.3	1.4	1.7
24	1.2	1.2	1.3	1.5
36	1.0	0.9	1.2	1.3
48	0.8	0.8	1.2	1.3

* FTIR absorption peak ratio: 1,507 cm⁻¹/895 cm⁻¹.

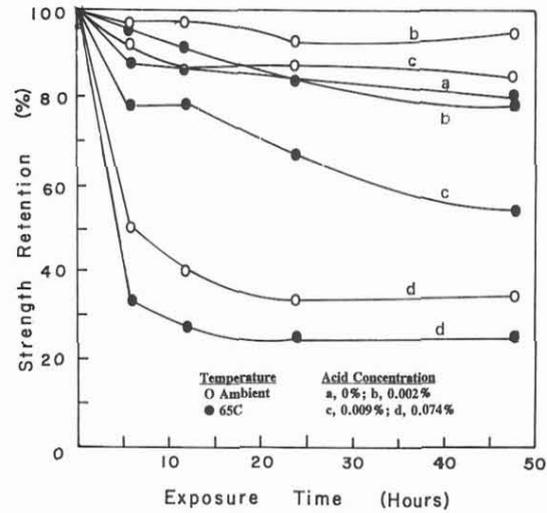


FIG. 1. Effect of acid rain on tensile strength of wood at ambient temperature and at 65 C. No change in tensile strength was observed for the control.

Mechanisms of degradation

Many factors are involved in wood deterioration in the polluted environment. The absorption of UV light and acid rain can lead to chemical changes on wood surfaces, and deterioration of tensile strength was experimentally proven. It was discussed previously that

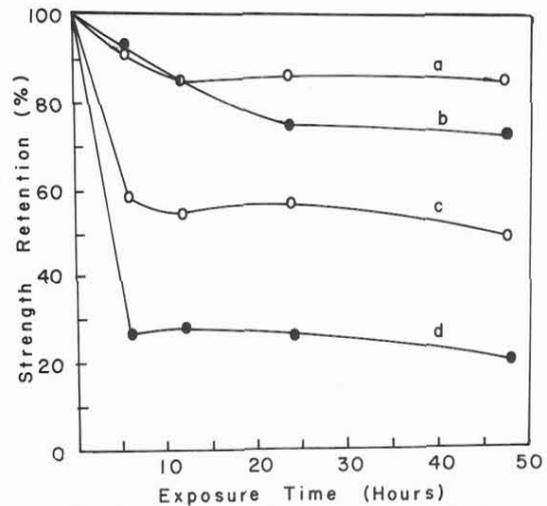


FIG. 2. Effect of acid rain on tensile strength of wood at ambient temperature in the presence of UV light. a, UV irradiated without acid; b, UV irradiated with 0.002% acid; c, UV irradiated with 0.009% acid; d, UV irradiated with 0.074% acid.

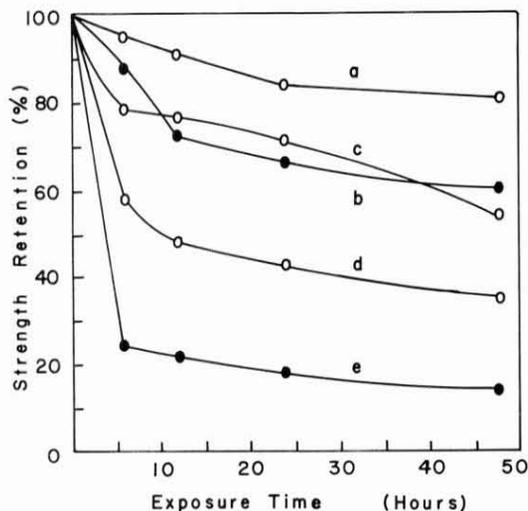


FIG. 3. Effect of acid rain on tensile strength of wood at 65 C. a, control at 65 C; b, UV irradiated without acid; c, UV irradiated with 0.002% acid; d, UV irradiated with 0.009% acid; e, UV irradiated with 0.074% acid.

photo-induced free radicals in wood are able to react with sulfur dioxide to produce various oxidized products (Hon and Feist 1993). They, in turn, further influence the color and surface properties. The presence of UV light may also accelerate oxidation of sulfur dioxide to sulfur trioxide, which will subsequently react with water to produce sulfuric acid. Sulfuric acid may also form by other catalytic processes involving sulfur dioxide, water, and a catalyst present in the atmosphere. Hence, three plausible mechanisms that can lead to surface degradation of wood are worth considering. They are summarized below:

- I. Wood + $h\nu$ → Wood Free Radicals
Wood Free Radicals + SO_2 → Oxidized Products
- II. $h\nu + \text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$
 $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$
 $\text{H}_2\text{SO}_4 + \text{Wood} \rightarrow \text{Degradation Products}$
- III. $\text{SO}_2 + \text{O}_2 + \text{Catalyst} \xrightarrow{\text{H}_2\text{O}} [\text{SO}_2 \cdot \text{H}_2\text{O}]$
 $[\text{SO}_2 \cdot \text{H}_2\text{O}] \rightarrow \text{H}_2\text{SO}_4$
 $\text{H}_2\text{SO}_4 + \text{Wood} \rightarrow \text{Degradation Products}$

CONCLUSIONS

Wood is sensitive to the environment in which it is exposed. In addition to UV light, acid rain seems to be an important element contributing to deterioration of wood surface quality and tensile property of wood. Experimental results showed that while carbonyl groups were generated in wood, lignin content simultaneously decreased when it was exposed to light; and this process was further enhanced when it was also exposed to acid spray. Either with or without ultraviolet light at 65 C wood deteriorated slightly faster than at ambient temperature. Acid further accelerated the degradation process. Wood lost its tensile strength in the presence of acid both at ambient temperature and at 65 C.

REFERENCES

- BANKS, W. B., AND P. D. EVANS. 1985. The role of water in the degradation of wood surfaces. Amer. Chem. Soc. 190 Annual Meeting. Abstr. Cell 0010. Chicago, IL.
- BREZONKI, P. L., E. S. EDGERTON, AND C. D. HENDRY. 1980. Acid precipitation and sulfate deposition in Florida. *Science* 208:1027-1029.
- EMBER, L. R. 1981. *Chem. Eng. News* 37:20.
- GOLDSTEIN, I. S. 1981. Chemicals from cellulose. Pages 101-124 in I. S. Goldstein, ed. *Organic chemicals from biomass*. CRC Press, Boca Raton, FL.
- HON, D. N.-S. 1991. Photochemistry of wood. Pages 525-555 in D. N.-S. Hon and N. Shiraishi, eds. *Wood and cellulosic chemistry*. Marcel Dekker, New York, NY.
- . 1992. Thermomechanical pulp and light: Photoactivity of α -carbonyl group in solid lignin. *J. Wood Chem. Technol.* 12:179-196.
- , AND S. T. CHANG. 1984. Surface degradation of wood by ultraviolet light. *J. Polymer Sci. Polymer Chem. Ed.* 22:2227-2241.
- , AND W. Y. CHAO. 1989. Effect of sulfur dioxide on wood surface quality. Pages 1037-1057 in C. Schuerch, ed. *Cellulose and wood: Chemistry and technology*. John Wiley and Sons, New York, NY.
- , AND W. C. FEIST. 1992. Hydroperoxidation in photoirradiated wood surfaces. *Wood Fiber Sci.* 24(4): 448-455.
- , AND ———. 1993. Interaction of sulfur dioxide and nitric oxide with photoirradiated wood surfaces. *Wood Fiber Sci.* 25(2):136-141.
- HOVLAND, J., G. ABRAHAMSEN, AND G. OGNER. 1980. Effects of artificial acid rain on decomposition of spruce needles and on mobilization and leaching of elements. *Plant Soil* 56:365-378.

- JOHNSON, W. J., AND G. E. CORDON. 1987. The chemistry of acid rain. American Chemical Society, Washington, DC.
- LIKENS, G. E., AND F. H. BORMAN. 1974. Acid rain. Serious regional environmental problem. *Science* 184(4142):1176-1179.
- PAPAROZZI, E. T. 1986. Effect of acid rain on woody plants and their products. Pages 332-342 *in* R. Baboian, ed. Materials degradation caused by acid rain. American Chemical Society, Washington DC.

NEW ADDRESS FOR SUBMITTING MANUSCRIPTS

In July 1994, Dr. John F. Siau will take over as Editor of WOOD AND FIBER SCIENCE. To effect the transition, Dr. Siau will start processing all new manuscripts received after January 1, 1994. They should be sent to him at the following address:

Dr. John F. Siau
Brooks Forest Products Center
Virginia Tech
Blacksburg, VA 24061-0503

All correspondence regarding manuscripts first received on or before December 31, 1993, should be addressed to the current Editor, Arno P. Schniewind.