

# THE EFFECT OF WOOD EXTRACTIVE CONTENT ON GLUE ADHESION AND SURFACE WETTABILITY OF WOOD

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## ABSTRACT

The effect of wood extractive content on glue adhesion and surface wettability was evaluated. Specimens of pine heartwood (*Pinus sylvestris*), stored at different times after surface planing, were assembled with a water-resistant polyvinyl acetate glue. The test material was classified according to its content of lipophilic extractives by chemical analyses. Glue adhesion parameters were assessed using two different test methods, a standard ASTM shear strength test and a nonstandard fracture test. Surface wettability was evaluated by contact angle measurements in parallel experiments. The results showed that, when the strength of the bonds was determined, the percentage adhesion failure increased with increasing extractive content for specimens exposed to water boiling test; but no such correlation was found in tests without water boiling. The correlation between glue bond strength and extractive content was poor. Surface storage time had no significant effect on the glue adhesion parameters. Surface wettability measurements revealed a complex relationship between extractive content and surface storage time.

**Keywords:** Adhesion, extractives, glue, softwood, wettability, wood.

## INTRODUCTION

It is commonly believed that wood adhesion problems, whether they relate to paint or glue adhesion, are likely to be more frequent in the case of resinous and stored wood surfaces than with low-resinous and freshly cut surfaces. Directly after cutting, any wood surface undergoes an inactivation process in which the wood extractives migrate to the surface forming a so-called "weak boundary layer," defined by Good (1972) as a layer of thickness greater than typical atomic dimensions, with a mechanical strength considerably less than that of the bulk substrate. A consequence of this is that a weak boundary layer may possibly prevent optimal interaction between glue or paint and the lignocellulosic substrate (Stehr 1999). The time-dependence of this in-

activation process is normally evaluated in terms of surface wettability by contact angle measurements and has been repeatedly described in the literature (Back 1991; Nussbaum 1999). A hypothesis is that the more extractives the wood contains and the longer the time that passes after cutting, the more complete is the developed weak boundary layer and the more unfavorable is the cut surface from an adhesion point of view. Although wettability measurements may be appropriate to follow the initial formation of a resinous weak boundary layer, such measurements may give information only about the hydrophobic/hydrophilic character of the outer molecular layers, and they are thus not necessarily informative regarding the weak boundary layer thickness. The effect of surface storage on

glue-bond strength has earlier been indicated in tensile strength tests with Douglas-fir glued with casein, where the strength was reduced at storage times longer than 2 months (Stumbo 1964). A linear relationship between surface wettability and glue-bond strength for various tropical woods glued with a urea formaldehyde resin and tested in shear was reported by Chen (1970), but no such correlation was obtained with a resorcinol formaldehyde resin.

If adhesion problems are related to wood extractive content, one might expect that adhesion failure would be more pronounced above a certain extractive content level. The most appropriate way to establish such an extractive content threshold value would be by comparing the wood extractive content with paint adhesion or glue-bond strength. Commonly used methods for evaluating paint adhesion to wood include peeling, pull-off, and shear tests (Ahola 1995; Boxall 1984; Holloway and Walker 1964; Kleive 1986; Williams et al. 1987). Corresponding methods for adhesively bonded joints normally include shear and tensile tests (Strickler 1968; Okkonen and River 1989; Stanger and Blomquist 1965).

In alternative methods based on fracture toughness tests, paint adhesion and glue-bond strength have been evaluated with double-cantilever-beam (DCB) specimens. An apparent advantage of the design of the DCB specimen for adhesion tests seems to be that initial crack formation can be directed to the paint/wood or glue/wood interphase by a notch. Fracture tests with DCB specimens (Mode I) have been used successfully for evaluation of wood adhesive joints. The effects of factors such as bondline thickness, wood anisotropy, cure time, surface roughness, and surface aging on adhesive joint fracture energy were investigated on phenol-resorcinol-bonded hard maple in studies with tapered DCB specimens by Ebewele et al. (1979, 1980, 1986). Storage of sanded surfaces for 3 to 4 weeks prior to bonding decreased the glue-bond strength compared to that achieved with unstored surfaces, although the difference was insignificant at the lowest degree of roughness (4  $\mu\text{m}$ ).

Fracture testing of wood adhesive joints has also been performed with composite contoured DCB specimens (River et al. 1989; Scott et al. 1992; Davalos et al. 1996). In a study where uniform DCB specimens of western red cedar were exposed to accelerated weathering for 0–4 weeks, paint adhesion was evaluated successfully with a coefficient of variation of 10% as compared with 15% for parallel shear block tests (Knaebe and Williams 1993). With a more close control of the grain angle and with the crack propagation monitored by computer, a coefficient of variation of less than 5% was obtained. A comparison of a block-shear strength test and a “tensile-splitting” test (a test with specimens resembling DCB) was equally effective in ranking a few adhesives after severe degradation treatments (Strickler 1968).

The aim of the present investigation has been to compare glue adhesion parameters such as glue-bond strength, glue adhesion failure, and wood surface wettability with wood extractive content. Tests were performed with two different glue-bond strength methods; a nonstandard fracture test with uniform DCB specimens and a standard shear strength test.

## EXPERIMENTAL

### *Wood material*

A package of 80 radially sawn planks of Scots pine (*Pinus silvestris*), each 63(tang.)  $\times$  100(rad.)  $\times$  4500(long.) mm in size were taken from the regular production of a large Swedish sawmill (Iggesund Timber) in August 1999. The planks were predominately taken from butt logs, but some middle logs were also included. The time between felling and sawing was not more than one month. Kiln-drying of the package was started within 24 h from the sawing and lasted for 195 h. The drying schedule was performed with an initial heating phase with saturated steam at a maximum dry-bulb temperature of 80°C. The final moisture content was 11%. The package arrived at its final destination within 12 days after the kiln-drying.

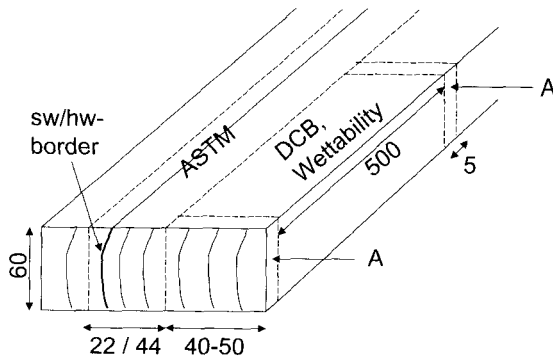


FIG. 1. Sketch showing sampling from a plank (only the first 0.5 m of the plank is shown). A = sample to extractive content analysis; sw/hw = sapwood/heartwood. All dimensions in mm.

Using a newly developed nondestructive technique based on near infrared spectroscopy (NIR) for the fast estimation of wood extractive content (Rosenqvist and Karlsson 1999), an approximate grading with respect to the main lipophilic extractive components in the heartwood at the butt end and the top end of each plank was made. Based on this grading, 20 planks with at least a 60-mm zone of heartwood and representing a broad range of total extractive content, were selected and placed in a cold storage room at  $-20^{\circ}\text{C}$  within a week from the arrival, until later investigations. All the selected planks were of high quality with no visible signs of blue stain or any other damage.

#### Glue adhesion tests

**Double cantilever beam (DCB).**—From each of the 20 selected planks, a 1.6-m length of heartwood with a radial width of 40–50 mm was cut from the plank butt end. This length was cut into three 0.5-m sections (see Fig. 1) from which coarse specimens,  $11.5 \times 10 \times 500$  mm in size, with strictly radial top surfaces were prepared. The coarse specimens were kept in plastics bags at  $-20^{\circ}\text{C}$  until the final specimen preparation when they were conditioned to the testing climate of  $21^{\circ}\text{C}$ , 50% RH for 2–3 days and 1.5 mm was cut off the coarse thickness to give a cross-section di-

mension of  $10.0 \times 10.0$  mm using a smoothing planer with a new, sharp cutter (Martin; Tersa T43 cutter; 9 m/min feed speed). The planed 500-mm lengths were cut into defect-free, straight-grained 115-mm specimens without knots and resin pockets.

The specimens that had been stored at  $21^{\circ}\text{C}$ , 50% RH for 0.5 h, 24 h, and 14 days after the planing, were glued in order to evaluate the surface inactivation process described in the Introduction. From each of the first two original 0.5-m sections, i.e., 0–0.5 m and 0.5–1.0 m, 6 glued specimen replicates were prepared for each storage time. In a few cases, where not enough defect-free specimens were available, specimens were instead taken from the third 0.5 m section (1.0–1.5 m). Glued specimens were marked so that the original plank number, 0.5 m section and storage time could be identified. Altogether 720 DCB specimens were prepared.

For final specimen preparation, two  $10.0 \times 10.0 \times 115$ -mm specimens (mates), randomly selected from the same original 0.5-m section, were assembled with a commercial water-resistant polyvinyl acetate (PVAc) glue with hardener (class D4 according to EN 204-1991). This glue type was chosen since it is extensively used in exterior applications such as window frames in Scandinavia. Glue was applied with a spatula on half the length of the radial top surface of one of the mates in an amount of  $150 \text{ g/m}^2$  (see Fig. 2). In order to obtain a distinct separation line between glued and non-glued zones, a 0.08-mm-thin Teflon tape was wound around one of the mates. A pressure of 0.08 MPa, which is just below the lowest recommended glue pressure, was applied for 15 min in a laboratory bench-scale press with a press area of  $115 \times 54$  mm. The relatively long notch (57.5 mm) in relation to the square cross section dimension is a standard geometry in uniform DCB tests (Hedner 1990).

In order to evaluate the effect of water exposure on glue adhesion, half the prepared specimens from each 0.5-m section and each storage time were treated in accordance with

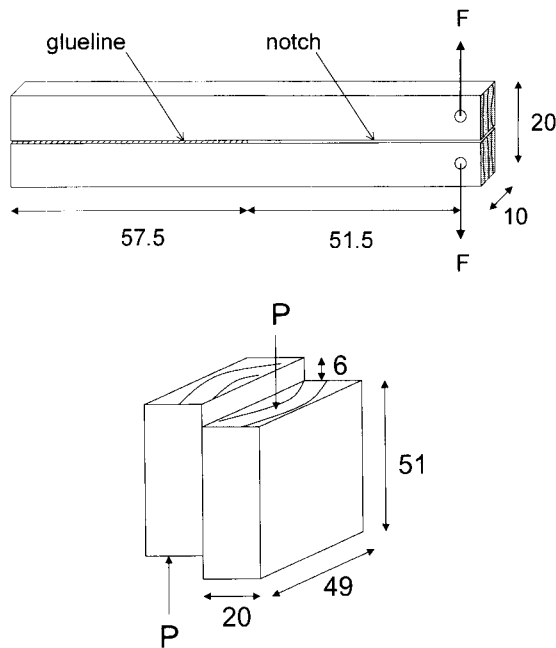


FIG. 2. (top) Uniform double cantilever beam (DCB) specimen used in fracture tests, and (below) ASTM specimen used in shear strength tests. All dimensions in mm.

a standard for evaluation of nonstructural wood adhesives (EN 204 1991). The treatment included 6 h immersion in boiling water followed by 2 h in cold water, after which the specimens were stored for 7 days in the testing climate before strength testing.

Strength testing was performed in a tensile testing machine (Alwetron TCT50) at a rate of traverse of 50 mm/min until breakage. Specimens were hinged in the fixture with metal pins inserted in 2.5-mm holes drilled in the non-glued specimen ends 6 mm from the end-grain. The maximum tensile force at failure was recorded. Data were sampled at 12-ms intervals.

The so-called adhesion failure, or more accurately *apparent* adhesion failure, defined as the total area of failure in the interface between glue and wood or in the glue line itself, was determined on one of the two mates of each strength-tested specimen. The adhesion failure area was colored by hand under a magnifier with a thin black ink marker, and com-

TABLE 1. ASTM specimen test groups.

Group	Storage time	Water exposure test
A	0.5 hour	no
B	0.5 hour	yes
C	24 hours	yes
D	14 days	no
E	14 days	yes

putational scanning and image analysis (ImageTool ver. 2.0) were then applied to calculate the adhesion failure percentage. The discrimination between black and non-black areas was distinct. The resolution of the image analysis was  $0.1 \times 0.1$  mm.

The density of the specimens was calculated using volumes and weights at the test climate corresponding to 9.5% moisture content.

**Block-shear test according to ASTM D 905.**—From 19 of the 20 selected planks, and immediately adjacent to the lengths cut for the DCB specimen, one or two 1.6-m lengths with a radial width of 22 mm were cut. At least 12 mm of the width was heartwood. The lengths were cut into five 350-mm sections with tangential top surfaces. The sections were numbered 1–5 starting from the plank butt end, and they were then put into plastic bags and stored at  $-20^{\circ}\text{C}$  until the final specimen preparation. After conditioning for three days at  $21^{\circ}\text{C}$ , 50% RH, 2 mm was cut off the section width on the pith side using the same planer conditions as for the DCB specimen preparation. Defect-free final specimen mates, each  $20(\text{rad.}) \times 49(\text{tang.}) \times 57(\text{long.})$  mm in size, were cut from each 350-mm section. As in the case with the DCB specimens, gluing was performed on specimens that had been stored at  $21^{\circ}\text{C}$ , 50% RH for 0.5 h, 24 h, and 14 days after the planing. A water-exposure test was also included (see below). Altogether five groups of assembled specimens designated A–E were prepared (see Table 1).

Because of the limited amount of test material available from each plank, only three specimen replicates (i.e., six mates), taken from different 350 mm sections according to the schematic description shown in Fig. 3,

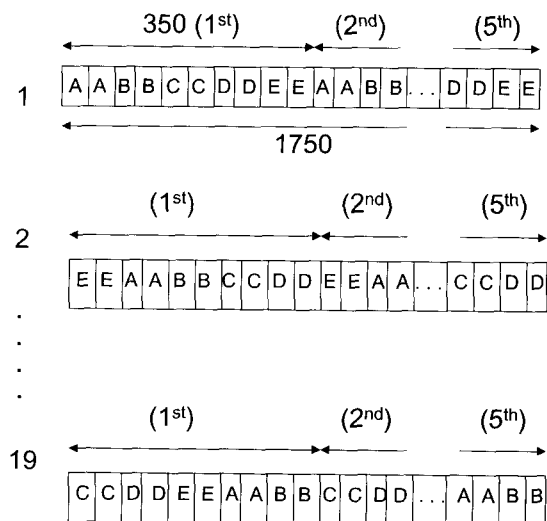


FIG. 3. Schematic description of selection of ASTM specimens for different test groups (A–E) from five 350-mm sections of 19 planks.

were prepared for each group A–E. In several cases where four or more 350-mm sections numbered 1–3 were available from the same plank, specimens were preferably taken from these sections instead of from the sections numbered 4–5, in order to reduce the variability of wood properties in the longitudinal direction.

The specimens were glued with the same PVAc glue ( $150 \text{ g/m}^2$ ) and press equipment as used in the DCB specimen preparation. The glue pressure, which was applied for 15 min, was 0.16 MPa. Assembled surfaces were always tangential pith-sides. Glued specimens were marked so that the original plank number, 350-mm section, and storage time could be identified. Finally, joint assemblies, with an overlapping area of  $45 \times 49 \text{ mm}$ , were prepared according to ASTM D 905 (1994) by removing 6 mm in the longitudinal direction from each specimen end by making a sawcut just through the glue line (see Fig. 2). A total of 285 ASTM specimen were prepared.

Water-exposure treatment prior to strength testing carried out according to a slightly modified standard boiling test described in ASTM D 3110 (1995). The treatment included 6 h

immersion in boiling water followed by drying for 20 h at  $63^\circ\text{C}$ , immersion again in boiling water for 4 h and thereafter cooling for 1 h in water at  $20^\circ\text{C}$ , after which the specimens were stored for 7 days in the test climate before strength testing.

Glue-bond strength was evaluated with a standard shear test under compression loading at a rate of 5 mm/min, and the maximum load was recorded. The same testing machine was used as for the DCB tests. Adhesion failure and wood density were determined as for the DCB specimens.

#### Wettability measurements

From each of the first two 0.5-m sections of each plank, three coarse specimens 500 mm in length, prepared in the same way as the DCB specimens, were conditioned for 2–3 days in the test climate of  $21^\circ\text{C}$ , 50% RH and thereafter planed to a thickness of 6.2 mm with a radial top surface. The lengths were finally cut into defect-free specimens  $6.2(\text{tang.}) \times 10(\text{rad.}) \times 80(\text{long.}) \text{ mm}$  in size. The wettability of the radial heartwood surfaces was evaluated by contact angle measurements, using an automatic contact angle tester (Fibro DAT 1122). Droplets ( $4 \mu\text{l}$ ) of pure chromatographic water were applied at 4 different positions along the specimen middle line, regardless of whether these places were earlywood or latewood. Measurements were repeated on three replicates, with one replicate from each coarse specimen, 0.5 h, 24 h and 14 days after planing. New specimens were used each time and each measurement took 30 s. A contact angle value expressed as the “constant wetting rate angle (cwra)” was evaluated according to Nussbaum (1999). The cwra represents the value when the change in contact angle ( $\theta$ ) per unit time becomes constant, i.e., when  $d\theta/dt = \text{constant}$ . Mean values were calculated from 12 cwra values (4 measurements/replicate).

#### Extractive content analysis

As the same time as the 1.6 m lengths were cut into three 0.5-m sections used for DCB

TABLE 2. *Lipophilic extractive content composition in mg/g dry wood. The four samples taken 0 m, 0.5 m, 1.0 m and 1.5 m from a plank butt end are denoted -1, -2, -3 and -4 respectively in the table. Limits of detection: Fatty acids, resin acids, ox. resin acids, sterols: <0.1 mg/g. Triglycerides, steryl esters: approx. 0.3–0.5 mg/g. n d = not detected.*

Plank no	Free fatty acids	Triglycerides	Resin acids	Oxidized resin acids	Sterols	Steryl esters	Total
1-1	9.2	0.4	51.7	3.6	0.15	1.1	66.1
1-2	7.2	0.4	37.6	1.8	0.15	1.1	48.2
1-3	7.5	0.6	30.9	1.4	0.15	1.3	41.8
1-4	6.6	0.4	21.2	0.9	0.14	1.3	30.6
2-1	8.8	n d	16.7	1.1	0.13	1.2	27.9
2-2	7.4	n d	9.5	0.8	0.12	1.4	19.1
2-3	6.7	n d	10.2	0.7	0.12	1.3	19.0
2-4	7.5	n d	9.5	0.7	0.13	1.5	19.4
3-1	9.9	0.4	29.2	1.4	0.14	1.0	42.0
3-2	8.4	0.4	21.5	1.0	0.13	1.0	32.3
3-3	8.2	0.3	19.3	0.9	0.13	1.0	29.8
3-4	7.9	0.6	15.1	0.9	0.13	1.1	25.7
4-1	4.0	n d	5.3	0.7	0.09	0.7	10.8
4-2	7.1	0.6	11.7	1.3	0.13	1.1	21.8
4-3	7.8	0.5	16.6	1.5	0.14	1.0	27.5
4-4	6.5	0.5	10.0	0.7	0.12	1.1	18.9
5-1	11.7	0.5	66.6	2.6	0.12	1.1	82.6
5-2	10.1	0.4	62.2	2.4	0.12	1.0	76.3
5-3	10.2	0.7	49.0	2.9	0.11	1.1	64.0
5-4	8.7	0.5	35.5	2.3	0.13	1.0	48.2
6-1	3.3	0.5	4.1	0.6	0.09	0.8	9.3
6-2	4.9	n d	5.7	0.6	0.11	1.2	12.5
6-3	4.9	n d	14.0	1.3	0.12	1.1	21.4
6-4	4.9	0.4	13.1	1.2	0.13	1.2	20.9
7-1	12.8	0.7	83.0	3.4	0.13	0.9	101.0
7-2	10.1	0.5	56.0	2.8	0.14	0.9	70.4
7-3	10.4	0.5	51.5	2.8	0.15	1.1	66.3
7-4	8.7	0.3	43.7	3.0	0.16	1.1	56.9
8-1	10.6	0.3	109	4.3	0.15	1.1	125.2
8-2	9.7	0.5	95.5	9.6	0.14	1.2	116.7
8-3	9.7	0.5	113	4.1	0.14	1.1	128.1
8-4	8.7	0.5	96.2	3.6	0.16	1.1	110.3
9-1	8.8	0.5	38.2	1.6	0.11	1.1	50.3
9-2	7.4	0.4	26.2	1.3	0.11	1.1	36.4
9-3	7.8	0.5	21.0	1.0	0.12	1.1	31.6
9-4	7.7	0.5	20.4	1.1	0.12	1.1	30.8
10-1	8.6	n d	11.7	0.9	0.11	1.1	22.4
10-2	8.1	0.3	7.9	0.6	0.12	1.2	18.4
10-3	6.7	n d	7.0	0.7	0.10	1.1	15.7
10-4	6.5	0.5	4.9	0.5	0.10	1.2	13.7
11-1	8.4	0.5	45.1	2.3	0.16	1.6	58.1
11-2	7.3	0.7	20.9	1.6	0.06	0.7	31.3
11-3	6.2	0.4	13.1	1.1	0.12	1.2	22.1
11-4	6.0	0.5	12.9	1.1	0.11	1.1	21.6
12-1	9.8	0.6	24.8	1.6	0.19	1.1	38.1
12-2	8.9	0.5	17.8	1.4	0.12	1.0	29.8
12-3	8.6	0.3	13.0	0.8	0.12	1.0	23.9
12-4	8.2	0.3	10.7	0.8	0.12	1.2	21.3
13-1	5.9	0.4	6.5	0.7	0.09	0.9	14.5
13-2	5.7	0.4	7.0	0.6	0.09	0.8	14.7

TABLE 2. *Continued.*

Plank no	Free fatty acids	Triglycerides	Resin acids	Oxidized resin acids	Sterols	Steryl esters	Total
13-3	5.6	0.3	6.0	0.7	0.09	0.9	13.5
13-4	5.8	n d	6.1	0.6	0.10	1.0	13.5
14-1	5.0	0.5	15.7	0.8	0.13	0.9	23.1
14-2	3.7	n d	5.6	0.4	0.11	0.8	10.7
14-3	3.2	n d	5.7	0.4	0.11	1.0	10.4
14-4	3.1	0.4	4.9	0.4	0.10	1.0	9.8
15-1	11.6	0.3	40.3	1.9	0.15	1.4	55.6
15-2	10.0	0.4	22.1	1.0	0.13	1.2	34.9
15-3	9.9	n d	23.4	1.2	0.13	1.4	36.1
15-4	10.8	0.4	19.5	1.0	0.14	1.5	33.3
16-1	16.1	0.4	112	15.1	0.16	0.9	144.4
16-2	16.0	0.6	105	10.0	0.20	1.0	133.2
16-3	12.0	0.7	67.6	4.9	0.15	0.9	86.3
16-4	11.3	0.5	67.9	3.3	0.16	1.0	84.3
17-1	10.3	0.2	98.1	4.0	0.17	1.2	113.8
17-2	8.9	0.5	84.2	4.4	0.16	1.2	99.4
17-3	7.6	0.2	74.3	3.0	0.14	0.9	86.2
17-4	8.9	0.4	84.8	2.5	0.14	1.0	97.7
18-1	5.1	0.5	14.9	1.7	0.17	1.0	23.4
18-2	4.9	n d	16.6	1.1	0.14	1.1	23.9
18-3	4.7	0.3	13.0	1.0	0.14	1.1	20.3
18-4	2.5	0.4	8.0	0.6	0.20	1.1	12.7
19-1	12.1	0.4	65.9	3.6	0.17	1.1	83.2
19-2	10.4	n d	59.3	2.5	0.16	1.0	73.3
19-3	10.0	n d	52.3	4.2	0.16	1.1	67.8
19-4	9.6	n d	43.9	2.6	0.15	1.1	57.4
20-1	9.4	n d	74.1	2.9	0.11	1.0	87.5
20-2	9.3	0.4	64.5	2.5	0.10	1.0	77.8
20-3	8.3	n d	40.2	1.7	0.10	1.1	51.4
20-4	8.3	0.3	32.3	1.6	0.10	1.1	43.8

specimen preparation, a 5–6 mm-thick (40–50) × 60-mm cross section slice, free from knots and resin pockets, were cut at 0, 0.5, 1.0 and 1.5 m from the butt end of each length. The slices were labeled and immediately put into plastic bags and stored at –25°C until further analysis.

The extractive content analysis of lipophilic compounds was performed by the Laboratory for Forest Products Chemistry at Åbo Akademi, Finland, in accordance with their elaborate methods (Ekman and Holmbom 1989; Örså and Holmbom 1994). The following steps were included in the analysis procedure: Wood slices were dried and ground in a Wiley mill to a homogeneous meal. Portions of 300 mg were extracted with ethanol under ultrasonic agitation for 2 min. After filtration and

dilution to an exact volume, an internal standard solution was added to 1–2 ml aliquots, which were then evaporated to dryness in a nitrogen atmosphere. Compounds included in the internal standard were heneicosanoic acid, betulin, 1,3-dipalmytol-2-oleyl-glycerol and cholesteryl heptadecanoate. The residues were silylated by the addition of (bis-(trimethylsilyl))-trifluoroacetamide and trimethylchlorosilane and heat treatment at 70°C. The silylated extracts were analyzed on two GC systems: HP-1 (Hewlett Packard) 25 m × 0.2 mm i.d., 0.11 mm film thickness for the determination of fatty acids, resin acids, and sterols and HP-1 6 m × 0.53 mm i.d., 0.15-mm film thickness for the determination of steryl esters and triglycerides. The components were identified by comparing retention times with those of ref-

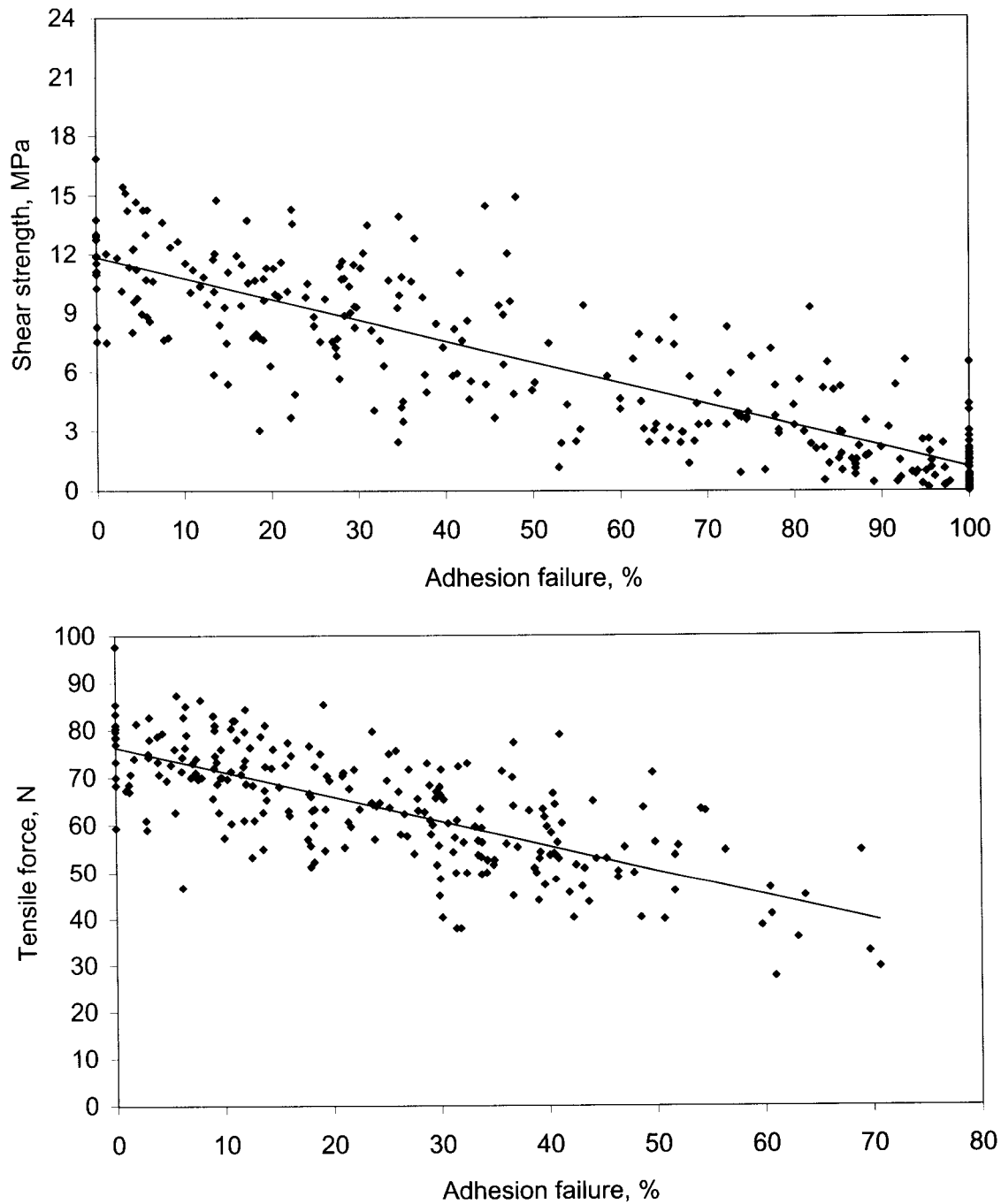


FIG. 4. Relationship between glue-bond strength and adhesion failure for (top) ASTM specimens (shear strength), and (below) DCB specimens (tensile strength). Each DCB data point represents the mean value of three replicates.



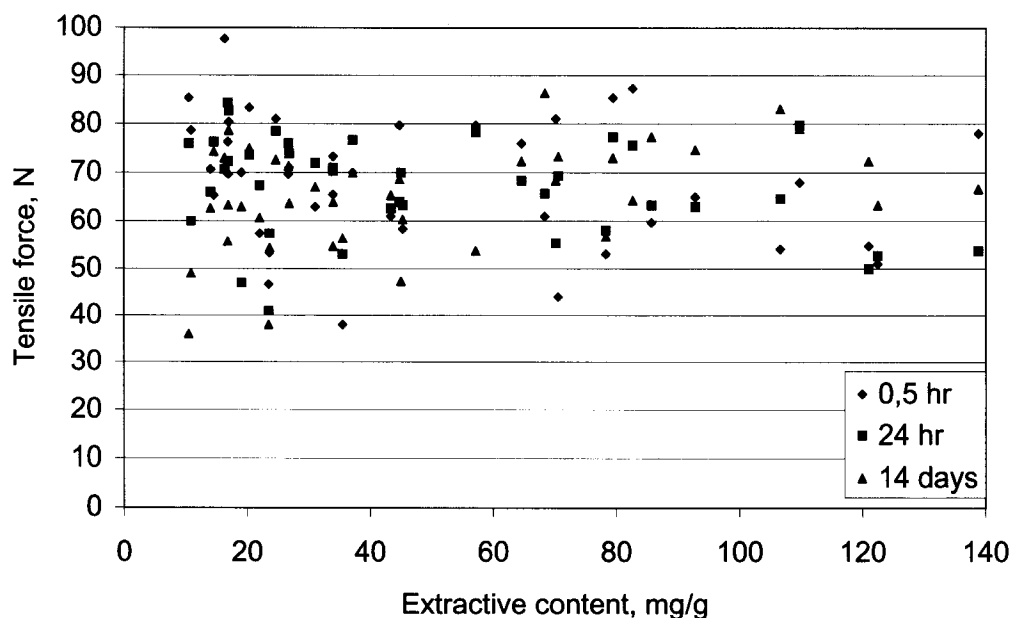


FIG. 5. Relationship between glue-bond strength (tensile force) and extractive content; non-water-exposed DCB specimens. Each data point represents the mean value of three replicates.

erence samples. After quantification of peak areas, the analyzed compounds were divided into six groups—fatty acids, triglycerides, resin acids, oxidized resin acids, sterols, and steryl esters—for which the results were expressed as the total amount of detected compounds.

#### RESULTS AND DISCUSSION

##### *Extractive content analysis*

The results of the extractive content determination are shown in Table 2. The variation in total extractive content between different planks is relatively large. Extractive content ranged from 10 to 145 mg/g dry wood. Samples taken from the butt end (0 m) of each plank predictably generally have a higher extractive content than the samples taken farther away in the longitudinal direction. At most, the butt end sample value was twice that of the 0.5-m sample value. Resin acids constitute the dominating part of the total extractives in most samples except for those samples with a low total content where free fatty acids and resin acids were at the same level.

To each specimen used in the glue-bond strength tests, adhesion failure evaluations and wettability measurements, a corresponding approximate extractive content value was assigned. This value was calculated by interpolating the data from the four analyses at 0, 0.5, 1.0, and 1.5 m. For DCB specimens and wettability specimens, the mean value of two 0.5-meter values was calculated. For ASTM specimens, for which the position in the longitudinal direction was known to within 0.1 m, a linear interpolation was used.

##### *Glue-bond strength vs. adhesion failure*

Correlations between glue-bond strength and adhesion failure are shown in Fig. 4 for the two test methods. A somewhat better correlation is obtained with the ASTM D 905 method (correlation coefficient =  $-0.849$ ) than with the DCB method (correlation coefficient =  $-0.716$ ).

##### *Correlations between glue-bond strength and extractive content*

The correlation between glue-bond strength and extractive content is in general poor. An

example is shown in Fig. 5 where mean values of non-water-exposed DCB specimens are plotted against extractive content including all components. Similar results are obtained for non-water-exposed and water-exposed specimens with both test methods. Further examination of the data showed that the correlations of glue bond strength (or adhesion failure) and extractive content did not vary with storage time. Attempts to find better correlations by plotting glue bond strength against the most hydrophobic components by excluding resin acids resulted in poorer correlations.

Earlier findings by Johansson (2000) have shown that more than 50% of the Scots pine tree population in Sweden contain less than 30 mg/g, and 10 to 20% contain more than 70 mg/g of lipophilic extractives. For further analysis of the experimental data, ASTM and DCB specimens were therefore divided into three groups with respect to their lipophilic extractive content.

Group 1:	less than 30 mg/g dry wood	40–43% of all specimens
Group 2:	30 to 70 mg/g	35–36% of all specimens
Group 3:	higher than 70 mg/g	21–25% of all specimens

The data were statistically evaluated by one-way ANOVA where the combined factor of extractive content group and storage time after planing was used. A multiple range test (LSD) where mean values were compared revealed a few significant differences at the 5% significance level: Water-exposed ASTM specimens from group 3 (highest extractive content) stored for 14 days had a lower glue-bond strength than group 1 specimens and, unexpectedly, non-water-exposed ASTM and DCB specimens from group 3 stored for 14 days had a higher glue-bond strength than specimens from group 1 and 2 (not shown in any figure).

The mean wood density was 540 kg/m<sup>3</sup> with a standard deviation of 55 kg/m<sup>3</sup>, which is a relatively limited density interval. No clear correlation was evident between wood density

and glue-bond strength. Correlation coefficients for all ASTM and DCB tests were 0.065 and 0.187 respectively. The wood density in the studied range thus seems not to be a decisive factor for the glue bond strength.

#### *Correlations between adhesion failure and extractive content*

The result of the adhesion failure evaluation of non-water-exposed specimens did not differ significantly from that of the glue-bond strength tests. For water-exposed specimens, however, there is undoubtedly a tendency for greater adhesion failure with increasing extractive content, particularly for the ASTM specimens. The extractive content vs. adhesion failure plot for the water-exposed ASTM specimens reveals a large scatter of data points over the whole adhesion failure range from 0 to 100% at extractive contents less than 35 mg/g, but few data are found at levels below 60% at higher extractive contents (see Fig. 6). A similar scattering was moreover also obtained with the corresponding glue-bond strength data (not shown here), thus showing that not all low-extractive content specimens were stronger than the assemblies made from wood with high extractive content. One-way ANOVA of the ASTM adhesion failure data, with the specimens divided into the three extractive content groups (see above), showed a clear trend with a greater degree of adhesion failure with increasing extractive content. Group 3 specimens, i.e., those with the highest extractive content, had a significantly greater degree of adhesion failure at a 0.1% significance level than group 1 at 24 h and 14 days storage time (see Fig. 7a). For comparison, the corresponding ANOVA for water-exposed DCB specimens is shown in Fig. 7b. Although significant differences with a higher degree of adhesion failure in group 3 than in group 1 at 0.5 and 24 h storage time are demonstrated, the existence of a clear correlation between extractive content and adhesion failure is not evident in these DCB results.

The effect of wood surface storage time on

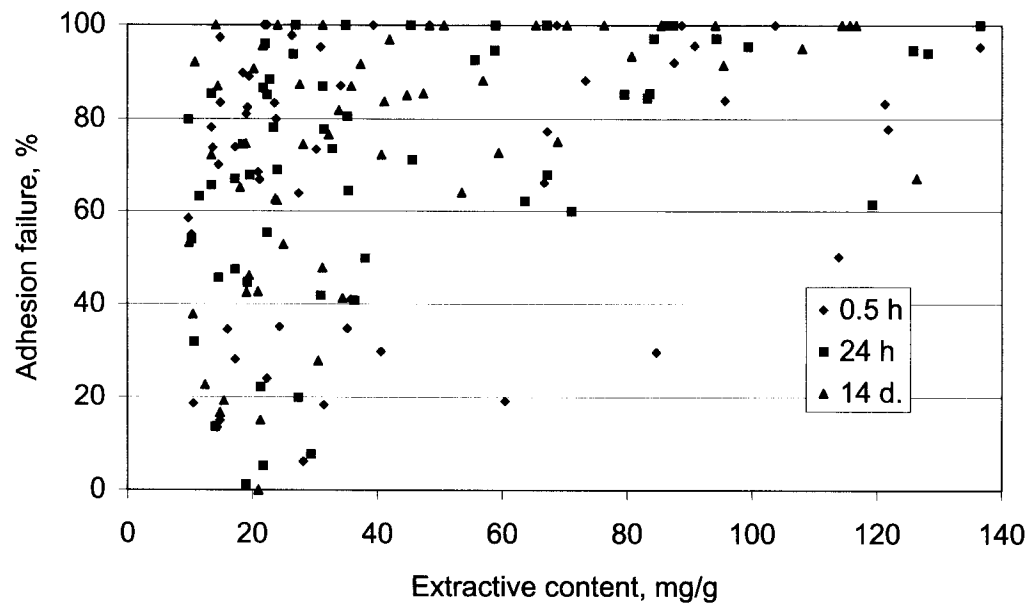


FIG. 6. Relationship between degree of adhesion failure and extractive content for water-exposed ASTM specimens.

adhesion failure is surprisingly low, and the discernible trend in Fig. 7 with increasing adhesion failure at longer storage time is not statistically significant at a 5% significance level. Mean adhesion failure values for all water-exposed DCB tests are 21, 26, and 30% for 0.5

h, 24 h, and 14 days respectively storage time. Corresponding values for water-exposed ASTM tests are 69, 71, and 74%.

The large variability in data for several test groups, evident in Fig. 7, is partly a result of the fact that each group includes specimens

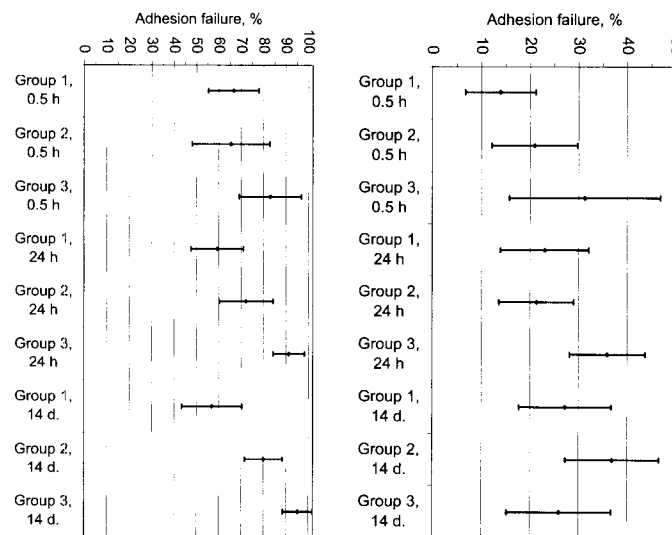


FIG. 7. Confidence intervals (95%) for mean values for tested combinations of extractive content group and storage time for water-exposed specimens according to (a) ASTM tests at left, and (b) DCB tests at right.

from different planks. The fact that relatively few specimens have no adhesion failure, i.e., 100% cohesive wood failure, even at low storage times may be attributed to the low glue pressure used.

Entirely different forces are applied in the two test methods, shear strength along the grain in the ASTM test and tensile strength perpendicular to the grain in the DCB test, and some differences in the results should be mentioned. Whereas adhesion failure data for non-water-exposed DCB and ASTM specimens are within the same range of 0–50%, a significant difference is obtained for water-exposed ASTM specimen data (40–100%) compared with DCB specimen data (0–50%). This difference may be explained by the fact that ASTM specimens undergo a more severe water-exposure test. In addition, the glue line in the tangentially bonded ASTM specimen is subjected to a larger strain than the glue line in the radially bonded DCB specimen. Accordingly, the average shear strength of non-water-exposed ASTM specimens, 10–15 MPa, is substantially higher than that for water-exposed specimens, 2–5 MPa. The corresponding difference in tensile force for DCB specimens is relatively small; 60–80 N for non-water-exposed and 55–70 N for water-exposed specimens.

It should be noted that two different material properties are evaluated with the two test methods: The ASTM shear strength test gives mostly information on the local bond strength of the glue line, whereas the DCB test provides information on fracture energy and stiffness. The preparation of DCB specimens aimed at straight-grained specimens, i.e., with a grain angle close to 0°. Other fracture test studies with glued wood, however, clearly indicate that more decisive results are obtained with a controlled grain angle of 3–6° (Knaebe and Williams 1993; Gagliano and Frazier 2000).

#### *Wettability measurements*

The results of the wettability measurements are plotted against wood extractive content in

Fig. 8. When average values of the wettability data are compared, higher contact angles are obtained at longer storage times, which is quite in line with the results of earlier studies (Nussbaum 1999). However, when the extractive content is also taken into account, the picture becomes much more complex. Whereas the contact angle on a surface stored for a short time before testing (0.5 and 24 h) appears to increase with increasing extractive content, the opposite relation with a decreasing contact angle at higher extractive contents is evident for surfaces stored for 14 days.

The explanation of the difference in behavior between short-term and long-term stored surfaces is likely to be found in factors related to the formation of a weak boundary layer, such as the time for extractives to migrate and—as a hypothesis—to spread over the surface, as well as to chemical changes in the already formed weak boundary layer. In earlier studies by Nussbaum (1999) it was demonstrated that the contact angle, measured on pine wood with an unknown extractive content and stored at 21°C, increased linearly during an initial phase until it started to level out after approximately 4 days. During this initial phase, the measured contact angle is probably directly correlated to the degree of spreading of extractives over the surface. After about a week, when a maximum contact angle is reached, the spreading process is probably completed. Assuming that this spreading will occur more rapidly at higher extractive contents, it seems reasonable to expect that, at short storage times, the contact angle will increase with increasing extractive content (see Fig. 8). At longer storage times, the situation is different. The decrease in contact angle with increasing extractive content for surfaces stored for 14 days may possibly be a result of air oxidation of the surface. If spreading occurs more rapidly at higher extractive contents, this may indicate that the extractives have been exposed to air for a longer time than in the case of the samples with lower contents, with a potentially greater degree of surface oxidation and thereby better surface wettability

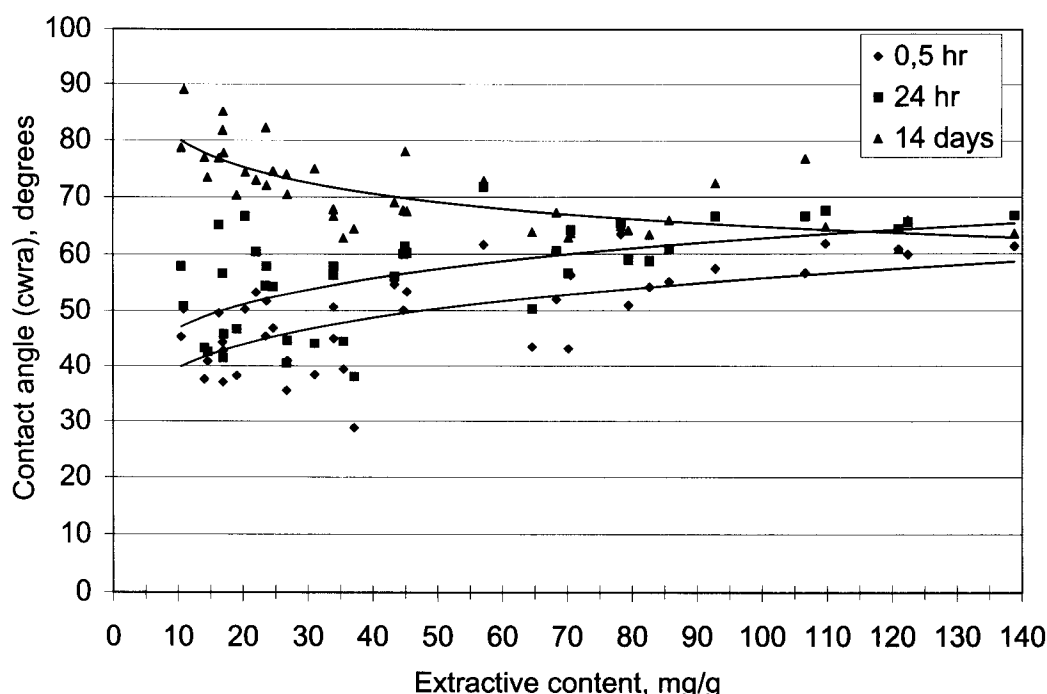


FIG. 8. Relationships between surface wettability and extractive content after different storage times. The contact angle is expressed as the "constant wetting rate angle (cwra)". Bottom, middle and upper lines represent 0.5 h, 24 h and 14 days data respectively.

as a result. Another factor that may be important in explaining differences in wettability between specimens of high and low extractive content is the fats/resin acid ratio. As shown in Table 2; this ratio decreases with increasing extractive content. Since fats (fatty acids and triglycerides) have a more hydrophobic character than resin acids, one may expect that when the spreading of extractives over the surface is completed, which seems to be the case after 14 days, a higher ratio, i.e., a higher proportion of fats, will lead to higher contact angle values. Yet another factor to take into account is the contamination effect that wood extractives have on the probe liquid (water), i.e., the fact that water-soluble extractives actually decrease the surface tension of a water drop applied onto a wood surface (Wälinder 2000).

No correlation is apparent when surface wettability is compared with glue-bond strength and adhesion failure data for DCB

specimens taken from the same original wood material, but this lack of correlation is not surprising considering the above results and the interpretation of how factors such as storage time and extractive content may affect the surface wettability. Wettability measurements may be useful for following the development of a weak boundary layer, but once such a layer is formed, wettability measurements are merely informative about the actual chemical nature of the top molecular layer. If the glue-bond strength is affected negatively with increasing weak boundary layer thickness, surface wettability measurements may be only of limited value.

It is important to emphasize that the contact angle on a wood surface is a phenomenological parameter influenced not only by surface thermodynamics (i.e., wetting properties) but also by factors such as surface roughness, heterogeneity, and porosity, as well as by contam-

ination effects caused by soluble extractives being taken up by the probe liquid.

#### CONCLUSIONS

Glue-bond strength tests performed under controlled wood moisture content conditions, involving two different methods—a fracture test and a block-shear strength test—show a linear correlation between glue-bond strength and the degree of adhesion failure for pine heartwood bonded with a water-resistant PVAc glue.

The hypothesis that the existence of a weak boundary layer of resinous extractives will affect wood adhesion properties negatively is only partly supported by the results obtained. There is no clear correlation between glue-bond strength and lipophilic extractive content for non-water and water-exposed specimens with surfaces stored for different times prior to assembly. Significant effects of different extractive content levels on the adhesion failure are found for water-exposed specimens. For ASTM shear strength tests in particular, the extent of adhesion failure is greater in groups of specimens with an extractive content higher than 70 mg/g dry wood than it is in groups with lower content. The lowest degree of adhesion failure is generally found for specimens with less than 30 mg/g. An indication of a higher degree of adhesion failure with increasing surface storage time is discernible, although this effect is not statistically significant.

Surface wettability measurements reveal a complex relationship between wood surfaces of different extractive contents and different storage times. The results clearly indicate that although surface wettability measurements are informative for following the development of resinous weak boundary layers, there is no apparent correlation between surface wettability and glue adhesion parameters.

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