STABILITY OF ACETYLATED WOOD TO ENVIRONMENTAL CHANGES

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(Received January 1993)

ABSTRACT

Acetylated wood is more dimensionally stable and resistant to biological attack than unacetylated wood. In this study, the stability of acetylated wood was tested under various pH, temperature, and moisture conditions. Ground acetylated southern yellow pine and aspen flakes were treated with buffer ranging from 2 to 8 pH, exposed at 24 C, 50 C, or 75 C for different periods, and tested for acetyl content. At 24 C, acetylated wood was more stable at pH 6 than pH 2, 4, or 8. At 50 C and 75 C, acetylated wood was more stable at pH 4 than at the other pH values. The half-life of acetylated wood continuously in contact with a buffered liquid at pH 6 and 24 C was approximately 30 years. For acetylated wood used under normal circumstances, the half-life would be expected to be much longer. Acetylated southern yellow pine and aspen flakes were also (1) kept at 90% relative humidity at 27 C for 6 years or (2) cycled (42-day cycle) between 90 and 30% relative humidity for 5 years. The loss of acetyl was less than 2% in both the constant and cyclic relative humidity tests. The stability of acetylated wood suggests that such wood can be used for products exposed to changes in humidity.

Keywords: Acetylation, stabilization, pH, moisture.

INTRODUCTION

Acetylation of wood is presently a commercial reality in Japan, soon will be a reality in the United Kingdom and Sweden, and, hopefully, will be realized in North America in the near future. Wood is being acetylated primarily to improve its dimensional stability and, to a limited extent, to improve its resistance to attack.

Since the bond formed by the reaction of acetic anhydride and the wood (cell-wall) polymers is an ester bond, splitting of the acetyl group has been questioned if the acetylated product is to be used over the course of many

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Wood and Fiber Science, 25(4), 1993, pp. 359–364

years. Esters of organic compounds are known to be susceptible to hydrolysis, especially under alkaline conditions. Tarkow et al. (1950) immersed acetylated birch veneers in a 9% solution of sulfuric acid at room temperature for 18 h. No loss in antishrink efficiency (ASE) was found after removal of the acid, and analysis of acetyl content showed no loss in acetyl. In the same acidic solution at 40 C, deacetylation did occur to some extent, as shown by a drop in ASE from 75% to 65%. The authors also subjected acetylated spruce veneers to 10 cycles of humidity changes from 30% to 97% relative humidity over a 4-month period. After the 10 cycles, no reduction in ASE occurred. In a final test, the authors suspended acetylated birch wood over a saturated solution of sodium chloride at 80 C for 3½ days. Again, no loss in ASE was observed.

Another source of information about acetyl stability can be found indirectly in the literature on wood aging. Hedges (1990) and Freedland (1990) reviewed the degradation of the carbohydrate fraction as a function of time and conditions. The carbohydrate fraction degrades at a much faster rate than does the lignin fraction, and the hemicelluloses degrade to a greater extent than does the cellulose. Acetyl is lost in the hemicellulose fraction but not completely. Kauri wood from New Zealand, for example, that was buried for 30,000 years under conditions that resulted in a 50% loss in hemicelluloses and a 60% loss in xylose, showed an 85% loss in acetyl content (Freedland 1990). Similar results have been reported with other woods under different conditions for varying periods.

The purpose of our research was to expose acetylated wood to varying pH, moisture, and temperature conditions and determine loss of acetyl. These data can be used to predict the expected life of an acetylated product under different use conditions.

MATERIALS AND METHODS

Preparation of specimens

Southern yellow pine and aspen wood flakes were acetylated using uncatalyzed acetic anhydride as previously described (Rowell et al. 1986). After final drying, the average analytically determined acetyl content (on a weight basis) was 20.2% for southern yellow pine flakes and 20.6% for aspen flakes.

pH and temperature conditions

Part of each flake type was ground to pass through a 10-mesh (2.0-mm) screen. Approximately 14 g of each ground sample was stirred into a 1-liter flask containing 0.5 liter of buffer solution at pH 2, 4, 6, or 8. The accuracy of the buffer solutions was checked with a pH meter at the start of the experiment and each time a sample was removed for analysis. The flasks were placed in one of three different temperature conditions: 24 C (room temperature) or a 50 C or 75 C water bath. At various times, ground wood samples were removed from the flasks and the acetyl contents determined by gas chromatography. Duplicate tests were run and the results averaged.

Humidity conditions

Part of each acetylated flake type was placed in a constant relative humidity (RH) room at 90% RH at 27 C. Samples were removed every 6 months and ground to pass a 10-mesh screen. Half of each sample was leached in water for 3 days; acetyl contents were determined for leached and unleached samples. Triplicate samples were run and the results averaged.

Another part of each acetylated flake type was cycled between constant 90% RH, 27 C and 30% RH, 27 C conditions. Each cycle consisted of 21 days at 90% RH and 21 days at 30% RH. At the end of each 42-day cycle, samples were removed and ground to pass a 10-mesh screen. Half the sample was leached in water for 3 days. Acetyl contents were determined for leached and unleached samples. Triplicate samples were run and the results averaged.

RESULTS AND DISCUSSION

Because of the limited number of specimens per individual test, statistical analysis of the data was not appropriate. The results present-

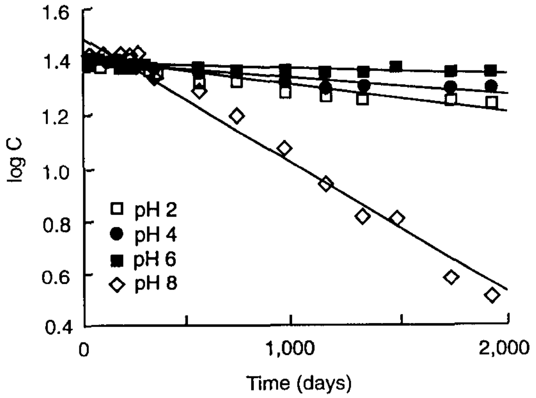

FIG. 1. Relationship between acetyl content and time over a pH range of 2 to 8 at 24 C for aspen.

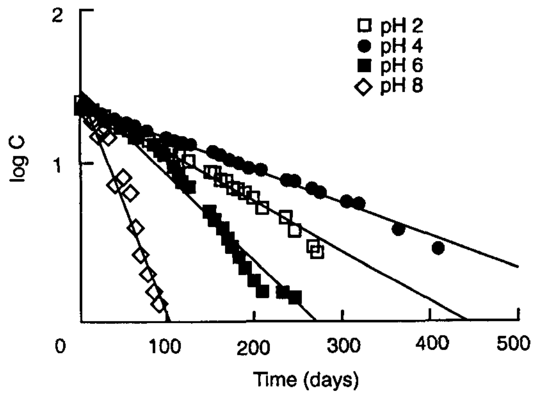

FIG. 3. Relationship between acetyl content and time over a pH range of 2 to 8 at 75 C for aspen.

ed here should be considered as indicative of trends that a larger, statistically valid experiment should confirm.

Assuming that the deacetylation of acetylated wood is dependent on the content of the acetyl groups, first-order reaction kinetics were used for all calculations. Figures 1 to 3 show the relationship between acetyl content and time for aspen over a pH range of 2 to 8 at 24 C, 50 C, and 75 C, respectively. Figures 4 to 6 show the same data for pine. These data show the great difference in stability of the acetyl group under acidic conditions as compared to slightly alkaline conditions.

From the slope of each plot in Figs. 1 through 6, it is possible to determine the reaction rate constant, k, for each pH and temperature. Figure 7 shows the relationship between reaction rate constant and temperature over a pH range of 2 to 8 for aspen, and Fig. 8 shows the same data for pine. Table 1 shows the rate constants for acetylated aspen and pine at 24 C, 50 C, and 75 C at pH values of 2, 4, 6, and 8. At 24 C, deacetylation occurred at the slowest rate at pH 6 and at the fastest rate at pH 8. At 50 C and 75 C, the slowest rate of deacetylation occurred at pH 4 and the fastest rate at pH 8. As expected, raising the temperature at each pH level greatly increased the rate of deacetylation. Also as expected, the acetyl groups were more stable under acidic conditions than basic.

The rate constants represent the bulk rate of

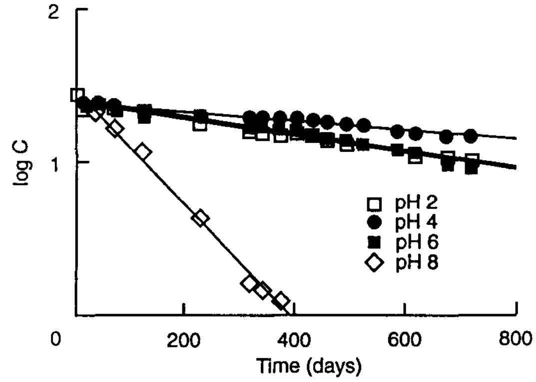

FIG. 2. Relationship between acetyl content and time over a pH range of 2 to 8 at 50 C for aspen.

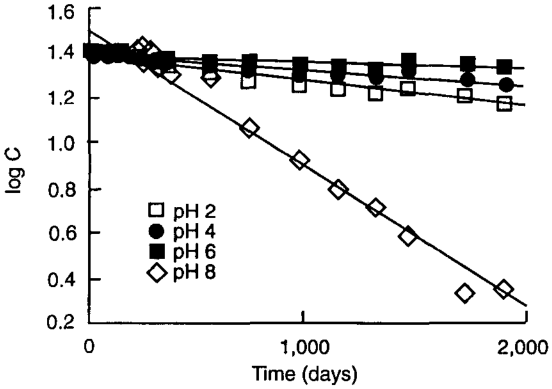

FIG. 4. Relationship between acetyl content and time over a pH range of 2 to 8 at 24 C for pine.

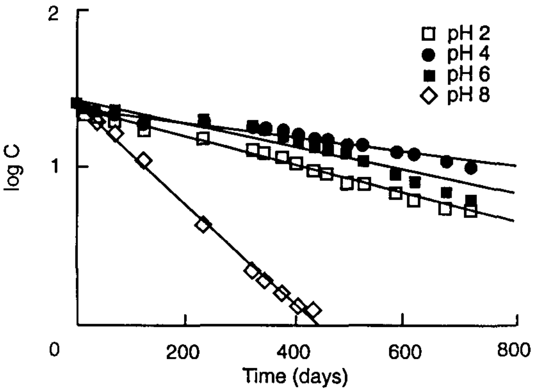

FIG. 5. Relationship between acetyl content and time over a pH range of 2 to 8 at 50 C for pine.

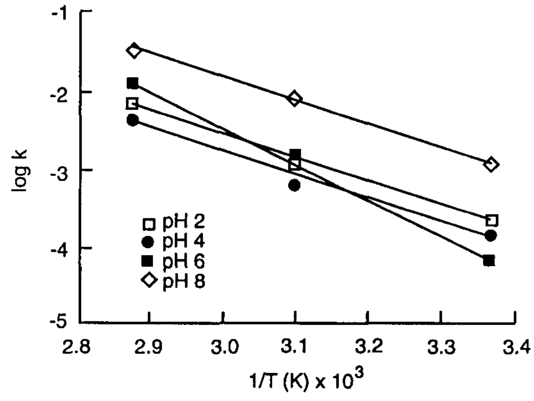

FIG. 7. Relationship between reaction rate constant (k) and temperature (1/T) over a pH range of 2 to 8 for aspen.

deacetylation of wood—that is, under the conditions used in these experiments, it is not possible to see the difference between the rate of deacetylation of the lignin fraction separately from the rate for the hemicelluloses. Because isolated lignin has been shown to acetylate faster than the hemicelluloses, it might be expected that their rates of deacetylation would be different (Rowell et al. in press). It is also interesting that the rate of deacetylation was essentially the same for the hardwood and softwood used in the study reported here. It might be expected that since they differ both in the content and type of hydroxyl groups in both lignin and hemicelluloses, the rate of deacetylation might be different.

Using the reaction rate constant, the half-life for the acetyl groups can be determined. When half the acetyl content is hydrolyzed, dimensional stability and biological resistance are reduced and the half-life data can be used as an indication of how long acetylated wood could be expected to perform in a given pH and temperature environment. Table 1 shows the half-life for aspen and pine at each pH and temperature used.

The half-life data suggest that wood acetylated to 20 weight percent gain would deacetylate to 10 weight percent gain in approximately 30 years at room temperature at pH 6. The dimensional stability or ASE of wood acetylated to about 10% is about 50% compared to

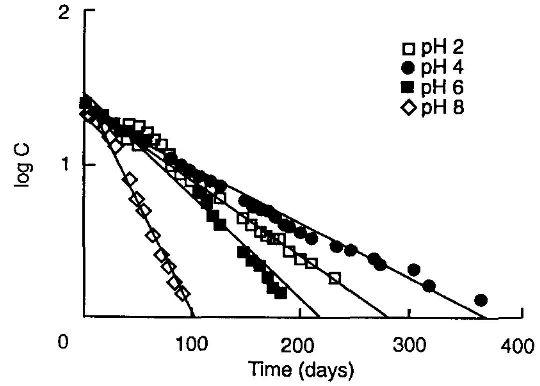

FIG. 6. Relationship between acetyl content and time over a pH range of 2 to 8 at 75 C for pine.

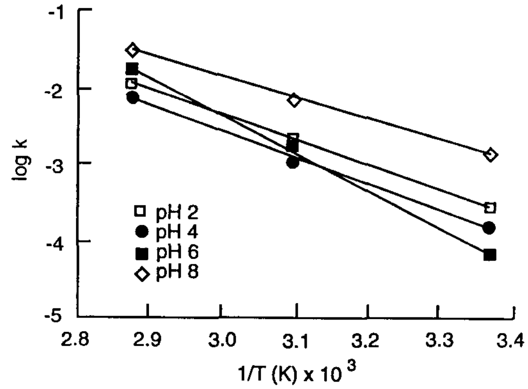

FIG. 8. Relationship between reaction rate constant (k) and temperature (1/T) over a pH range of 2 to 8 for pine.

TABLE 1. *Rate constant and half-life of acetylated aspen and pine at different pH and temperature conditions.*

Sample	Temperature (C)	pH	Rate constant $[k \times 10^{3}$ $(da^{-1})]$	Half-life (days)
Aspen	24	2	0.23	3,083
		4	0.15	4,697
		6	0.06	10,756
		8	1.11	623
Pine	24	2	0.26	2.640
		4	0.15	4,630
		6	0.06	10,900
		8	1.40	500
Aspen	50	2	1.18	590
		4	0.66	1,050
		6	1.29	540
		8	8.51	80
Pine	50	2	2.07	340
		4	1.06	650
		6	1.71	410
		8	7.31	95
Aspen	75	2	7.33	95
		4	4.78	145
		6	12.60	55
		8	32.50	21
Pine	75	2	11.30	61
		4	8.41	82
		6	15.50	45
		8	32.20	22

85% for wood acetylated to 20 weight percent gain.

From the slope of the plots in Figs. 7 and 8, it is possible to calculate the activation energy for the deacetylation at each pH. Table 2 shows the activation energy for aspen and pine at each pH level used in these experiments. The activation energy is about 90 kJ/mole at pH 6, 65 kJ/mole at pH 4, 60 kJ/mole at pH 2, and 55 kJ/mole at pH 8.

Table 3 shows the acetyl content for aspen and pine flakes kept at 90% RH and 27 C for 6 years. Within experimental error limits, very little acetyl content was lost during this time. So little acetyl was lost that rate constants, half-life estimates, and activation energy calculations could not be determined. It is interesting to note that whereas untreated flakes darkened as a result of attack by microorganisms in the 90% RH room within 2 weeks, the acetylated flakes were still their original color after 6 years.

TABLE 2. *Activation energy for deacetylation of aspen and pine over temperature range of 24 C to 75 C.*

Sample	pH	Activation energy (kJ/mole)
Aspen	2	63
	4	68
	6	93
	8	53
Pine	2	58
	4	58
	6	89
	8	57

Table 4 shows the acetyl content for aspen and pine flakes cycled between 90% and 30% RH at 27 C. Since each cycle represents 42 days, a total of 41 cycles represents about 4.7 years. As with the flakes kept at constant RH, very little loss of acetyl was observed after the cyclic RH conditions.

The acetyl values in Tables 3 and 4 for leached and unleached samples are essentially the same, showing that no soluble acetate-containing compounds were formed during the experiments.

CONCLUSIONS

Results from these experiments show that acetylated wood is much more stable under slightly acid conditions as opposed to slightly alkaline conditions. Acetylated wood should be stable for a very long time under normal air temperatures and humidity. In addition, the stability of acetylated wood under conditions of high or cyclic humidity suggests that such wood can be used for products exposed to changes in humidity.

The data can be used to predict the stability of acetylated wood or other biobased fiber composites at any pH and temperature combination to estimate the life expectancy of the product in its service environment. However, it must be remembered that data for this study were collected using either finely ground powder or small fiber. As a result, a very large

TABLE 3. *Acetyl content of aspen and pine flakes after exposure to 90% relative humidity at 27 C.*

	Acetyl content (%) after various periods (months)							
Sample	0	3	6	12	24	48	60	72
Aspen								
Unleached	20.1	19.4	19.3	18.7	18.2	18.5	18.4	18.3
Leached	19.5	19.6	19.4	19.1	17.1	17.3	18.13	18.6
Southern Pine								
Unleached	18.4	18.5	18.0	17.6	16.6	16.2	17.3	16.9
Leached	18.4	18.0	18.2	17.7	16.6	16.4	17.8	16.8

TABLE 4. *Acetyl content of aspen and pine flakes after relative humidity cycles.*

	Acetyl content (%) after cycle (no.)				
Sample	0	13	21	33	41
Aspen					
Unleached	17.9	18.1	17.1	17.8	17.1
Leached	17.9	18.1	17.1	18.8	16.9
Pine					
Unleached	18.6	18.2	16.2	18.0	16.5
Leached	18.6	17.3	16.1	16.1	17.0

surface area came into contact with the various pH and temperature environments. We expect that these data represent the fastest possible degradation rates and that composites made from acetylated fiber would degrade at a much slower rate since there would be much less surface contact. This is known to be the case in archaeological wood, in which acetyl groups have been very stable over thousands of years and little loss of acetyl has been observed.

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