

EFFECT OF EXTREME PH ON BOND DURABILITY OF SELECTED STRUCTURAL WOOD ADHESIVES

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Abstract. This is the second part of a two-part study aimed at examining the effect of extreme adhesive pH on bond durability. The first part dealt with short-term exposure and this second part dealt with long-term exposure. This part also included an examination of wood degradation by adhesive pH. Nine structural wood adhesives (four high-pH phenol-formaldehyde [PF], one intermediate pH phenol-resorcinol-formaldehyde [PRF], two low-pH melamine-formaldehyde [MF], and two low-pH melamine-urea-formaldehyde [MUF]) were studied in terms of their pH effect on wood-adhesive bond durability using Douglas-fir wood substrate with specimens tested in block shear. The block shear specimens were initially subjected to vacuum-pressure treatment under water, followed by exposure, while wet at 50°C for 0, 4, 8, 12, and 17 mo. There were indications that the wood layer closest to the bond line, which contained included glue, had higher solubility compared with those farther from the bond line. This suggests that wood degradation and/or adhesive decomposition occurred and was considered to be induced by the adhesive alkalinity or acidity under the long-term exposure conditions. The PF showed the best durability performance followed, in decreasing order, by PRF and MF/MUF. The latter adhesives degraded completely after an exposure period of 8–17 mo. The four PF adhesives passed the shear strength and wood failure requirements of the well-known North American structural wood-adhesive standards indicating that their high pH had no significant detrimental effect on the wood-adhesive bond durability after the 17-mo exposure period despite being subjected to multiple cyclic tests. This observation was not apparent for the PRF, and the pH effect was considered inconclusive for the MF/MUF since they degraded during the exposure period. The results of this study provide support to wood-adhesive standards that do not impose restriction on the upper spectrum of the pH range, and would be useful to adhesive standard developers. These results also serve as background information for adhesive companies in their formulation of wood adhesives as well as for bonded wood product manufacturers in their use of adhesives and for builders in their use of bonded wood products.

Keywords: Structural wood adhesives, adhesive pH, long-term exposure, block shear test, bond durability.

INTRODUCTION

Current structural wood-adhesive standards differ in their specifications for adhesive pH limitations in the alkaline and/or acidic regions of the spectrum. For example, in American Society for Testing and Materials (ASTM) D 2559 (2011c), Canadian Standards Association (CSA) O112.6 (1977a), CSA O112.9 (2010a), and CSA O112.10 (2010b) standards, the specified lower pH limit of the cured adhesive film is 2.5 and there is no upper pH limit. On the other hand, an upper pH limit of 11.0 appears in CSA O112.7 (1977b) in addition to the lower limit of 2.5. Draft standard ISO/DIS 20152.1 (2009) restricts lower dry film pH to 3.0 and upper film pH of 11.0. Some standards, such as ASTM D 2559 and

CSA O112.9, are intended for evaluating adhesives for wood and wood-based products that may be repeatedly exposed to moisture, and are expected to withstand design stresses when wet. Adhesives at extremely high or low pH levels could be corrosive and their potential impact on wood properties, especially in the presence of moisture, is a concern that motivated the establishment of the pH limits.

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. Usually, a low pH predominantly affects the holl cellulose,

whereas a high pH mainly affects the lignin (Stamm 1964; Haygreen and Bowyer 2003) contents of the wood. Thus, a low pH may have a more detrimental effect on wood strength than a high pH.

It is well known that most wood adhesives are catalyzed by acidic or alkaline additives to ensure rapid curing, which, in turn, affects the quality of the resulting bond. The effect of pH on the long-term durability of the wood-adhesive bond is influenced by other factors, including adhesive type, wood species, exposure time (ET), and exposure conditions. Wood components may be hydrolyzed or degraded in highly acidic or alkaline conditions.

Zhang et al (2011) did a comprehensive review on the effect of pH on bond quality. Notable of these included the works of Gillespie and River (1975) who reported that yellow birch and Douglas-fir (DF) plywood shear specimens stored for 4 yr at 27°C and 30% RH lost little, if any, strength, when bonded with nonacidic adhesives, but showed appreciable strength loss when bonded with acidic adhesives. Similarly, Raknes (1976, 1981) reported that acidic phenol-formaldehyde (PF) adhesives started showing signs of failure after 10-15 yr, probably due to acid damage to the wood, while alkali resorcinol-formaldehyde (RF) adhesives still retained satisfactory strength. Kline et al (1947) 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 (1946) also found that with acid-catalyzed intermediate-temperature-setting (ITS) PF at moderate RH exposure conditions, the more acidic adhesives caused deterioration of the wood adjacent to the bond line, whereas the alkaline-catalyzed adhesives did not show this effect.

Green et al (2005) observed that structural solid-sawn lumber, laminated veneer lumber (LVL) bonded with PF, and laminated strand lumber (LSL) bonded with isocyanate exposed at 82°C and 80% RH showed reductions in bending strengths after 12-24 mo of exposure. They concluded that acid hydrolysis of hemicellulose,

especially arabinose, was the fundamental cause of strength loss resulting from thermal degradation. The products became more acidic with ET, and arabinose showed the largest and most consistent decrease with duration of exposure.

Blomquist (1949/1962) investigated the effect of alkalinity of hot-pressed PF, ITS PF, and room-temperature-setting RF on the wood-adhesive bond in yellow birch and DF plywood specimens at different exposure conditions over a period of 2-3 yr. Exposure at room conditions had no significant effect on the durability of the specimens regardless of the alkalinity of the adhesive, whereas exposure at high RH/room temperature or cyclic high/low RH was the most damaging condition to the most alkaline hot-pressed PF. On the other hand, Santos et al (2003) reported that there was no adverse effect on the bond durability of thermosetting adhesives at a curing pH value from 12.0 to 13.5 for bonding *Araucaria* sheets. Zimmerman et al (2007) showed that 5-h exposure of spruce wood to 10% and 18% sodium hydroxide (NaOH) or 24% potassium hydroxide at room temperature resulted in slight reductions in hemicellulose components and, in most cases, significant reductions in bending strength and stiffness.

More recently, a study by Zhang et al (2011) indicated that adhesive pH, test condition, and wood species showed significant effects on the block shear strength and wood failure of specimens made from DF and black spruce woods bonded with structural adhesives of varying pH and tested under short-term exposure. The melamine-based adhesives such as MF and MUF were found to be less durable than the phenol-based adhesives such as PF and PRF, and that the latter did not have a negative impact on the strength of the specimens. Similarly, Wang et al (2013) found that the tensile strength and wood failure of specimens decreased after 4-7 mo of exposure to acidic conditions but did not change significantly under alkaline conditions.

Wang et al (2010) found that wood has the ability to buffer and mitigate the effects of strongly acidic or alkaline environments produced near the bond line by adhesives. This would help

mitigate the potentially adverse effects of extreme pH adhesives on wood-adhesive bond quality. Aspen wood had a greater effect on adhesive pH than spruce and DF. In addition to the buffering effect of the wood, Huang et al (2010) found that for alkaline adhesives exposed to wet service conditions, hydroxyl ions could diffuse away from the bond line, thus resulting in the decrease in alkalinity. A similar but less effective process, whereby hydrogen ions diffused away from the bond line, occurred with acidic adhesives. It is likely that due to the above effects, spruce and DF samples exposed to strongly acidic and alkaline buffered solutions for three months did not show appreciable changes in chemical composition by wet chemical analysis. However, they observed that samples bonded with an alkaline adhesive showed dissociation of carboxylic acid groups in hemicelluloses to a distance of 150-300 μm from the center of adhesive bond lines, but no effects on wood chemistry were observed around acidic adhesive bond lines. Similarly, Wang et al (2013) found that, in aspen lap shear specimens which were bonded with PF (film pH value of 12.8) and soaked in different buffer solutions of pH 2.0-12.5 for up to 7 mo, the acidic buffer solutions with a pH range between 2.0 and 3.0 did not cause a measurable chemical change in the wood, whereas losses in hemicellulose and lignin were found when exposed to basic buffer solutions when the pH value was greater than 11.0.

The specified adhesive pH in wood-adhesive standards is usually that of the cured adhesive film. The standard test method for film pH determination of both room temperature and elevated temperature setting adhesives is described in ASTM D 1583 (2011b) (curing for 4 h at 66°C, followed by 1 h at 150°C for a hot setting resin, or curing at room temperature overnight for a room-temperature setting resin). Similarly, CSA O112.6 (1977a) describes a method for determining the film pH of high-temperature curing PF and PRF (curing for 1 h at 102-105°C). Zhang et al (2010) described other methods of measuring cured film pH (cured resin squeezed out of glue lines during hot pressing from block

shear assemblies) as well as alkalinity/acidity of liquid-form adhesives.

In view of the potential long-term implications and the lack of technical rationale for the existing pH limits in the adhesive standards, there is a need to assess and properly document the appropriateness of these limits. Until then, this would mean adopting conservative limits for wet service conditions and relaxed limits only for products intended for dry service, where there is a history of good performance from composite and other engineered wood products.

This study was conducted to better understand the role and need for pH limits on the cured adhesive film with respect to the development of adhesive standards that ensure good long-term performance, and at the same time, permit innovative adhesive systems to be developed and used in the most appropriate applications. The main objective was to evaluate the effect of extreme pH of acidic and basic adhesives on wood-adhesive bond durability, assessed by a block shear test, after long-term exposure to different environmental conditions. This information will be used to help determine whether there is a need to place stricter pH limitations on adhesives used in structural glued wood products, especially under wet service conditions.

MATERIALS AND METHODS

Adhesives

Four commercial high-pH adhesives (denoted as PF-1, PF-2, PF-3 and PF-4) and one intermediate pH PRF adhesive (denoted as PRF having a pH value of around 10.0) were obtained from various adhesive manufacturers. The hardener for PRF was 20-25% powder slurry of which the major components were paraformaldehyde and walnut shell flour. A commercial low-pH MF adhesive with methylated melamine was made into two formulations (denoted as MF-1 and MF-2) with different pH by varying the weight ratios of resin to hardener. The main component of the hardener was aluminum chloride. Another commercial low-pH MUF adhesive

was also made into two formulations (denoted as MUF-1 and MUF-2) with different pH by adding different levels of hardener. The hardener was slurry composed mainly of formic acid and resorcinol. For the MUF and MF, the ratios of adhesive to hardener were within the range recommended by the adhesive manufacturer. Table 1 provides information on the wood adhesives used in the study.

Wood Substrate

The wood species used in the study was DF (*Pseudotsuga menziesii*). The lumber samples (2 in. × 4 in. × 8 ft. [51 mm × 102 mm × 244 cm]) were obtained from Tembec in Elco, British Columbia, Canada. All of the lumber samples were conditioned at 65% RH and 21°C to achieve EMC of about 12%. From these samples, billets measuring 32 mm thick × 88 mm wide × 820 (or 600) mm long were cut. Only the billets that met the visual wood quality and density requirements of CSA O112.9 (2010a) were selected for the study. The wood density range was 0.61–0.74 g/cm³ based on 12% MC. About 74% of the billets fell in the density range of 0.63–0.69 g/cm³. The billets were surfaced on both faces to a thickness of about 21 mm, and stored at 65% RH and 21°C prior to use.

Experimental Design

The experimental design consisted of two factors: adhesive type with different curing pH values and ETs. Nine adhesives with their corresponding cured film pH are shown in Table 1. Solid wood test specimens (without adhesive) were used as a control in this study, thus providing a total of 10 levels for the adhesive factor, while the ETs factor had a time interval of 0, 4, 8, 12, and 17 mo.

Each treatment combination had at least 20 replications, giving a subtotal of at least 1000 block shear test specimens. In addition, at least 20 test specimens were prepared for the adhesive-type factor for a total of at least 200 specimens for testing in the dry condition, which also serve as control. Thus, a grand total of at least 1200 test specimens were prepared for the study.

Preparation of Block Shear Specimens

A hot press was used to cure the adhesives in accordance with the adhesive manufacturer's recommendations. The target temperature in the bond line was 100°C.

For the solid wood, some block shear specimens were heated at 100°C for 24 h to be compared with unheated specimens.

Table 1. Wood adhesives used in the study and pH^a of the cured adhesive film.

Adhesive identification	Adhesive type	Actual weight ratio of adhesive-to-hardener	Non-volatile content (% w/w)	Cured adhesive film pH
PF-1	PF ^b	n/a ^f	43.0 ^h	12.79 (0.04) ⁱ
PF-2	PF	n/a	45.0	12.76 (0.05)
PF-3	PF	n/a	44.0	12.44 (0.04)
PF-4	PF	n/a	45.0	12.11 (0.05)
PRF	PRF ^c	2.2:1.0 (6.0:1.0) ^g	47.0	10.58 (0.03)
MF-1	MF ^d	100:10	54.0	3.72 (0.04)
MF-2	MF	100:20	51.5	3.60 (0.03)
MUF-1	MUF ^e	100:25	62.9	2.92 (0.07)
MUF-2	MUF	100:30	61.0	2.78 (0.11)

^a Determined in accordance with CSA O112.6-M (1977a) in a previous study (Zhang et al 2011).

^b Phenol-formaldehyde.

^c Phenol-resorcinol-formaldehyde.

^d Melamine-formaldehyde.

^e Melamine-urea-formaldehyde.

^f Not applicable.

^g Weight ratio of adhesive-to-hardener based on solids content.

^h Each value is an average of two replicates.

ⁱ Each value is an average of three replicates, and the value in parenthesis is standard deviation.

Conditioning of Specimens for Dry Test

The specimens were conditioned at 65% RH and 21°C to reach EMC of about 12%. They were stored in these conditions until they were tested.

Long-Term Exposure Treatment of Specimens

The specimens were initially subjected to a vacuum-pressure (VP) treatment as described in CSA O112.10 (2010b). They were placed in an impregnation tank, and a metal screen sheet placed over them and weighted down. Tap water (~20°C) was introduced into the tank to immerse the specimens. A vacuum of 635 mm Hg (85 kPa) was applied for 30 min, followed by a pressure of 550 kPa for 120 min. After impregnation, the pressure was released and excess water was wiped from the specimen surfaces.

Except for the specimens designated for the 0 ET, the rest of the specimens were double sealed in plastic bags, and placed in a chamber maintained at 50°C for different ETs as indicated above. At each designated ET, the specimens were removed from the chamber, and they (including those designated for 0 ET) were weighed and then dried in an oven at 60°C to their original weight. The redried specimens were conditioned at 65% RH and 21°C for about 3 wk to allow them to equilibrate to the desired MC of approximately 12%.

Testing and Evaluation of Wood Failure

Shear test was conducted in a control environment of 65% RH and 20°C. The specimens were tested in shear by compression loading using a shear test device described in ASTM D 905 (2011a). The loading with a continuous motion of the movable head at a rate of 10 mm/min was applied to failure. After testing, the specimens were dried at 105°C for at least 24 h until constant weight was reached, before wood failure assessment and MC measurement. Wood failure was determined using the guidelines described in ASTM D 5266 (2011d). Wood failure was

also defined as “deep wood failure” or “shallow wood failure” depending on the depth of the fracture, which is possibly related to the inherent strength of the wood or the enhanced wood strength caused by the adhesive. The deep wood failure was invariably several to many cells away from the adhesive layer, whereas the shallow wood failure was invariably within the first one or two layers of cells beyond the adhesive layer. In addition, the fracture path was strongly influenced by the grain angle and growth ring structure as observed for the deep wood failure as compared with the shallow wood failure.

The MC of the specimens was determined by the oven-drying method, ie, the weight of the specimens were taken before and after oven-drying. The MC was calculated as the weight difference before and after oven-drying divided by the oven-dry weight.

Scanning Electron Microscopic Examination of Wood-Adhesive Bond

This examination was performed to assess whether there was adhesive penetration into the wood. The bond lines of shear specimens bonded with PRF and MUF-1 were examined.

A thin wood section measuring 5 mm × 10 mm in cross section was cut by a microtome along the grain direction from an unbroken shear specimen, showing the exposed end grain with the bond line. The wood section was placed in a vacuum oven under 25-in. pressure (635 mm Hg) for at least 24 h to remove the moisture. The exposed end grain of the wood section was coated with palladium, and then examined under a Jeol 840A scanning electron microscope (SEM).

Evaluation of Wood Degradation in Bonded Area by Adhesive pH Conditions

The wood adjacent to the bond line is expected to undergo some degradation by hydrolysis under extreme adhesive pH conditions after long-term exposure to high humidity and temperature. The degraded wood or low-molecular-weight sugars were extracted with 1% NaOH

solution. The quantity of extracted wood was used to estimate the extent of wood degradation.

The shear specimens used for this evaluation were those bonded with PF (PF-1), PRF, and MUF (MUF-1) after exposure to 12-mo duration. They had approximately 12% MC after conditioning at 65% RH and 21°C.

Estimation of Adhesive Weight in Bond Line

The adhesive weight in the bond line can be estimated from the adhesive remaining in the broken shear specimen by the following equation:

$$R_{wt} = L \times W \times Sr \times Nv \times (1 - Rsq)$$

where R_{wt} = adhesive weight in a broken shear specimen (g), L = length of specimen along the grain direction (cm), W = width of specimen (cm), Sr = adhesive spread rate of mixed adhesive (g/cm^2), Nv = nonvolatile content of adhesive (%), and Rsq = quantity of cured adhesive squeezed out of the bond line (%), which was estimated from the pressed assembly before trimming.

Sample Preparation for NaOH Extraction

The wood meals for extraction were prepared from the tested shear specimens. The wood meals were taken from approximately 0.5 mm from each of the bond line (some wood meals included glue from portion of the bond line) using a disc saw. The wood meals with included glue were referred to as interface wood meals. Additional wood meals were taken at 7 mm from the bond line, and these were considered as control wood meals.

For each adhesive, about 10 g of wood meal was prepared from a number of tested shear specimens randomly selected.

Extraction Procedure

The extraction procedure used was based on the Technical Association of the Pulp and Paper

Industry (TAPPI) Test Method T-212 (2007a). The procedure is as follows:

1. The wood meals were ground to pass through a 0.5-mm screen in accordance with TAPPI T-257 (2002).
2. Two test samples of 2.0 g (± 0.1 g) were weighed to the nearest 1.0 mg. Each sample was placed in a 250-mL Erlenmeyer flask.
3. A sample for MC determination was also weighed in accordance with TAPPI T-264 (2007b).
4. A 100 mL (± 1 mL) of 1% NaOH solution was added in the Erlenmeyer flask and stirred with a glass rod.
5. The Erlenmeyer flask was covered with a watch glass and placed in a water bath and maintained at 97-100°C for 60 min. The water level in the bath was maintained above that of the mixture in the flask.
6. After 60 min, the wet residue was transferred to a tarred filtering crucible, and washed with 100 mL of hot water.
7. A 25 mL of 10% acetic acid was added into the residue and allowed to soak for 1 min before removal. This step was repeated with a second 25 mL of 10% acetic acid.
8. The residue was washed finally with hot water until acid free.
9. The crucible with the residue was placed in an oven at 105°C ($\pm 3^\circ\text{C}$) and dried to a constant weight, and then cooled in a desiccator for 30 min and weighed.

Data Analysis for the Shear Test Results

Since the sample size for the block shear test was uneven for each test condition, the least square means outlined in the SAS statistical program (1996) was used.

RESULTS AND DISCUSSION

SEM Analysis of Wood-Adhesive Bond

The morphology of the bond line of a bonded specimen is influenced by adhesive spread rate, adhesive solids content, and processing

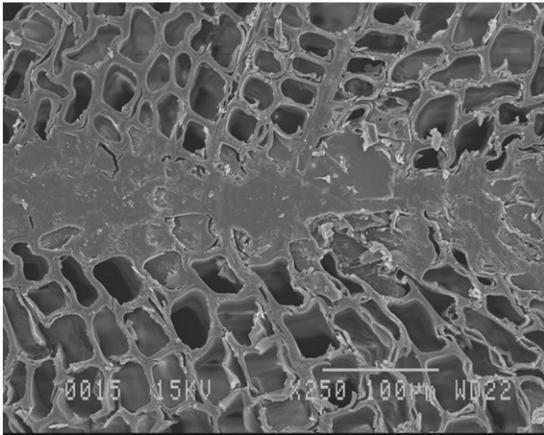


Figure 1. Scanning electron microscope image of bonded Douglas-fir specimen with phenol-resorcinol-formaldehyde adhesive ($\times 250$).

parameters such as wood MC, assembly time, temperature, pressure, and press time. The SEM images of the bond lines of the DF specimens bonded with PRF and MUF are shown in Figs 1 and 2.

Based on the spread rate used, the solids content of the adhesive in the bond line was in the range 0.018-0.022 g/cm². If the adhesive did not penetrate into the wood substrates and remained at the bond line, the thickness of the bond line would be around 140-180 μm with the density of 1.2 g/cm³ for the cured adhesive. Based on

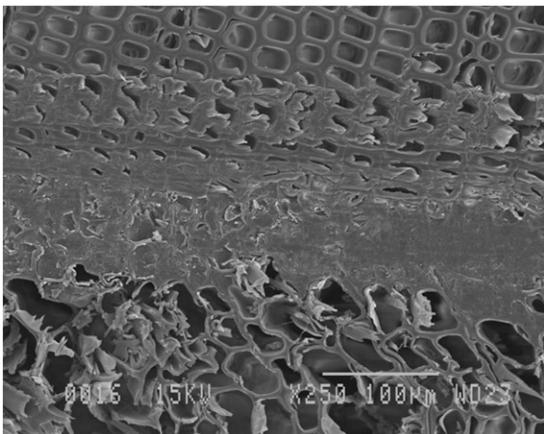


Figure 2. Scanning electron microscope image of bonded Douglas-fir specimen with melamine-urea-formaldehyde-1 adhesive ($\times 250$).

the SEM images, the bond line thickness was less than 100 μm . Thus, the actual bond line thickness was thinner than the theoretical one, which implied that some adhesive had penetrated into the wood substrates. The amount of adhesive squeezed out of the bond line during pressing would obviously also contribute to a thinner bond line. The depth of adhesive penetration into the wood was not determined in this study.

Wood Degradation in Bonded Area by Adhesive pH Conditions

Quantity of adhesive remaining in broken shear specimen. Based on the adhesive spread rate, adhesive nonvolatile content, and amount of adhesive squeezed out of the bond line, the quantity of adhesive remaining in the broken shear specimen was estimated by the equation described in the methodology section. The test results obtained from the above calculations are given in Table 2.

NaOH solubility of bonded area. The results of the 1% NaOH extraction of the broken shear specimens are presented in Table 3. In general, the solubility or quantity of extractable materials increased with increasing ET for the three adhesives. Also, the extraction values observed for the 0 ET were lower compared with those of the dry condition. The difference was probably attributed to the leaching of part of the water-soluble components from the 0 ET shear specimens during the VP treatment.

For the dry and 0 ET, the extraction values were lower for the sample with included glue than that without included glue for all three adhesives.

Table 2. Wood meals for 1% NaOH extraction.

Adhesive ID	Wood meal at the bond line		Wood meal away from the bond line	
	Adhesive (% wt)	Wood (% wt)	Adhesive (% wt)	Wood (% wt)
PF-1	16.7-17.4	82.6-83.3	0.0	100
PRF	14.0-14.7	85.3-86.0	0.0	100
MUF-1	13.7-14.5	85.5-86.3	0.0	100

MUF, melamine-urea-formaldehyde; PF, phenol-formaldehyde; PRF, phenol-resorcinol-formaldehyde.

Table 3. 1% NaOH solubility of wood meals.

Adhesive	Exposure treatment (dry/month)	Wood meal at the bond line (% wt)	Wood meal away from the bond line (% wt) ^a
PF-1	Dry	18.42 (1.79)	25.92 (0.35)
	0	15.20 (2.74)	23.50 (3.44)
	4	18.57 (4.40)	24.71 (0.32)
	8	23.63 (0.26)	23.60 (0.19)
	12	28.46 (0.31)	26.10 (0.03)
PRF	Dry	16.15 (0.03)	22.97 (4.57)
	0	14.58 (0.08)	17.19 (0.12)
	4	19.96 (2.00)	20.09 (0.30)
	8	22.57 (0.03)	23.10 (0.39)
	12	24.81 (0.16)	23.67 (0.45)
MUF-1	Dry	18.72 (1.12)	19.79 (2.58)
	0	16.56 (0.38)	18.86 (0.68)
	4	21.47 (0.09)	19.55 (1.00)
	6	23.27 (0.08)	23.39 (0.58)
	8	29.40 (0.40)	25.25 (0.04)
	12	28.44 (0.54)	26.81 (0.75)

MUF, melamine-urea-formaldehyde; PF, phenol-formaldehyde; PRF, phenol-resorcinol-formaldehyde.

^a Values in parentheses are the standard deviations.

However, with increasing ET, the extraction value of the sample with included glue generally increased faster than that without included glue.

The extraction data for the 0 ET were used as a reference to normalize the extraction data for the other exposure conditions. The normalization of solubility was performed as follows:

$$\text{Normalized NaOH solubility} = 1\% \text{ NaOH solubility} / 1\% \text{ NaOH solubility at 0 ET}$$

The normalized solubility values obtained from the above calculations are shown in Fig 3 as a function of ET. After 12-mo ET, the samples without included glue showed increases in solubility of 42%, 38%, and 11% for the MUF, PRF, and PF, respectively (Table 3). For the samples with included glue, the corresponding solubility increases were 72%, 70%, and 87%.

The above observations indicate that the NaOH solubility after 12-mo ET was much higher for the samples with included glue compared with those without included glue regardless of adhesive type. These results indicate that the adhesives could also be decomposing with increasing ET and/or that the interaction between the adhesive and wood could accelerate the decomposi-

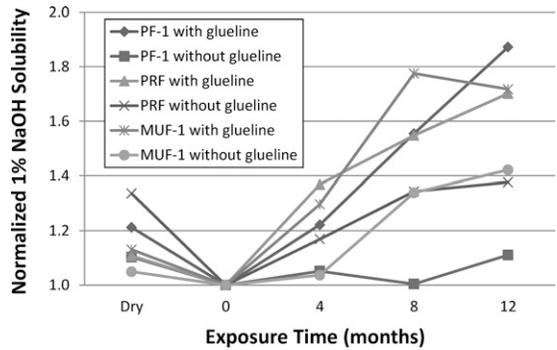


Figure 3. Normalized 1% NaOH solubility of bonded specimens with adhesives (phenol-formaldehyde-1, phenol-resorcinol-formaldehyde, and melamine-urea-formaldehyde-1).

tion of the wood. It is suggested that further studies be conducted in this area to ascertain the actual mechanism involved in the decomposition or solubility process.

Analysis of the Block Shear Strength Test Results

Phenol-based adhesives. High pH levels are used for phenol-based adhesives. The shear strengths of the bonded specimens and those of the solid wood at the dry condition and after

varying ET are shown in Fig 4. The solid wood showed the highest shear strength at the dry condition. However, in general, the PF adhesives appeared to show comparable shear strengths with those of the solid wood after the various ET conditions. This indicates that within the 17-mo ET, the bond quality of the high-pH adhesives still remained good. At the 0 ET, the shear strengths of the bonded specimens all dropped compared with those obtained at the dry condition. However, after 4-mo ET, the shear strengths appeared to increase compared with those of the 0 ET, except for the PRF adhesive. This could be attributed to the continued curing of the PF adhesives (PF-1 to PF-4) after the exposure. It has been indicated that heat exposure could result in post

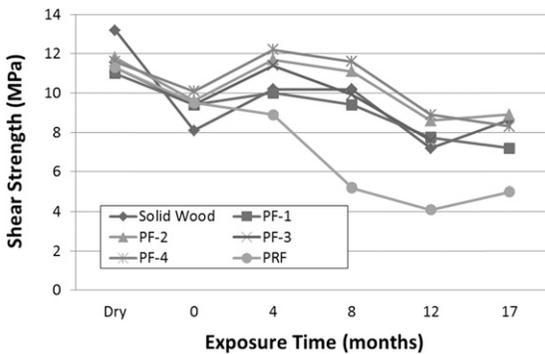


Figure 4. Shear strengths at different exposure times for solid wood (Douglas-fir) and high and intermediate pH adhesives (phenol-formaldehyde-1 [PF-1], PF-2, PF-3, PF-4, and phenol-resorcinol-formaldehyde).

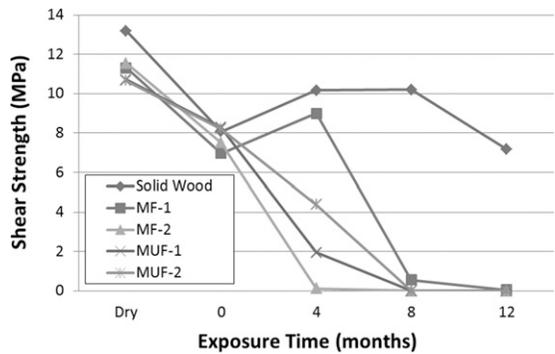


Figure 5. Shear strengths at different exposure times for the solid wood (Douglas-fir) and low-pH adhesives (melamine-formaldehyde-1 [MF-1], MF-2, melamine-urea-formaldehyde-1 [MUF-1], and MUF-2).

cure effect in PF adhesives (Houwink and Salomon 1967). PF usually requires greater heat energy to cure compared with PRF. Further prolonged exposure resulted in a decreasing trend of the shear strength.

The observed decrease in strength for the solid wood was likely due to the weathering effect of the exposure condition on the wood. On the other hand, the strength losses for the bonded specimens suggest that either the wood layer adjacent to the bond line was being affected by the adhesive or that the adhesive itself was also breaking down and this effect was different between the PF and the PRF adhesives. The PRF adhesive appeared to be less durable than the high-pH PF adhesives.

Melamine-based adhesives. Both MF and MUF are normally cured under a low pH value. The shear strengths of the bonded specimens and those of the solid wood at the different conditions are shown in Fig 5. In the dry condition, statistical analysis indicated that the average shear strengths of the bonded specimens were comparable, and that their shear strengths were significantly greater than at the 0 ET. At 0 ET, there were also no significant differences in shear strengths among the bonded specimens and the solid wood.

With longer ET, the shear strengths of the bonded specimens decreased very rapidly. After

8-mo ET, the shear strengths of the MUF adhesives (MUF-1 and MUF-2) and the MF adhesive (MF-2) dropped to zero, and that of the other MF adhesive (MF-1) also dropped to practically zero after 12 mo. The difference in durability between MF-1 and MF-2 was probably due to the difference in the amount of hardener used. These results indicate that the low-pH adhesives were degrading rapidly as the ET was increased.

Linear estimate of the shear strength loss rate during the exposure period. An estimate of the rate of loss in shear strength for the solid wood and the bonded specimens was made by linear regression analysis. The results of the analysis are summarized in Table 4. The loss rate was represented by the slope of the regression line. The solid wood showed the lowest rate of decrease (about -0.05 MPa/month), followed in increasing order, by the PF adhesives (-0.11 to -0.17 MPa/month), PRF adhesive (-0.32 MPa/month), and the MF/MUF adhesives (-0.54 to -1.04 MPa/month). On the average, the rates of strength loss of the MF/MUF and the PRF adhesives were about six times and twice, respectively, faster than the PF adhesives.

After 17-mo ET, the shear strengths of the PF adhesives ranged from about 7.2–8.9 MPa (1044–1291 psi). Considering that the median shear strength requirement of CSA O112.10 (2010b) after one cycle of VPD treatment, which is the same as 0 ET in the present tests,

Table 4. Estimated shear strength loss rate during the exposure period.

Adhesive		pH of cured film	Rate of strength loss ^a (MPa/month)
Code	Type		
PF-1	PF ^b	13.2	-0.158
PF-2	PF	12.8	-0.108
PF-3	PF	12.9	-0.172
PF-4	PF	12.7	-0.167
PRF	PRF ^c	10.8	-0.321
MF-1	MF ^d	3.6	-0.537
MF-2	MF	2.4	-0.937
MUF-1	MUF ^e	2.9	-1.040
MUF-2	MUF	2.8	-1.020
Solid wood			-0.047

^a Represented by the slope of the regression line.

^b Phenol-formaldehyde adhesive.

^c Phenol-resorcinol-formaldehyde adhesive.

^d Melamine-formaldehyde adhesive.

^e Melamine-urea-formaldehyde adhesive.

is only 6.5 MPa (943 psi), the above results are relatively good and acceptable despite subjecting the specimens to an extended period of time. On the other hand, the intermediate pH PRF adhesive yielded a residual strength of only about 5.0 MPa (725 psi) for the same ET.

It would be interesting to extend these tests beyond ET of 17 mo, particularly for the PF adhesives. This would help build up more confidence on the effect of high pH on long-term wood-adhesive bond durability.

In the present tests, the effect of pH of the low-pH adhesives on the strength of the wood is considered inconclusive. It would be interesting to test other low-pH adhesives that are more durable than those tested in this study.

Solid Wood Thermally Treated and Untreated

The shear strength results for the heated and the untreated (unheated) solid wood specimens are shown in Fig 6. Statistical analysis indicated that the thermal treatment significantly reduced the shear strength of the specimens at the dry condition.

After 2-mo ET, the shear strengths decreased significantly, but no significant difference was observed between the untreated and thermally

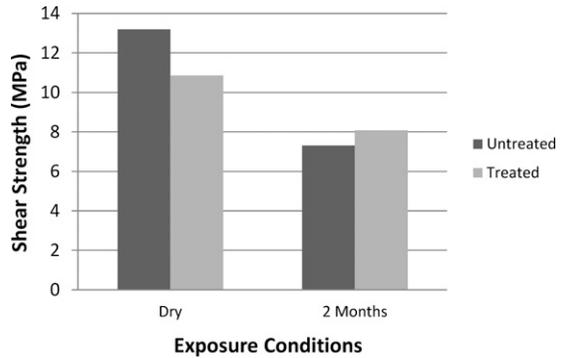


Figure 6. Shear strengths of thermally treated and untreated solid wood specimens.

treated specimens. It is interesting to note that the effect of thermal treatment on the wood shear strength appeared to be minimized after a moderately long ET. This indicates that the thermal treatment could impart some degree of durability to the solid wood. This could be related to the decreased wettability of the thermally treated wood as observed by Casilla et al (1981).

Analysis of the Block Shear Wood Failure Test Results

Phenol-based adhesives. The wood failure results for the five adhesives at the various conditions are shown in Fig 7. Statistical analysis indicated that there were no significant differences in wood failure among all five adhesives at the dry and 0 ET conditions.

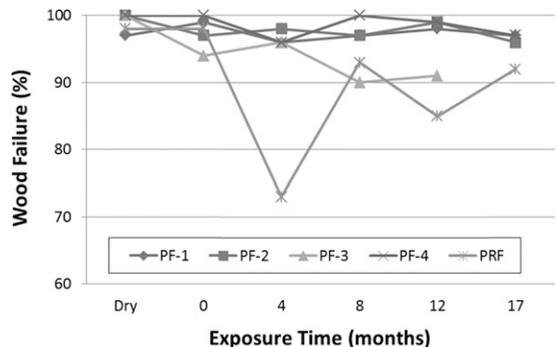


Figure 7. Wood failures at different exposure times for the high and intermediate pH adhesives (phenol-formaldehyde-1 [PF-1], PF-2, PF-3, PF-4, and phenol-resorcinol-formaldehyde).

The wood failures for the PF adhesives remained constant and relatively high (close to 100%) throughout the 17-mo ET, although PF-3 showed lower values at the 8- and 12-mo ET. Considering that the average wood failure requirement of ASTM D 2559 standard (ASTM 2011c) is 75% and that the median wood failure requirement of CSA O112.9 (2010a) and CSA O112.10 (2010b) is 85% after some wet exposure conditioning prior to testing, the above results are relatively good and acceptable. It was observed that the shallow wood failure component of the total wood failure of the PF adhesives was very low (<28%) at all ET, and thus their high shear strengths were probably associated with deep wood failure.

The PRF adhesive did not exhibit the same constant wood failure as that observed above for the PF adhesives, and that, in general, it showed consistently lower deep wood failure component than the PF adhesives. For example, it yielded only about 73% average wood failure after 4-mo ET and 85% after 12-mo ET. Thus, the pH effect observed for the PF adhesives could not be postulated for the PRF adhesive. It is more probable, with its large decrease in shear strength coupled with its inconsistent and relatively low wood failures, that the PRF adhesive itself was exhibiting some degradation.

Melamine-based adhesives. The wood failure results for the four low-pH adhesives at the various conditions are shown in Fig 8. Statistical

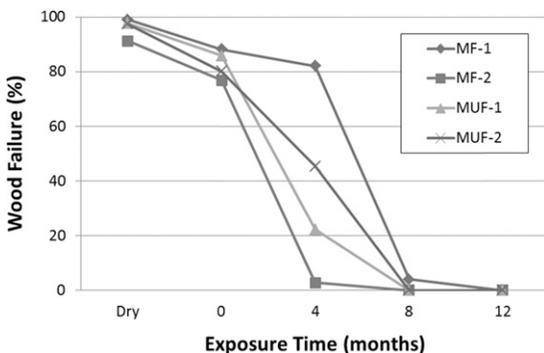


Figure 8. Wood failures at different exposure times for the low-pH adhesives (melamine-formaldehyde-1 [MF-1], MF-2, melamine-urea-formaldehyde-1 [MUF-1], and MUF-2).

analysis indicated that there were no significant differences in wood failure among the four adhesives at the dry condition.

At 0 ET, there were small observed differences in wood failure among the adhesives, but after 4-mo ET the differences became much larger. At the later ET, MF-1 showed the highest average wood failure of about 82% followed, in decreasing order, by MUF-2 (45%), MUF-1 (22%), and MF-2 (3%).

After 8-mo ET, all four adhesives lost their bonding ability as indicated by their very low average wood failures ranging only from 0 to 4%. After 12-mo ET, no wood failure was observed for all four adhesives, ie, all the specimens delaminated before or after drying.

These results indicate that the low-pH adhesives (MF and MUF) were degrading during the long-term exposure period. Thus, their effect on the wood in terms of their acidity is inconclusive from this shear testing.

Correlation between Cured Adhesive Film pH and Block Shear Properties of Bonded Specimens

Efforts were made to examine whether there is correlation between the pH of the cured adhesive film and the block shear test results of the bonded specimens. In this connection, the shear strength, total wood failure, and its components (shallow wood failure and deep wood failure)

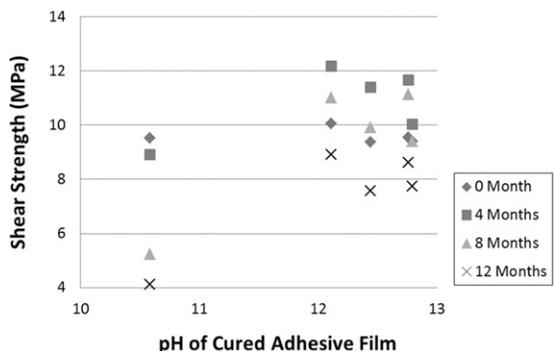


Figure 9. Block shear strength as a function of cured film pH of high and intermediate pH adhesives.

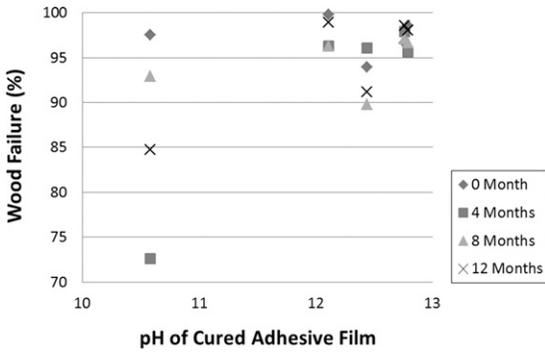


Figure 10. Total wood failure as a function of cured film pH of high and intermediate pH adhesives.

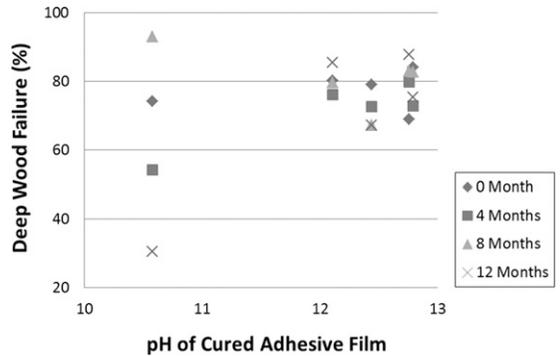


Figure 12. Deep wood failure as a function of cured film pH of high- and intermediate-pH adhesives.

were plotted against cured adhesive film pH. The plots for the high and intermediate pH adhesives are shown in Figs 9-12. In all of the four plots, there appeared to be no apparent correlation between the pH and shear strength or wood failure.

Similar plots for the low-pH adhesives also did not show apparent correlations between cured film pH and shear strength, total wood failure, shallow wood failure, or deep wood failure.

It is suggested that further studies be conducted along this area, perhaps including adhesives with cured film pH close to neutral and pH 13 and above.

CONCLUSIONS

The 1% NaOH solubility test of small-layer samples taken close to the bond line of block

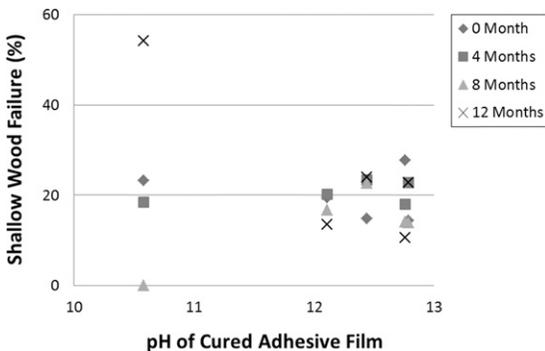


Figure 11. Shallow wood failure as a function of cured film pH of high- and intermediate-pH adhesives.

shear specimens bonded with PF, PRF, and MUF indicates that aside from wood degradation there is also the potential of adhesive decomposition induced by adhesive chemistry and exposure conditions.

Among the three groups of adhesives studied, the high-pH PF adhesives have the best durability performance followed, in decreasing order, by the intermediate pH PRF adhesive and the low-pH MF/MUF adhesives, when exposed to wet and moderately high temperature conditions for a period of up to 17 mo.

The PF adhesives exhibit the lowest average rate of decrease in shear strength, followed in increasing order, by the PRF adhesive and the MF/MUF adhesives, during the exposure period. The rate of strength loss of the MF/MUF is about six times, and that of the PRF two times, faster than that of the PF. All the PF adhesives pass the shear strength requirement of the CSA O112.10 standard and the wood failure requirements of ASTM D 2559, CSA O112.9, and CSA O112.10 standards after the 17-mo exposure period.

The above observation is not apparent for the PRF adhesive. It is more probable, with its large decrease in shear strength coupled with its inconsistent and relatively low wood failures, that the adhesive itself is exhibiting greater degradation. For the MF/MUF adhesives, the effect of pH is considered inconclusive since they degrade completely after 12 mo or even shorter duration of exposure.

REFERENCES

- American Society for Testing and Materials (ASTM) (2011a) Standard test method for strength properties of adhesive bonds in shear by compression loading. D 905-08. American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 15.06, West Conshohocken, PA.
- American Society for Testing and Materials (ASTM) (2011b) (Reapproved 2008). Standard test method for hydrogen ion concentration of dry adhesive films. D 1583-01. American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 15.06, West Conshohocken, PA.
- American Society for Testing and Materials (ASTM) (2011c) Standard specification for adhesives for bonded structural wood products for use under exterior exposure conditions. D 2559-10a. American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 15.06, West Conshohocken, PA.
- American Society for Testing and Materials (ASTM) (2011d) (Reapproved 2005). Standard practice for estimating the percentage of wood failure in adhesive bonded joints. D5266. American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 15.06, West Conshohocken, PA.
- Blomquist RF (1949) (Reaffirmed 1962) Effect of alkalinity of phenol- and resorcinol- resin glues on durability of joints in plywood. Report No. R1748. USDA Forest Service, Forest Products Laboratory, Washington, DC.
- Canadian Standards Association (CSA) (1977a) Phenol and phenol-resorcinol resin adhesives for wood (high-temperature curing). O112.6-M. Canadian Standards Association, Rexdale, ON.
- Canadian Standards Association (CSA) (1977b) Resorcinol and phenol-resorcinol resin adhesives for wood (room- and intermediate-temperature curing). O112.7-M. Canadian Standards Association, Rexdale, ON.
- Canadian Standards Association (CSA) (2010a) Evaluation of adhesives for structural wood products (exterior exposure). O112.9-04. Canadian Standards Association, Mississauga, ON.
- Canadian Standards Association (CSA) (2010b) Evaluation of adhesives for structural wood products (limited moisture exposure). O112.10-08. Canadian Standards Association, 2010. Mississauga, ON.
- Casilla RC, Chow S, Steiner PR (1981) An immersion technique for studying wood wettability. *Wood Sci Technol* 15:31-43.
- Gillespie RH, River BH (1975) Durability of adhesives in plywood: Dry-heat effects by rate-process analysis. *Forest Prod J* 25(7):26-32.
- Green DW, Evans JW, Hatfield CA, Byrd PJ (2005) Durability of structural lumber products after exposure at 82°C and 80% relative humidity. Forest Products Laboratory Res. Paper FPL-RP-631. Forest Service USDA Forest Products Laboratory, Washington, DC.
- Haygreen JG, Bowyer JL (2003) Forest products and wood science: An introduction. 4th ed. Iowa State University Press, Iowa City, IA.
- Houwink R, Salomon G (eds) (1967) Adhesion and adhesives. 2nd ed, Vol. 2, Applications. Elsevier Publishing Co., Amsterdam, London, New York. 590 pp.
- Huang Z, Cooper P, Wang X, Wang XM, Zhang Y, Casilla R (2010) Effects of conditioning exposure on the pH distribution near adhesive-wood bond lines. *Wood Fiber Sci* 42(2):219-228.
- International Organization for Standardization (ISO)/TC 165 (2009) Timber structures: Bond performance of adhesives. Part 1: Basic requirements. DIS 20152.1. International Organization for Standardization, Geneva, Switzerland.
- Kline GM, Reinhart FW, Rinker RC, De Lollis NJ (1947) Effect of catalysts and pH on strength of resin-bonded plywood. *Modern Plastics* 7:123-128, 196-202.
- Raknes AE (1976) Long-term durability of glues for load-bearing timber constructions: Results after 10 years of exposure. *Norsk Skogindustri* 30(6):168-171, 175-176.
- Raknes AE (1981) Long-term durability of structural adhesives for wood: Results after 15 years' exposure. *Norsk Skogindustri* 35(10):260, 270-273.
- Santos CB, Pimenta AS, Vital BR, de A. Barbosa LC (2003) Effect of pH variation and synthesis temperature on the performance of thermosetting adhesive formulations based on demethylated wood creosote-formaldehyde. *R. Arvore, Vicosa-MG* 27(4):551-559.
- SAS Institute (1996) Statistical analysis system. SAS Institute, Inc., Cary, NC.
- Stamm AJ (1964) Wood and cellulose science. The Ronald Press Co., New York, NY.
- Technical Association of the Pulp and Paper Industry (TAPPI) (2002) Sampling and preparing wood for analysis. T-257 cm-02. Technical Association of the Pulp and Paper Industry, Technology Parkway, South Norcross, GA.
- Technical Association of the Pulp and Paper Industry (TAPPI) (2007a) One percent sodium hydroxide solubility of wood and pulp. T-212 om-07. Technical Association of the Pulp and Paper Industry, Technology Parkway, South Norcross, GA.
- Technical Association of the Pulp and Paper Industry (TAPPI) (2007b) Technical Association of the Pulp and Paper Industry. Preparation of wood for chemical analysis. T-264 cm-07. Technical Association of the Pulp and Paper Industry, Technology Parkway, South Norcross, GA.
- Wang X, Huang Z, Cooper P, Wang XM, Zhang Y, Casilla R (2010) The ability of wood to buffer highly acidic and alkaline adhesives. *Wood Fiber Sci* 42(3):398-405.
- Wang X, Huang Z, Cooper P, Wang XM, Zhang Y, Casilla R (2013) Effects of pH on lap-shear strength for aspen veneer. *Wood Fiber Sci* 45(3):294-302.
- Wangaard FF (1946) Summary of information on the durability of woodworking glues. Forest Products Laboratory Report No. 1530 (Revised in 1956 as Durability of water-resistant woodworking glues). USDA Forest Products Laboratory, Washington, DC.

- Zhang Y, Wang XM, Casilla R, Cooper P, Huang Z, Wang X (2010) Impact of curing condition on pH and alkalinity/acidity of structural wood adhesives. *J Appl Polym Sci* 117:2888-2898.
- Zhang Y, Wang XM, Casilla R, Cooper P, Huang Z, Wang X (2011) Evaluation of block shear properties of selected extreme-pH structural adhesives by short-term exposure test. *J Appl Polym Sci* 120:657-665.
- Zimmerman T, Richter K, Bordeanu N, Sell J (2007) Arrangement of cell-wall constituents in chemically treated Norway spruce tracheids. *Wood Fiber Sci* 39(2):221-231.