Impact of Curing Condition on pH and Alkalinity/Acidity of Structural Wood Adhesives

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ABSTRACT: Nine formulations were selected for evaluating the effect of different curing methods on pH and alkalinity or acidity of various structural wood adhesives. These included four phenol–formaldehyde (PF) resins with high pH, one phenol–resorcinol–formaldehyde (PRF) resin with intermediate pH, two melamine–urea–formaldehyde (MUF) resins, and two melamine–formaldehyde (MF) resins with low pH. The four curing methods used in the study were: (1) curing at 102–105°C for 1 h (based on CSA O112.6-1977), (2) four-hour curing at 66°C followed by 1-hour curing at 150°C (based on ASTM D1583-01), (3) curing at room temperature overnight (based on ASTM D 1583-01), and (4) cured adhesive squeezed out from glue lines of bonded shear block samples. The effect of the different methods on pH and alkalinity/acidity of the cured adhesive depended strongly on the individual adhesives. For the PF, the alkalinity was different for the different formulations in the liquid form, while in the cured form, the difference in the alkalinity depended on the curing method used. The MF and the MUF were the adhesives most affected by the method used. In particular, the MUF showed much higher cured film pH values when cured by method 2 compared to the other three methods, while both the cured MF and MUF exhibited quite variable acidity values when cured with the different methods. The PRF showed reasonably uniform cured film pH but varying acidity values when cured with the different methods. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2888–2898, 2010

Key words: structural wood adhesives; alkalinity; acidity; pH; phenolic resin; melamine–urea–formaldehyde resin; curing conditions

INTRODUCTION

Hot setting thermoset phenol–formaldehyde (PF) resin is a major adhesive used to manufacture I-joist (LVL flange) and LVL products. One of the characteristics of this type of adhesive is its high pH, which can be as high as 13.0.

There is concern that adhesives in which the pH is either too low or too high may be detrimental to the mechanical properties of the wood and impact the service life of the glued-wood product. On the other hand, pH specifications that are unnecessarily restrictive may limit the range of adhesive technology available to glued-wood product manufactures, or increase the cost of adhesives. This is one of the main issues that was debated in the Canadian Standards Association (CSA) Wood Adhesive Sub-Committee (SC).

It was hypothesized that high pH could create a corrosive environment that would negatively affect the mechanical properties of the wood adjacent to the bond line, particularly in the presence of moisture. Different adhesive standards allow high adhesive film pH, ranging from pH 11 in the CSA O112.7[1] to no upper limit in the CSA O112.6[2] and ASTM D 2559.[3] However, there is no documented information on how these standards ended up with no upper pH limit. For adhesives used in bonded products for dry service conditions or limited moisture exposure, such as under CSA O112.10,[4] there is reason to believe that an upper pH limit may not be necessary. This would be consistent with the current ASTM D 2559 limit and the use of high pH PF in structural composite lumber [e.g. Laminated Veneer Lumber (LVL)], which are qualified under ASTM D 5456[5] and intended for dry service conditions. For products suitable for wet service, it is recognized that high pH PF adhesives have been used in plywood under exterior or wet service conditions; however, it is uncertain if the end use conditions (moisture and structural loading) are comparable to those

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anticipated for products that may be used under wet service conditions (e.g. glulam), which is the default moisture exposure conditions covered by CSA O112.9.[6]

For acidic adhesives, pH 2.5 is the lower limit specified in CSA O112.6, O112.7, and ASTM D 2559. However, there is no evidence on how this limit was determined. If there is evidence to show that there is degradation occurring in the wood at pH 2.5, it makes more sense to use a higher lower limit. However, there is at least one adhesive, which exhibits a film pH just above 2.5.[7]

ASTM D 1583[8] describes a standard test method for hydrogen ion concentration of dry adhesive films for both room temperature and elevated temperature setting adhesives. Similarly, CSA O112.6 has a standard method for determining the cured film pH of high temperature curing PF and PRF.

The aforementioned standard test methods for the determination of pH involve different adhesive film preparations and curing methods, which could give different results for a given resin sample. There are also concerns that not only pH, but also buffering capacity (alkalinity or acidity) may significantly impact the adhesion performance. Because there is no standard method for the determination of alkalinity and acidity of wood adhesives, it was necessary to develop such a method in this study.

There are three types of linkages involved in a wood–adhesive bond, namely: adhesive layer, wood–adhesive interface, and wood layer adjacent to the adhesive layer. The latter is probably more susceptible to the negative effects of extreme pH for long term exposure. The wood substance in wood cell walls is composed of holocellulose (40–44% cellulose and 15–35% hemicellulose) and 18–35% lignin.[9] Usually, a low pH affects predominantly the holocellulose, while a high pH affects predominantly the lignin.[9,10] Thus a low pH may have a more detrimental effect on wood strength than a high pH.

Kline et al.[11] observed strength losses in plywood with aging at pH values less than about 4 for urea–formaldehyde adhesives and 3.5 for PF adhesives. Wangaard[12] also found that with acid-catalyzed intermediate-temperature-setting PF at moderate humidity exposure conditions, the more acidic adhesives appeared to cause deterioration of the wood adjacent to the bond line. The alkaline-catalyzed adhesives did not show this effect. Similar observations were made by Eickner[13] on bonding compreg-to-compreg with three types of adhesives (alkaline intermediate-temperature-setting PF, room temperature-setting RF, and acidic PF) exposed to 93°C and 20%RH. He found that the alkaline intermediate-temperature-setting PF and the room temperature-setting RF retained relatively high strengths after 1 year of exposure, while those glued with the acidic PF lost strength. Moreover, a Weyerhaeuser[14] application guide on Microllam® laminated veneer lumber (LVL) scaffold plank indicates that the most hazardous acidic chemical solutions to wood are those that have pH less than or equal to 3.

Hse[15] examined the effects of several PF adhesive properties, including pH, on the bond quality of southern pine plywood. The pH of the liquid adhesive ranged from 10.5 to 12.1. However, the corresponding cured adhesive film pH would likely be higher based on the observations by Blomquist[16] and Kline et al.[11]. The relationships of pH to wet shear strength and wood failure were found to be parabolic. It is interesting to note that from the regression equations generated, the maximum values of wood failure and shear strength were found to correspond to liquid adhesive pH 11.0 and 10.7, respectively. The author indicated that it was unlikely that pH altered the wood substrate sufficiently to influence the quality of bonding. Santos et al.[17] examined the effects of pH and synthesis temperature on the performance of thermosetting adhesive formulations based on demethylated wood creosote-formaldehyde when used in bonding *Araucaria angustifolia* sheets. The pH's of the adhesive formulations were 12.00, 12.25, 12.50, 12.75, 13.00, 13.25, and 13.50. The dry and wet shear strengths were observed to be positively correlated linearly with increasing pH. However, no trend was observed between pH and wood failure. These results indicated that within the pH range studied, the adhesive probably did not have an adverse effect on the wood.

It is believed that either high or low pH of an adhesive could influence its bond durability and performance when the engineered wood product is used, especially under wet conditions. Key questions are whether the pH requirements are necessary and if so, whether they need to be the same for CSA O112.6, O112.9, and O112.10 and whether they should be harmonized with ASTM D 2559. Because of the potential long term implications and the lack of technical rationale for the existing limits, it is proposed that the appropriateness of these limits be assessed and properly documented.

The objective of this article was to investigate different test methods for measuring pH, alkalinity and/or acidity of cured adhesive films, and cured adhesives. Results of additional studies in this collaborative project between FPInnovations – Forintek Division and University of Toronto will be reported separately. They address impacts of high and low pH on wood and adhesive bond quality.

MATERIALS AND METHODS

Adhesives

Four high pH PF adhesives (R-I, R-II, R-III, R-IV) and one intermediate pH PRF adhesive (R-V) were supplied by adhesive manufacturers. In addition, one commercial low pH MUF adhesive was made into two formulations (R-VI and R-VII) of different pH values by adding different levels of hardener. Also a commercial low pH MF adhesive was made into two formulations (R-XI and R-XII) having different pH values. For the MUF and MF, the ratios of resin to hardener were within the range recommended by the adhesive manufacturers. Information on the adhesives used in this study is given in Table I.

Determination of pH of cured adhesives

Measurements of adhesive pH are normally performed for neat liquid adhesive, liquid adhesive mix, and cured adhesive film. In our study, the pH of the wood adhesives was measured from both the cured adhesive film and the cured adhesive squeezed out from glue lines of bonded block shear samples. Several methods were adopted to cure the adhesive for pH measurement in this study: method 1—curing for 1 h at 102–105°C (based on CSA O112.6-1977 for hot setting resins), method 2—curing for 4 h at 66°C, followed by 1 h at 150°C (based on ASTM D 1583-01 for hot setting resins), method 3—curing at room temperature overnight (based on ASTM D 1583-01 for room temperature setting resins), and method 4 - cured resin squeezed out of glue lines during hot pressing from block shear assemblies).

The procedure for sample preparation and pH measurement is as follows: (1) the adhesive was cured with the methods described above; (2) the cured adhesive was ground to pass through a No. 40 (425 μm) sieve, except cured adhesives R-XI and R-XII with method 3 because it was very difficult for them to pass the No. 40 sieve after grinding; (3) exactly 2 g of the ground particles was weighed in a small standard PE vial with cap, and 10 mL distilled water was added; (4) the mixture was thoroughly stirred for 20 min at room temperature and tightly sealed in a container and kept for over 24 hours; and (5) the pH was measured with a Corning Pinnacle 530 pH meter according to ASTM D 1583.

Determination of nonvolatile contents of adhesives

A representative sample was taken and placed in a clean and dry container that was tightly sealed to avoid evaporation of volatile matter and/or picking up atmospheric moisture. For each analysis, two flat bottomed aluminum pans (ID 50 ± 5 mm, rim height 8–10 mm) were used for weighing the adhesive sample. The nonvolatile contents of the adhesives were measured according to CSA O112.6. For each pan, the nonvolatile content was calculated as follows:

$$\mathit{Nonvolatile\ Content}(\%) = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \qquad (1)$$

where: m_1 was the mass of empty pan (mg); m_2 was the mass of pan with loaded sample (mg); and m_3 was the mass of pan plus residue (mg).

The nonvolatile content of the adhesive sample was expressed as an average of two values obtained to the nearest 0.05%.

Determination of alkalinity and acidity of liquid and cured adhesives

As there is no published standard test method used to determine the alkalinity and acidity of liquid or cured adhesives, a method was developed based on ASTM D 1067[18] and GB/T 14,074-2006.[19] This involved the development of a titration curve that

TABLE I
The Wood Adhesives Used in the Project and pH of the Cured Adhesives

Resin ID	Adhesive suppliers	Resin type	pH of Liquid adhesive[a]	pH of cured adhesive films[b]				Weight ratio of resin to hardener
				Method 1	Method 2	Method 3	Method 4	
R-I	A	PF	12.70	12.79 (0.04)	13.15 (0.05)		13.11 (0.04)	n/a[c]
R-II	B	PF	12.10	12.76 (0.05)	12.81 (0.07)		12.15 (0.07)	n/a
R-III	C	PF	11.80	12.44 (0.04)	12.87 (0.09)		12.00 (0.04)	n/a
R-IV	C	PF	11.55	12.11 (0.05)	12.69 (0.05)		11.95 (0.08)	n/a
R-V	D	PRF	10.00	10.58 (0.03)	10.84 (0.03)	10.09 (0.05)	10.51 (0.05)	2.2 : 1.0
R-VI	B	MUF	2.90	2.92 (0.07)	6.91 (0.09)	2.94 (0.05)	4.98 (0.02)	100 : 25
R-VII	B	MUF	2.70	2.78 (0.11)	7.00 (0.50)	2.78 (0.11)	4.99 (0.06)	100 : 30
R-XI	D	MF	3.90	3.72 (0.04)	3.63 (0.22)	3.93 (0.03)	3.98 (0.02)	100 : 10
R-XII	D	MF	3.70	3.60 (0.03)	2.39 (0.06)	3.71 (0.01)	3.84 (0.01)	100 : 20

[a] pH measured after mixing the adhesive with hardener.
[b] The result is the average of three replicates, and the values in parenthesis are standard deviations.
[c] n/a − not applicable.

properly identified the inflection points by adding a standard acid or alkali to the sample in small increments, and a pH reading was taken after each addition. The cumulative volume of solution added was plotted against the observed pH values. Sulfuric acid (0.5*N*) and sodium hydroxide (0.5*N*) were used as the standard reagents in titration.

The hydrogen or hydroxyl ions present in the adhesive were neutralized by titration with a standard alkali (acidity) or acid (alkalinity). Test Method A of ASTM D 1067-06 was found to be the most precise and accurate method. It was used to develop an electrometric curve (sometimes referred to as pH curve), which defined the acidity or alkalinity of the sample and indicated the inflection points and buffering capacity. In addition, the acidity or alkalinity can be determined with respect to any pH of particular interest.

When sodium carbonate is neutralized by sulfuric acid, the first inflection point is at pH 8.3 and the second is at pH 3.9 (GB/T 14,074-2006). The inflection point corresponding to the complete titration of carbonic acid salts is very close to 3.9 (ASTM D 1067-06). For high pH adhesives, including cured films and cured adhesives, and wood adducts, the inflection point could be different from 3.9. For development and comparison purposes, we set several end points of pH (3.9, 3.5, 3.0, and 2.5) to calculate the alkalinity.

When phthalic acid is neutralized by sodium hydroxide, the inflection point corresponding to the complete titration of phthalic acid salt is very close to pH 8.6 (ASTM D 1067-06). For adhesives, including cured films and cured adhesives, and wood adducts, the inflection point could be different from 8.6. Again, it was desirable to set several end points of pH (8.9, 10, 10.5, 11, and 11.5) to calculate the acidity.

The titration procedure for determining acidity or alkalinity of adhesives is detailed below:

1. For liquid adhesives, 5 gm liquid adhesive sample was weighed (accurately to 0.1 mg) and placed in 250 mL volumetric flask. The volumetric flask was filled with distilled water to the mark, and shaken well to distribute the adhesive uniformly in solution.
2. For cured adhesives, 2 gm 40-mesh sample was weighed (accurately to 0.1 mg) and placed in a 250 mL or 200 mL Erlenmeyer flask with stopper. The Erlenmeyer flask was filled with 100 mL distilled water, sealed with stopper and shaken well. After 72 h, titration was applied.
3. The combination pH electrode was mounted in an integral unit. The electrodes were placed in a beaker and the pH meter was calibrated using a reference buffer having designated pH values (7 and 4, or 7 and 10, or 4 and 10 as applicable). The electrodes were first rinsed with reagent water, and then drained completely. The samples prepared above were used for the pH measurements. A magnetic stirrer was used to mix the solution thoroughly, and the pH was measured in accordance with ASTM Test Methods D 1293.[20]
4. For the liquid adhesive, 100 mL of the solution was transferred from the volumetric flask into a 250 mL beaker. A magnetic stirrer was used to mix the solution thoroughly. A 0.5*N* acid solution (for alkalinity) or 0.5*N* alkali solution (for acidity) was added in increments of 0.1 mL or less. The solution was mixed thoroughly. The pH was determined when the mixture had reached equilibrium as indicated by a constant reading. The titration was continued until the desired end point for the titration curve was obtained.
5. For the cured adhesive, 0.5*N* acid solution (for alkalinity) or 0.5*N* alkali solution (for acidity) was added in increments of around 0.1 mL per minute (this means adding x mL standard solution and waiting for 10x min to read the pH). The titration was continued until pH 2.5 was reached for alkalinity and 11.5 for acidity.

For the liquid adhesive, the alkalinity (acidity), in milli-equivalents per gram, was calculated using eq. (2) as follows:

$$Alkalinity(acidity), (meq/g) = \frac{c \times V}{m \times \frac{B}{250}} \tag{2}$$

where: meq/g was the milliequivalent per gram; c was the normality of the standard sulphuric acid (or sodium hydroxide); V was the volume of standard sulphuric acid (or sodium hydroxide) required for the titration (mL); m was the sample mass in aqueous solution (here $\sim$ 5 gm); and B was the sample volume titrated (here 100 mL).

For the cured adhesive, the alkalinity (acidity), in milli-equivalents per gram, was calculated using eq. (3).

$$Alkalinity(acidity), (meq/g) = \frac{c \times V}{m} \tag{3}$$

where: meq/g was the milliequivalent per gram; c was the normality of the standard sulfuric acid (or sodium hydroxide); and m was the sample mass in aqueous solution (here $\sim$ 2 gm).

RESULTS AND DISCUSSION

The pH of cured film and squeezed-out cured adhesives

High pH adhesives

The pH values of the cured films of the high pH adhesive took a few days to reach equilibrium pH. The pH values at different curing conditions are summarized in Table I. Of the five adhesives, only Resin R-V could be cured at room temperature. The pH values of the cured films obtained with method 2 were higher than those obtained with method 1. This was probably attributed to the higher curing temperature used in the former method. The results obtained from method 4 were also different from those obtained from methods 1 and 2. This was probably due to the differences in assembly procedures recommended by the different adhesive manufactures. Table I definitely shows that curing condition had a significant effect on pH.

The pH obtained from method 4 (using the squeezed-out adhesive from the glue line from block shear assemblies) was different from that obtained from the adhesive in the glue line because the resin did not experience the same curing conditions as the temperature profiles were different. It should be pointed out that it was very difficult to collect a pure cured adhesive sample from the glue line without any wood component attached since the glue line was very thin. However, the pH measured from method 4 could provide a clue for estimating the pH of the glue line. The trend in pH of the cured films using method 4 was estimated to be: R-I > R-II > R-III ≥ R-IV> R-V, which varied from 13.11 to 10.51.

Low pH adhesives

The pH values of the cured films of the low pH adhesives measured with the four methods also took a few days to stabilize. This indicates that the cured adhesives either underwent hydrolysis in the aqueous solution or the acid components in the ground particles took time to dissolve in the water. The pH obtained at different curing conditions is summarized in Table I.

The pH changed dramatically with different curing conditions. For adhesives R-VI and R-VII, the pH increased from 2.92 to 6.91 and from 2.78 to 7.00 when measured with methods 1 and 2, respectively. However, for R-XI and R-XII, the pH decreased from 3.72 to 3.63 and from 3.60 to 2.39 when measured with methods 1 and 2, respectively. The pH of the cured films was lower than 3.0 when measured with methods 1, 2, or 3 and was always higher than 3.0 (around 4 or 5) when measured with method 4.

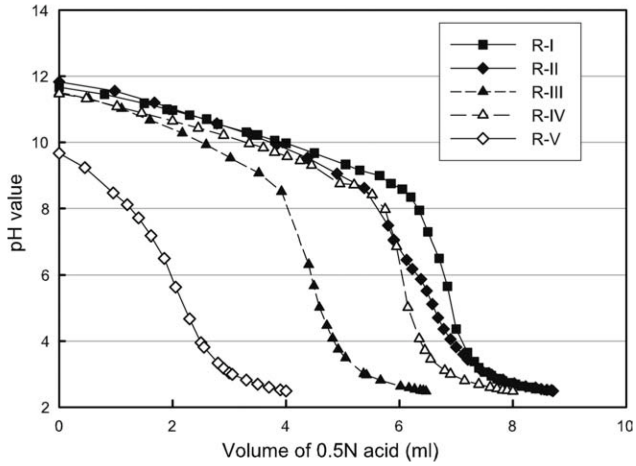

Figure 1 Cumulative volume of acid solution vs. pH for high pH adhesives (liquid form).

Alkalinity of high and intermediate pH adhesives with different curing conditions

High pH adhesives in liquid form

The titration curves (cumulative titration volume against pH) for the adhesives in liquid form are depicted in Figure 1. In general, the pH decreased at a fast rate with the addition of acid solution after a pH around 8 was reached and slowly decreased when the pH reached about 4. The inflection point was obtained from the relationship between pH and acid solution added.

As indicated above, the inflection point corresponding to the complete titration of carbonic acid salts is very close to pH 3.9 in water. The inflection points for the five resins studied were between 4 and 6. The alkalinities at various selected pH end points are presented in Table II. The alkalinities at the end points 3.0 to 3.9 were similar, and were higher at 2.5. This suggests that selecting the end point between 3.9 and 3.0 is reasonable for obtaining the actual alkalinity. The end point 2.5 could exceed the actual alkalinity.

Cured films of high pH adhesives according to method 1

The titration curves are depicted in Figure 2. The titration curves of the cured films were different from those of the adhesives in liquid form. In the titration of adhesives in the liquid form, it was easier to reach constant values after adding a certain amount of acid standard solution. In the titration of the cured adhesives, the pH was not stable, i.e., the rate of addition of acid solution had an effect on the pH; also the pH changed with time. In this study, the addition rate of acid solution was set at × mL per 10 × min. The pH of the cured adhesives decreased with the addition of acid solution more gradually than for those in the liquid form. As it was very

TABLE II
Alkalinity of PF and PRF Adhesives in the Liquid and Cured Forms at Different Conditions

Items	Unit	PF and PRF resins[a]				
		R-I	R-II	R-III	R-IV	R-V
Nonvolatile content	% (wt/wt)	43.0	45.0	44.0	45.0	47.0
Resin type		PF	PF	PF	PF	PRF
pH end point		Based on liquid content				
3.9	meq/g	1.81 (0.04)	1.72 (0.02)	1.21 (0.13)	1.40 (0.13)	0.52 (0.10)
3.5	meq/g	1.83 (0.01)	1.77 (0.04)	1.36 (0.12)	1.43 (0.11)	0.57 (0.07)
3.0	meq/g	1.85 (0.09)	1.80 (0.19)	1.39 (0.04)	1.45 (0.02)	0.63 (0.01)
2.5	meq/g	2.00 (0.05)	1.99 (0.05)	1.51 (0.05)	1.54 (0.05)	0.72 (0.05)
pH end point		Based on nonvolatile content				
3.9	meq/g	4.21 (0.06)	3.82 (0.03)	3.00 (0.18)	3.12 (0.18)	1.10 (0.15)
3.5	meq/g	4.26 (0.02)	3.92 (0.06)	3.09 (0.16)	3.17 (0.16)	1.21 (0.10)
3.0	meq/g	4.30 (0.13)	3.99 (0.25)	3.17 (0.06)	3.22 (0.03)	1.35 (0.02)
2.5	meq/g	4.66 (0.07)	4.42 (0.07)	3.43 (0.07)	3.43 (0.07)	1.53 (0.07)
pH end point	Method 1					
3.9	meq/g	3.45 (0.05)	3.40 (0.03)	3.04 (0.03)	2.47 (0.05)	0.64 (0.05)
3.5	meq/g	3.53 (0.05)	3.54 (0.04)	3.18 (0.05)	2.60 (0.06)	0.71 (0.07)
3.0	meq/g	3.71 (0.05)	3.68 (0.06)	3.36 (0.04)	2.76 (0.04)	0.81 (0.06)
2.5	meq/g	3.87 (0.05)	3.85 (0.05)	3.51 (0.06)	2.90 (0.05)	0.87 (0.05)
pH end point	Method 2					
3.9	meq/g	3.11 (0.30)	3.93 (0.30)	3.31 (0.31)	2.61 (0.08)	0.49 (0.03)
3.5	meq/g	3.61 (0.03)	4.13 (0.28)	3.57 (0.17)	2.79 (0.05)	0.60 (0.06)
3.0	meq/g	3.84 (0.06)	4.40 (0.21)	3.80 (0.12)	3.02 (0.01)	0.73 (0.06)
2.5	meq/g	4.15 (0.12)	4.87 (0.03)	4.15 (0.01)	3.31 (0.08)	0.88 (0.14)
pH end point	Method 4					
3.9	meq/g	2.62	2.64	2.12	1.88	0.82
3.5	meq/g	2.83	2.79	2.30	2.05	0.91
3.0	meq/g	3.03	2.99	2.53	2.26	0.99
2.5	meq/g	3.31	3.22	2.78	2.49	1.08

[a] Each data accompanied with parentheses is the average of at least two replicates and the values in parentheses are standard deviations. Each data without accompanying parentheses is only one test value.

difficult to get the actual inflection point, it was better to set the pH end point to obtain the alkalinity value for the cured resins. The alkalinities at various end points are summarized in Table II.

The adhesives cured with method 1 generally had lower alkalinity than those in the liquid form (based on nonvolatile content), with the exception of R-III. This phenomenon could be attributed to at least two reasons. Firstly, at certain conditions, some sodium hydroxide or other alkali compounds were probably entrapped in the cured fine particles, and it took time for the alkali to dissolve in the solution to react with the acid. Secondly, the structure of the phenolic compounds was probably altered after curing resulting in the pH change, thus affecting the alkalinity.

Cured films of high pH adhesives according to method 2

The titration curves obtained with method 2 were similar to those obtained with method 1 as shown in Figure 2. The alkalinities at various pH end points are given in Table II.

The cured adhesives gave lower alkalinity than those in liquid form based on nonvolatile content. Adhesive R-V showed similar alkalinity for the cured films prepared with methods 1 and 2. Except for R-V, the other cured adhesives with method 2 showed higher alkalinity at the end pH of $\leq$ 3.5 than that with method 1. This indicates that the adhesive structure and curing procedure have an effect on the alkalinity of the resins.

Cured films of high pH adhesives according to method 3

Method 3 involved curing the resin at room temperature. This method could not be applied to the high pH PF resins as they require curing at elevated temperatures. Only the PRF resin was capable of being cured at room temperature. It was difficult to determine the inflection point from the titration curve. Thus, several pH end points were designated for the calculation of alkalinity for comparison purposes. The alkalinities at the end points 3.9, 3.5, 3.0, and 2.5 were 0.92, 1.03, 1.15, and 1.33 meq/g, respectively.

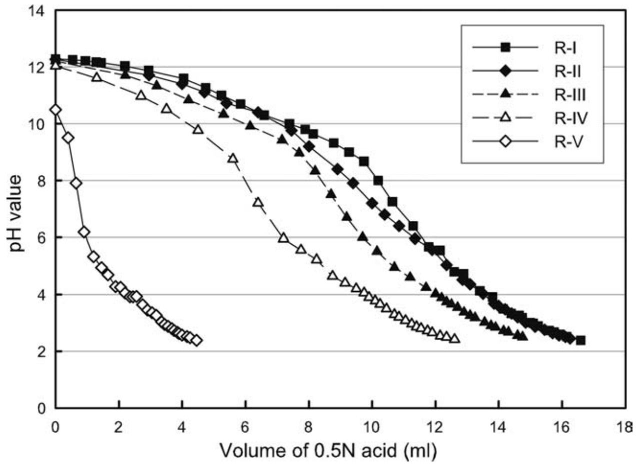

Figure 2 Cumulative volume of acid solution vs. pH for the high pH adhesives (the cured films were prepared with method 1).

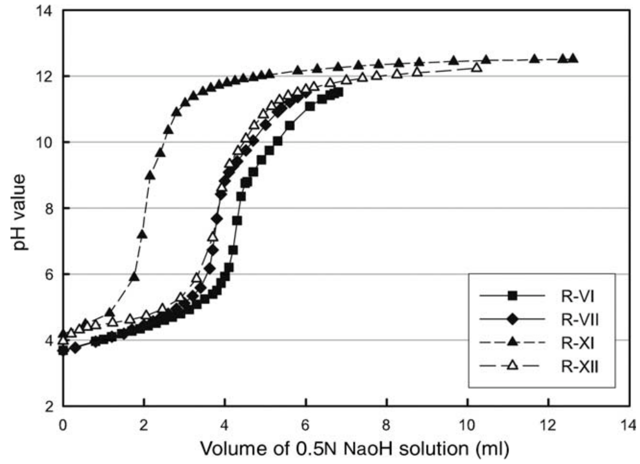

Figure 3 pH vs. cumulative volume of NaOH solution for the low pH adhesives (liquid form).

These values were slightly lower than those obtained in the liquid form based on nonvolatile content.

Cured films of high pH adhesives according to method 4

The alkalinities at various pH end points are given in Table II. For all the PF adhesives, the alkalinity with method 4 was lowest, suggesting that a portion of the alkali compound probably penetrated into the wood altering the composition of the cured adhesive, and/or that a portion of the alkali compound reacted with the wood components during pressing, thus reducing the alkalinity.

For R-V, the trend was as follows: adhesive in liquid form (based on nonvolatile content) > cured film with method 3 > cured film with method 4 >

TABLE III
Relative Alkalinity[a] of PF and PRF Adhesives in the Liquid and Cured Forms at Different Conditions

Items	Unit	PF and PRF resins[a]				
		R-I	R-II	R-III	R-IV	R-V
Nonvolatile Content	% (wt/wt)	43.0	45.0	44.0	45.0	47.0
Resin type		PF	PF	PF	PF	PRF
pH end point		Based on Nonvolatile content of adhesives in liquid form				
3.9		1	1	1	1	1
3.5		1	1	1	1	1
3.0		1	1	1	1	1
2.5		1	1	1	1	1
pH end point	Method 1	Cured film of adhesive (CSA O112.6–1977 hot setting resins)				
3.9		0.82 (0.02)	0.89 (0.01)	1.01 (0.06)	0.79 (0.05)	0.58 (0.09)
3.5		0.83 (0.01)	0.90 (0.02)	1.03 (0.06)	0.82 (0.05)	0.59 (0.08)
3.0		0.86 (0.03)	0.92 (0.06)	1.06 (0.02)	0.86 (0.01)	0.60 (0.05)
2.5		0.83 (0.02)	0.87 (0.02)	1.02 (0.03)	0.85 (0.02)	0.57 (0.04)
pH end point	Method 2	Cured film of adhesive [ASTM D 1583–01 (hot setting resins)]				
3.9		0.74 (0.07)	1.03 (0.08)	1.10 (0.12)	0.84 (0.05)	0.45 (0.07)
3.5		0.85 (0.01)	1.05 (0.07)	1.16 (0.08)	0.88 (0.05)	0.50 (0.06)
3.0		0.89 (0.03)	1.10 (0.09)	1.20 (0.04)	0.94 (0.01)	0.54 (0.05)
2.5		0.89 (0.03)	1.10 (0.02)	1.21 (0.02)	0.97 (0.03)	0.58 (0.10)
pH end point	Method 4	Cured adhesive squeezed out from glue line during hot press				
3.9		0.62 (0.01)	0.69 (0.01)	0.71 (0.05)	0.60 (0.04)	0.75 (0.11)
3.5		0.66 (0.01)	0.71 (0.02)	0.74 (0.04)	0.65 (0.04)	0.75 (0.07)
3.0		0.70 (0.02)	0.75 (0.05)	0.80 (0.02)	0.70 (0.02)	0.73 (0.04)
2.5		0.71 (0.02)	0.73 (0.02)	0.81 (0.02)	0.73 (0.02)	0.71 (0.05)

[a] The relative alkalinity is calculated as cured adhesive alkalinity divided by adhesive alkalinity in liquid form, and the relative alkalinity is set as 1 at different pH end points. The values in parentheses are standard deviations.

TABLE IV
Acidity of the Low pH Adhesives in the Liquid and Cured Forms at Different Conditions

Items	Unit	Low pH adhesives[a]			
		R-VI	R-VII	R-XI	R-XII
Nonvolatile Content	% (m/m)	62.9	61.0	54.0	51.5
Resin type		MUF	MUF	MF	MF
pH end point		Based on liquid content			
8.9	meq/g	0.96 (0.05)	1.11 (0.09)	0.53 (0.03)	0.99 (0.04)
10.0	meq/g	1.10 (0.11)	1.29 (0.13)	0.60 (0.05)	1.09 (0.04)
10.5	meq/g	1.16 (0.13)	1.36 (0.14)	0.63 (0.01)	1.14 (0.03)
11.0	meq/g	1.21 (0.15)	1.45 (0.19)	0.65 (0.02)	1.19 (0.04)
11.5	meq/g	1.25 (0.12)	1.48 (0.23)	0.64 (0.01)	1.24 (0.03)
pH end point		Based on nonvolatile content			
8.9	meq/g	1.53 (0.07)	1.81 (0.14)	0.98 (0.06)	1.91 (0.06)
10.0	meq/g	1.75 (0.17)	2.12 (0.18)	1.12 (0.08)	2.12 (0.06)
10.5	meq/g	1.84 (0.19)	2.24 (0.20)	1.17 (0.02)	2.22 (0.05)
11.0	meq/g	1.93 (0.22)	2.37 (0.27)	1.20 (0.03)	2.31 (0.06)
11.5	meq/g	1.99 (0.18)	2.43 (0.30)	1.19 (0.02)	2.40 (0.05)
pH end point	Method 1	Cured film of adhesive (CSA O112.6–1977 Hot setting resins)			
8.9	meq/g	0.82 (0.07)	0.86 (0.10)	0.34 (0.06)	0.78 (0.12)
10.0	meq/g	0.83 (0.12)	0.89 (0.15)	0.48 (0.06)	0.97 (0.16)
10.5	meq/g	0.82 (0.15)	0.90 (0.13)	0.51 (0.06)	1.03 (0.19)
11.0	meq/g	0.82 (0.15)	0.89 (0.18)	0.52 (0.06)	1.07 (0.19)
11.5	meq/g	0.79 (0.13)	0.84 (0.22)	0.50 (0.06)	1.09 (0.20)
pH end point	Method 2	Cured film of adhesive [ASTM D 1583–01 (Hot setting resins)]			
8.9	meq/g	0.05 (0.02)	0.04 (0.01)	0.19 (0.01)	0.28 (0.12)
10.0	meq/g	0.18 (0.02)	0.18 (0.03)	0.22 (0.01)	0.33 (0.14)
10.5	meq/g	0.27 (0.01)	0.26 (0.04)	0.22 (0.02)	0.36 (0.14)
11.0	meq/g	0.31 (0.02)	0.30 (0.05)	0.22 (0.02)	0.38 (0.14)
11.5	meq/g	0.29 (0.02)	0.28 (0.06)	0.22 (0.04)	0.44 (0.11)
pH End Point	Method 3	Cured film of adhesive [ASTM D 1583–01 (Cold setting resins)]			
8.9	meq/g	1.00	1.08	0.70	1.23 (0.17)
10.0	meq/g	1.02	1.10	0.85	1.41 (0.22)
10.5	meq/g	0.99	1.10	0.90	1.53 (0.26)
11.0	meq/g	1.02	1.09	0.92	1.59 (0.26)
11.5	meq/g	0.98	1.06	0.92	1.63 (0.24)
pH end point	Method 4	Cured adhesive squeezed out from glue line during hot press			
8.9	meq/g	0.06	0.06	0.47	0.86
10.0	meq/g	0.11	0.11	0.53	0.98
10.5	meq/g	0.15	0.15	0.57	1.07
11.0	meq/g	0.17	0.17	0.59	1.16
11.5	meq/g	0.15	0.14	0.59	1.24

[a] For the ratio of resin to hardener, refers to Table I.

cured film with method 1 $\geq$ cured film with method 2. The alkalinities of the cured adhesives at different conditions compared with those of the corresponding adhesives in liquid form are given in Table III. Different curing conditions definitely impact the alkalinity of the cured adhesives.

Acidity of low pH adhesives with different curing conditions

Adhesives in liquid form

The titration curves for the adhesives in liquid form are shown in Figure 3. The pH increased with the addition of sodium hydroxide solution. The pH increased at a fast rate between pH 6 and 9 and then tended to level off at pH over 10. The inflection points for the resins R-VI, R-VII, R-XI, and R-XII were $\sim$ 7.6, $\sim$ 7.6, $\sim$ 8.9, and $\sim$ 8.6, respectively. As indicated above, the inflection point corresponding to the complete titration of the phthalic acid salt is very close to pH 8.6. The acidities obtained at various end points at 20°C are listed in Table IV.

The acidity of the adhesives increased with end point from 8.9 to 11.5. Considering the standard deviation values, it appeared that there was no significant difference in the acidity values between end

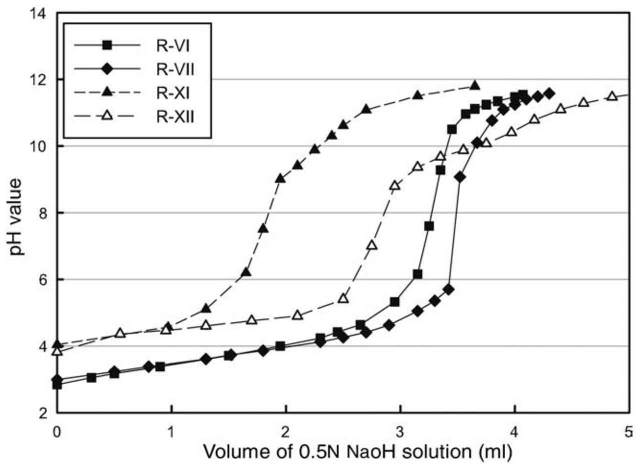

Figure 4 pH vs. cumulative volume of NaOH solution for the cured low pH adhesives (the cured filmswere prepared with method 1).

points 8.9 and 10. R-VI and R-VII showed higher standard deviations than R-XI and R-XII. This could be related to the difference in the storage time of one of the adhesive components. The shortest storage time for at least one component of R-VI and R-VII is only two months, while that of the component of R-XI and R-XII is six months. The chemical structure could change during storage and could affect the curing properties, which, in turn, could affect the acidity of the adhesive. It is suggested that future work in this area would include an examination of the effect of storage time on the functionality and performance of adhesives. It would be reasonable to use the end point pH between 8.9 and 10 for determining the acidity.

Cured adhesives films according to method 1

The titration curves are shown in Figure 4. The pH increased with the addition of sodium hydroxide solution similar to that of the adhesives in the liquid form. The acidity at various end points is presented in Table IV.

The acidities of the cured resins were much lower compared with those in the liquid form. For example, the acidity of Resin VI decreased from 1.53 meq/g in the liquid form to 0.82 meq/g for the cured adhesive at the end point of 8.9. This was probably attributed to: (1) evaporation of some of the inorganic or organic acid during curing and (2) the reaction between MF or MUF and the curing agents changed the chemical structures of the adhesive components during curing resulting in the change in the pH of the material.

Cured adhesives films according to method 2

The acidities at various end points are summarized in Table IV. The acidities of the cured adhesives obtained with method 2 were much lower than those obtained with method 1. This observation indicates that temperature probably plays an important role in changing the molecular structure of the adhesive and/or causing some of the acidic components to evaporate faster at the temperature of 150°C.

Cured adhesives films according to method 3

The titration curves obtained with method 3 were similar to those obtained with method 1 as shown in Figure 4. The acidities at various pH end points are given in Table IV. The sequence of acidity for the adhesives determined with the different methods were: liquid form > cured film with method 3 > cured film with method 1 > cured film with method 2. These results indicate that the curing procedure had a significant effect on the acidity of the adhesives.

Cured adhesives films according to method 4

The acidities are given in Table IV. The acidity of the different adhesives showed the following trend: R-XII > R-XI > R-VII ≈ R-VI. The relative acidities of the cured adhesives with different curing conditions at different end points are listed in Table V. The liquid form gave the highest acidity followed, in descending order, by method 3 (room temperature curing) and method 1. Methods 2 and 4 gave the lowest values.

Correlation between alkalinity and/or acidity and pH of cured adhesives

Alkalinity vs. pH of cured high pH adhesives

The alkalinities as a function of pH of the cured high pH adhesives obtained with the different methods are shown in Figures 5–7. Alkalinity had a very good correlation with pH of cured film with method 1. In general, the higher the pH of the cured adhesive, the higher was the alkalinity. However, this trend was not observed with methods 2 and 4.

Acidity vs. pH of cured low pH adhesives

In general, the correlation between pH and acidity of the cured low pH adhesives showed that the lower the pH of the adhesive, the higher was the acidity. However, this relationship was not as strong as that observed for the alkalinity–pH relationship for the high pH adhesives. The test results in Table I and Table IV showed that the curing methods had a significant effect on the pH and acidities of the cured adhesives. It is suggested that further studies be conducted aimed at developing a standard test

TABLE V
Relative Acidity[a] of the Low pH Adhesives in the Liquid and Cured Forms at Different Conditions

Items	Unit	Low pH adhesives[a]			
		R-VI	R-VII	R-XI	R-XII
Nonvolatile Content	% (m/m)	62.9	61.0	54.0	51.5
Resin type		MUF	MUF	MF	MF
pH end point		Based on nonvolatile content of resin in liquid form			
8.9		1	1	1	1
10.0		1	1	1	1
10.5		1	1	1	1
11.0		1	1	1	1
11.5		1	1	1	1
pH end point	Method 1	Cured film of adhesive (CSA O112.6–1977 Hot setting resins)			
8.9		0.54 (0.05)	0.48 (0.07)	0.35 (0.06)	0.41 (0.06)
10.0		0.47 (0.08)	0.42 (0.08)	0.43 (0.06)	0.46 (0.08)
10.5		0.45 (0.09)	0.40 (0.07)	0.44 (0.06)	0.46 (0.09)
11.0		0.42 (0.09)	0.38 (0.09)	0.43 (0.05)	0.46 (0.08)
11.5		0.40 (0.09)	0.35 (0.10)	0.42 (0.05)	0.45 (0.08)
pH end point	Method 2	Cured film of adhesive [ASTM D 1583–01 (Hot setting resins)]			
8.9		0.03 (0.01)	0.02 (0.01)	0.19 (0.02)	0.15 (0.06)
10.0		0.10 (0.02)	0.08 (0.01)	0.20 (0.02)	0.16 (0.07)
10.5		0.15 (0.02)	0.12 (0.02)	0.19 (0.02)	0.16 (0.06)
11.0		0.16 (0.02)	0.13 (0.03)	0.18 (0.02)	0.16 (0.06)
11.5		0.15 (0.02)	0.12 (0.03)	0.18 (0.03)	0.18 (0.05)
pH end point	Method 3	Cured film of adhesive [ASTM D 1583–01 (Cold setting resins)]			
8.9		0.65 (0.04)	0.60 (0.05)	0.71 (0.07)	0.64 (0.09)
10.0		0.58 (0.06)	0.52 (0.05)	0.76 (0.07)	0.67 (0.11)
10.5		0.54 (0.06)	0.49 (0.05)	0.77 (0.04)	0.69 (0.12)
11.0		0.53 (0.07)	0.46 (0.06)	0.77 (0.05)	0.69 (0.11)
11.5		0.49 (0.05)	0.44 (0.06)	0.77 (0.04)	0.68 (0.10)
pH end point	Method 4	Cured adhesive squeezed out from glue line during hot press			
8.9		0.04 (0.01)	0.03 (0.01)	0.48 (0.06)	0.45 (0.05)
10.0		0.06 (0.01)	0.05 (0.01)	0.47 (0.06)	0.46 (0.05)
10.5		0.08 (0.01)	0.07 (0.01)	0.49 (0.04)	0.48 (0.05)
11.0		0.09 (0.01)	0.07 (0.01)	0.49 (0.04)	0.50 (0.05)
11.5		0.08 (0.01)	0.06 (0.01)	0.50 (0.04)	0.52 (0.04)

[a] The relative acidity is calculated as cured adhesive acidity divided by adhesive acidity in liquid form, and the relative acidity of adhesives in liquid form is set as 1 at different pH end points. The values in parentheses are standard deviations.

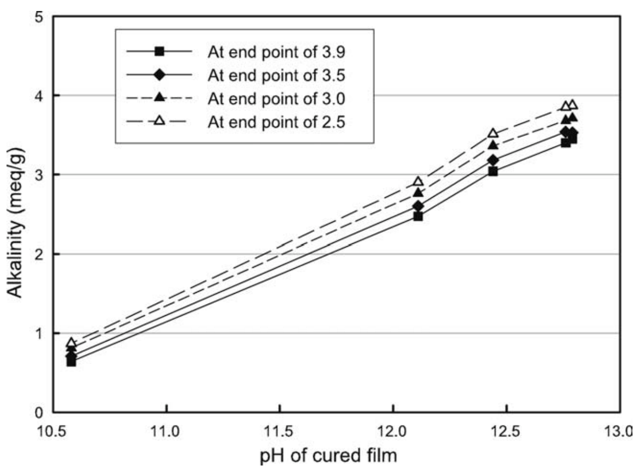

Figure 5 Alkalinity vs. pH for the adhesives cured with method 1.

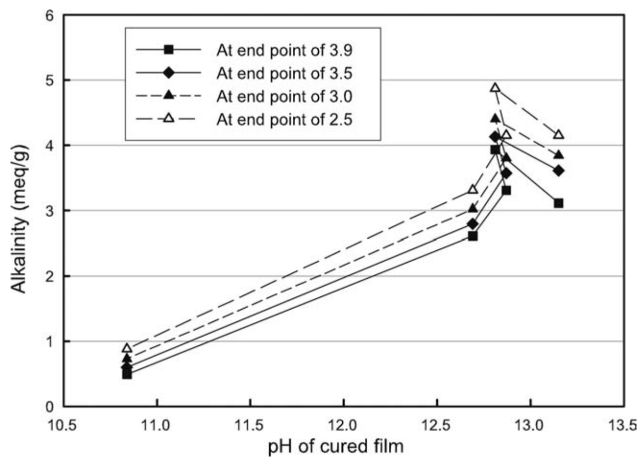

Figure 6 Alkalinity vs. pH for the adhesives cured with method 2.

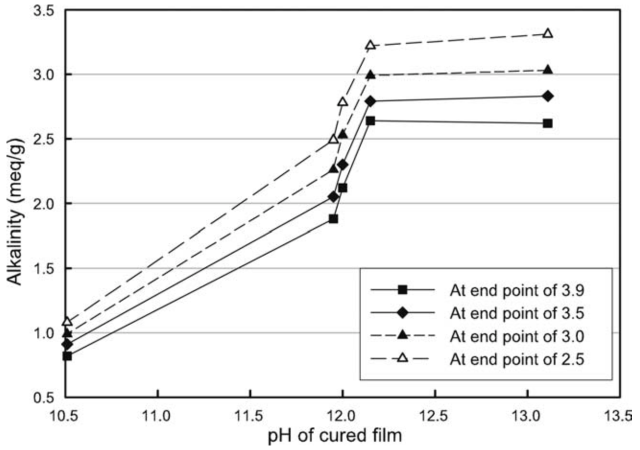

Figure 7 Alkalinity vs. pH for the adhesives cured with method 4.

method to better characterize structural wood adhesives in terms of their acidities.

CONCLUSIONS

Curing condition and adhesive form (liquid or cured) influence the pH and alkalinity/acidity of the cured adhesive film. The effect depends strongly on the individual adhesive type. The low pH adhesives, particularly the MUF, are more affected than the high and intermediate pH adhesives. When considered as a group (i.e., adhesives of low or high pH), a relationship exists between alkalinity and cured pH and between acidity and cured pH.

The determination of alkalinity or acidity of adhesives by titration is more difficult when performed with a cured film than with a liquid sample. Thus, in standards requiring the determination of adhesive alkalinity or acidity, it is suggested that the test should be performed on the liquid adhesive instead of on the cured adhesive film.

The findings from this study suggest that in the preparation of cured adhesive film for pH determination, the curing method that is similar or close to that used in the manufacture of the glued-wood product should be adopted. Further studies and/or discussions should be made in this area.

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