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Tannin-based cold-setting adhesives for face lamination of wood

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Tannin-based adhesives, in which 50–70 percent of resorcinol in PRF resins was substituted by tannin from pecan nut pith, were formulated for face-lamination of wood under cold-setting conditions. Synthesized tannin-based resins were also modified by further addition of pecan tannin. Bonds were tested in block-shear on the wood of Douglas-fir, spruce and southern pine according to AITC-107 and AITC-110 standards. Some of these tannin-based adhesive formulations meet the strength and wood failure requirements when bonding Douglas-fir and spruce.

Tannin-Klebstoffe für kalthärtendes Kleben von lamelliertem Holz

Tannin-Klebstoffe, in welchen 50–70% Resorcin durch den Gerbstoff des Pecanobaums ersetzt wurde, wurden für Kaltverklebung von lamelliertem Holz angewandt. Die Gerbstoffharze wurden noch zusätzlich durch die Zugabe von Tannin modifiziert. Die Eigenschaften der Klebverbindungen wurden nach den AITC-107 und AITC-110-Normen auf dem Holz der Douglasie, Fichte und Süd-Kiefer geprüft. Bei einzelnen für das Kleben von Douglasie und Fichte angewandten Klebstoffmischungen entsprechen der Holzbruchanteil und die Scherfestigkeit den Normen.

1 Introduction

Use of natural materials for substitution of synthetic polymers has been an object of numerous research studies (Hemingway et al., 1989). The reason for this was the oil crisis in the early 1970s, as well as the emerging ecological awareness (see e.g. FAO, Food and Agriculture Organization).

A detailed study of the chemistry (Tišler, 1992) and use (Tišler, 1985) of spruce tannin, showed that spruce bark extract can partly replace urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde resins in the manufacture of adhesives used for plywood, fiberboards, and particleboards. In Australia and New Zealand, a number of research projects focused on the possibility of using *Pinus radiata* bark extract in the manufacture of particleboards. Quebracho bark extract is reported as having been used by the plywood industry in Finland. Successful laboratory tests on the use of bark extract of Douglas-fir, hemlock, spruce (*Picea* spp.), fir (*Abies* spp.) and numerous species of pine (*Pinus* spp.) have been reported in articles reviewing this area (Porter and Hemingway, 1989; Pizzi 1983). In South Africa, acacia bark extract is used to replace a part of phenol and resorcinol in adhesives used for particleboards and plywood panels, as well as for laminated wood (Pizzi, 1983).

Because prices of phenol are relatively low in the United States, research there has focused on the possibility of using tannin as a substitute for resorcinol where it sells for about $2.00/lb. In the preparation of phenol-resorcinol-formaldehyde adhesives for finger-jointing and face lamination, loblolly pine (*Pinus taeda* L.) bark extract has been used (Hemingway and Kreibich, 1984). Because of the high yield and quality of the extract, adhesives were also formulated from a tannin obtained from pecan nut pith (Kreibich, 1993; Kreibich and Hemingway, 1996). In the present study, 50% or more of resorcinol was substituted by tannin from pecan nut (*Caraya illinoensis*) pith in adhesives formulated for face lamination of wood.

2 Materials and methods

2.1 Materials

2.1.1 Phenol, formaldehyde, resorcinol and catalyst

In the synthesis of phenol-resorcinol-formaldehyde resins, the following materials were used:

Phenol – 99%, technical, product of E. Merck, Darmstadt
Formaldehyde – 37%, technical, solution stabilized by 10% methanol, product of E. Merck, Darmstadt
Resorcinol – 99%, technical, product of E. Merck, Darmstadt.

The reaction was catalysed using a 50% NaOH water solution which was added in two equal parts.

2.1.2 Tannin

For the synthesis of tannin-based resins, tannin from pecan nut (*Caraya illinoensis*) pith was used (PX Inc.

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product Resorcinex Pecan Tannin 9901L) obtained by sulphite extraction (McGraw et al., 1992). The tannin solution had a viscosity 2480 cPs, pH 6.13, and a solids content of 41%.

2.1.3 Curing agent and filler

Technical paraformaldehyde by E. Merck, Darmstadt, in addition to various amounts of Borden's, FM-260, Springfield, OR, was used as the curing agent.

2.2 Methods

2.2.1 Synthesis of phenol formaldehyde (PF) and phenol-resorcinol-formaldehyde (PRF) resin

Synthesis of the resins was carried out in a 1000 ml kettle. The synthesis was catalysed by sodium hydroxide, a first part added at the beginning of synthesis, and a second part after 60 min of reaction at a temperature of 68 to 72 °C. Resin viscosity changes during the syntheses were measured using Gardner tube standards, and with a Brookfield viscometer after the completion of the synthesis.

A phenol-formaldehyde prepolymer was synthesized first. Here, 1 mol of formaldehyde, 1.05 mol of phenol, 0.5 mol of water and 0.073 mol of NaOH were heated from 30 to 70 °C at a uniform rate over a 30 min period after which another 0.073 mol of NaOH was added and temperature was raised to 90 °C. The reaction mixture was held at 90 °C until a Gardner viscosity of *G* was reached.

For synthesis of PRF1, the phenol-formaldehyde prepolymer described above was cooled to 70 °C and resorcinol (0.267 mol) was added. The reaction mixture was heated to reflux temperature at a uniform rate over a 20 min period. The reflux temperature was held for 90 min and then decreased to 90 °C and heated further until a Gardner viscosity of *U* was reached.

For synthesis of PRF2, the phenol-formaldehyde prepolymer described above was combined with water (0.7 mol) and resorcinol (0.267 mol of resorcinol) at 70 °C and the mixture was heated to reflux temperature at a uniform rate over a 20 min period. After 60 min, the temperature was dropped to 85 °C and held at that temperature until a Gardner viscosity *U* was reached. After a further 15 min at 85 °C the reaction mixture was cooled to 20 °C.

For PRF3, the phenol-formaldehyde prepolymer described above was combined with resorcinol (0.267 mol) at 65 °C and the reaction mixture was heated to 95 °C at a uniform rate over a 20 min period. After heating at 95 °C for 120 min, the kettle was cooled to 20 °C. Characteristics of the synthesized PRF resins and conditions of synthesis are shown in Table 1.

Table 1. Conditions of synthesis and characteristics of PRF resins
Tabelle 1. Bedingungen der Synthese und Eigenschaften der PFR-Harze

	PRF 1	PRF 2	PRF 3
Formaldehyde/phenol	0.95	0.95	0.95
Formaldehyde/phenol + resorcinol	0.759	0.759	0.759
NaOH/phenol	0.14	0.14	0.14
Viscosity (cPs)	534	700	800
pH	8.2	9.8	8.5
Solids content (%)*	62	59	61
M_w	2865	2550	2613
M_n	459	690	646
M_w/M_n	6.25	3.69	4.05

* 1 h/135 °C

2.2.2 Synthesis of tannin-based resins

In syntheses that followed, the quantities of pecan tannin (hereinafter:tannin) shown in Table 2 were added to the phenol-resorcinol (PRF) polymer syntheses to examine the hypothesis that tannin might be a suitable substitute for resorcinol when cooked into a PRF resin. Tannin was added at different temperatures in four equal portions. Resins were synthesized according to temperature programs shown in Figs. 1–3. Characteristics of tannin-based resins are given in Table 2. Upon the completion of synthesis, tannin-based resins were clear and homogenous in appearance, and their viscosity was appropriate for formulation of cold-setting laminating adhesives.

Table 2. Conditions of Synthesis and characteristics of Tannin-based resins
Tabelle 2. Bedingungen der Synthese und Eigenschaften der Gerbstoff-Harze

	Tannin based resins					
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
PRF resin (g)[a]	12.2	12.2	11.8	11.8	12.2	12.2
Tannin (g)[a]	12.2	12.2	11.8	7.4	15.5	12.2
Water (g)[b]	10	11	4.3	4.3	7.5	5.2
Ethanol (g)[b]	5	0	7	4.3	4.3	5.2
pH	8.4	8.6	9.0	9.1	8.7	8.8
Viscosity (cPs)	2300	2600	800	1800	1600	1900
Solid content (%)[c]	56	58	58	51	49	54
Free phenol	Trace	Trace	Trace	Trace	Trace	Trace
Free formaldehyde	<1%	<1%	<1%	<1%	<1%	<1%
M_w	3345	3597	3011	3514	3254	3483
M_n	501	545	542	605	444	446
M_w/M_n	6.68	6.60	5.55	5.81	7.30	7.80

[a] solid content; [b] per 100 g PRF of liqued resin; [c] 1 h/135 °C

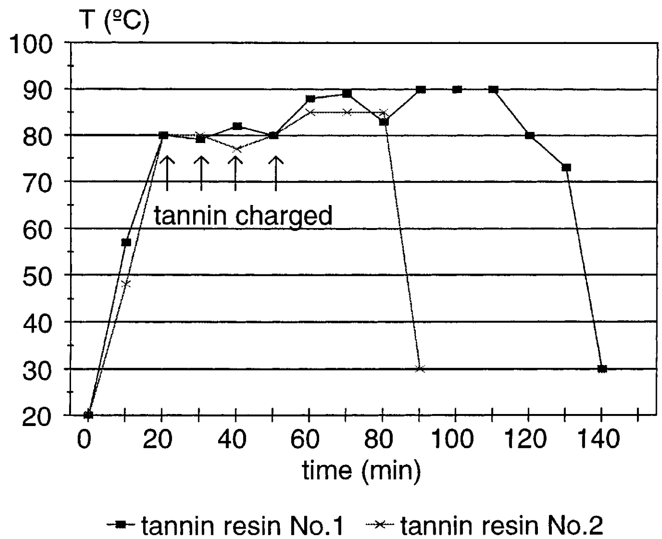

Fig. 1. The temperature programs of tannin-based resin No. 1 and tannin-based resin No. 2
Bild 1. Temperaturverlauf während der Synthese der Gerbstoffharze Nr. 1 und Nr. 2

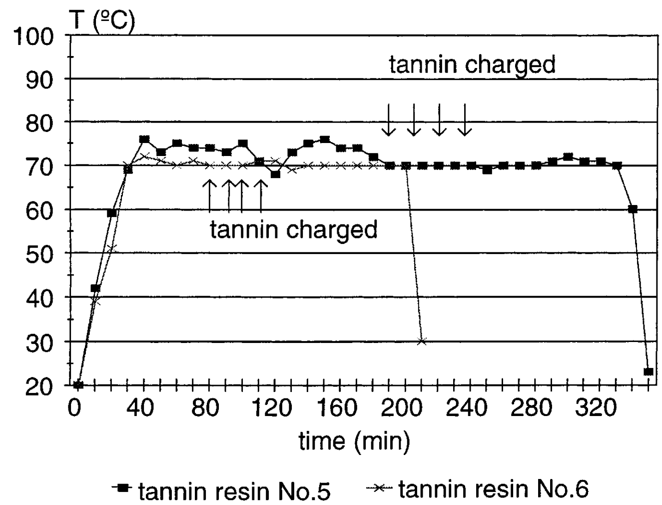

Fig. 3. The temperature programs of tannin-based resin No. 5 and tannin-based resin No. 6
Bild 3. Temperaturverlauf während der Synthese der Gerbstoffharze Nr. 5 und Nr. 6

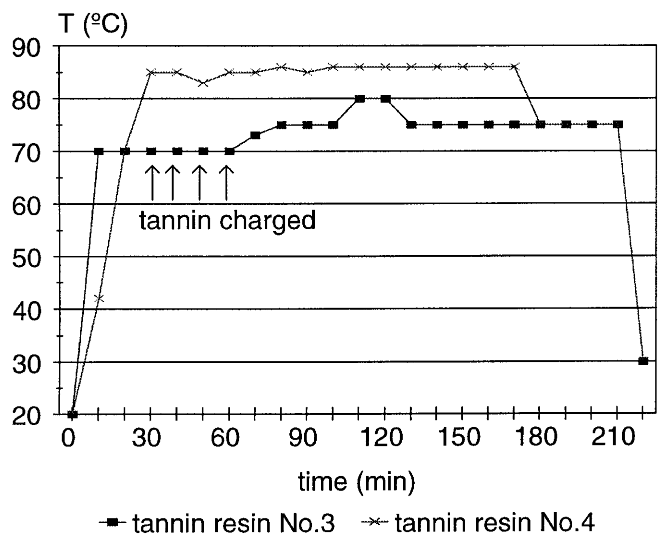

Fig. 2. The temperature programs of tannin-based resin No. 3 and tannin-based resin No. 4
Bild 2. Temperaturverlauf während der Synthese der Gerbstoffharze Nr. 3 und Nr. 4

2.2.3
Determination of free phenol and formaldehyde

Free phenol in resins was determined qualitatively, by means of Si-gel thin-layer chromatography using benzene/acetone (7:3) as the mobile solvent. Formalin/H_2SO_4 with heating was used as visualition reagent.

The free formaldehyde content in resins was determined by titration, using the hydroxylamine hydrochloride method.

2.2.4
Gel permeation chromatography

The number average molecular weight (Mn) and weight average molecular weight (Mw), as well as polydispersity, were determined by HPLC Waters Associates, model 440 with a Differential refractometer R 401. A Shodex GPC AD 800/P micro-styragel column was used with dimethyl formamide at 1 ml/min flow rate. Chromatograms were plotted with an Omini Scribe^{TM} recorder and evaluated by computer. The results are shown in Tables 1 and 2.

2.3
Tannin-based adhesives

Douglas fir, southern pine and spruce were used as wood substrates. The moisture content of specimens of 152.4 × 152.4 × 25.4 mm panels was 12 ± 1%. The texture of all specimens was radial, or radial–tangential. The surface of specimens was planed 24 h prior to bonding.

On the basis of parallel tests, where a commercially available PRF (Borden's LT-75) was modified by tannin (unpublished results), it was established that adhesive penetration and consequent strength of adhesive bond is improved in the case of bonding southern pine if the wood surface had been modified by a 10% NaOH solution. The solution was manually applied to the surface of southern pine wood 10 min before applying the adhesive.

Tannin-based adhesives with the following basic compositions were examined:

	Solid content (g)
Tannin-based resin	22.52
Filler (Borden's FM-260)	4.20
Catalyst NaOH (50%)	1 and 2
Curing agent (paraformaldehyde)	2 and 4

The adhesives were prepared immediately prior to the application on both faces of the specimens. Detailed compositions of individual tannin-based resins are given in Tables 3–5 (Sect. 3.1). The quantity of adhesive varied (260 g to 320 g/m^2) because adhesive squeezed out from

Table 3. Properties of glue bonds of tannin-based adhesived – bonding wood of Douglas-fir
Tabelle 3. Eigenschaften der Klebverbindungen mit Gerbstoff-Klebstoffen beim Kleben von Douglasienholz

Sample no.	Tannin resin used	Para-form. (g)	NaOH (g)	DRY samples		VPS samples	
				Shear strength (kPa)	Wood failure %	Shear strength (kPa)	Wood failure %
1	No. 1	2	2	7743	100	4241	80
2	No. 1	4	4	7984	89	3564	45
5	No. 2	2	2	6991	100	3192	50
7	No. 2	4	4	11501	78	5902	50
15	No. 4	2	2	7591	92	4723	77
16	No. 4	4	2	8894	89	3048	75
23	No. 5	2	2	6902	60	3712	30
24	No. 5	4	4	10843	85	5532	15
29	No. 6	2	2	9816	75	3558	5
30	No. 6	4	4	5507	35	5498	35

Table 4. Properties of glue bonds of tannin-based adhesived – bonding wood of spruce
Tabelle 4. Eigenschaften der Klebverbindungen mit Gerbstoff-Klebstoffen beim Kleben von Fichtenholz

Sample no.	Tannin resin used	Para-form. (g)	NaOH (g)	DRY samples		VPS samples	
				Shear strength (kPa)	Wood failure %	Shear strength (kPa)	Wood failure %
14	No. 3	4	2	7088	99	3082	56
20	No. 4	2	2	7488	90	2406	58
21	No. 4	4	4	7095	47	1025	28
22	No. 4	4	2	7681	88	3689	37
27	No. 5	2	2	5012	85	3829	76
28	No. 5	4	4	7134	69	2788	60
33	No. 6	2	2	7196	80	3213	50
34	No. 6	4	4	7867	98	3808	98

Table 5. Properties of glue bonds of tannin-based adhesived – bonding wood of southern pine
Tabelle 5. Eigenschaften der Klebverbindungen mit Gerbstoff-Klebstoffen beim Kleben von Kiefernholz

Sample no.	Tannin resin used	Para-form. (g)	NaOH (g)	DRY samples		VPS samples	
				Shear strength (kPa)	Wood failure %	Shear strength (kPa)	Wood failure %
6	No. 2	2	2	8874	69	3178	15
8	No. 2	4	4	8763	85	4626	40
9	No. 3	2	2	11335	50	4289	10
10	No. 3	2	4	7571	45	3406	5
11	No. 3	2	6	8894	80	2448	13
12	No. 3	4	2	8164	84	3896	35
17	No. 4	2	2	8481	75	3847	40
18	No. 4	4	2	7984	80	4151	43
19	No. 4	4	4	8171	75	4144	40
25	No. 5	2	2	7876	57	3441	47
26	No. 5	4	4	5054	78	2485	60
31	No. 6	2	2	5700	90	3415	67
32	No. 6	4	4	6890	75	3301	30

adhesive bond. The time between adhesive application and pressing was 1–2 min. Bonding was carried out at room temperature (22 ± 2 °C) in a Carver laboratory press, which was modified by means of Raymond–Kaller pneumo-hydraulic system (model KG 3000), which exerted a constant pressure of 1035 kPa. Press time was 60 min.

2.4 Modified tannin-based adhesives

Synthesized tannin-based resins were also modified by further addition of pecan tannin (Resorcinex Pecan Tannin-9901L). These adhesives are referred to as modified tannin-based adhesives.

Modified tannin-based adhesives with the following basic compositions were examined:

	Solid content (g)
Tannin-based resin	10.28 or 11.26
Filler (Borden's FM-260)	4.20
NaOH (50%)	1 and 2
Resorcinex Pecan Tannin (9901L)	12.24 or 11.26
Curing agent (paraformaldehyde)	2 and 4

These adhesives were prepared immediately prior to bonding. Due to the quick reaction between tannin and formaldehyde in the presence of NaOH, attention was paid to the open assembly time of the adhesive. Precise quantities of components, which were modified for each individual specimen, are shown in Tables 6–8 (Sect. 3.2). Bonding was carried out over the period of 60 min under identical experimental conditions as in the case of bonding with tannin-based adhesives.

3 Results and discussion

The boards were cut into standard shear block specimens tested for shear strength and wood failure according to AITC-107 and AITC-110 standards after conditioning of not less than 24 h.

The quality of adhesive bonds was assessed against the requirements of ASTM D2559 standard, which requires wood failure in excess of 75% and shear strength in the case of bonding southern pine wood with 12% moisture content to be in excess of 9040 kPa, while in the case of Douglas fir wood with 12% moisture content it should be in excess of 7380 kPa. The specified values apply to dry specimens. In the case of VPS specimens, wood failure should not be less than 75%. The values given in Table 3 are average values obtained from 9 specimens.

Table 6. Properties of glue bonds of modified tannin-based adhesived No. 1, No. 2, No. 3 and No. 4 (12,24 g solid content of tannin-based resin, 10,28 g solid content of pecan tannin), tannin-based resin No. 5 and No. 6 (11,26 g solid content of tannin-based resin, 11,26 g solid content of pecan tannin) – bonding wood of Douglas-fir
Tabelle 6. Eigenschaften der Klebverbindungen mit den modifizierten Gerbstoff-Klebstoffen Nr. 1, Nr. 2, Nr. 3 und Nr. 4 (12,24 g Trockensubstanz des Gerbstoff-Harzes, 10,28 g Trockensubstanz des Gerbstoffes), den modifizierten Gerbstoff-Klebstoffen Nr. 5 und Nr. 6 (11.26 g Trockensubstanz des Gerbstoff-Harzes; 11,26 g Trockensubstanz des Gerbstoff-Harzes) beim Kleben von Douglasienholz

Sample no.	Tannin resin used	Para-form. (g)	NaOH (g)	DRY samples		VPS samples	
				Shear strength (kPa)	Wood failure %	Shear strength (kPa)	Wood failure %
35	No. 1	2	2	6812	99	3537	75
36	No. 1	4	4	10094	88	4716	48
39	No. 2	2	2	6626	95	3565	75
41	No. 2	4	2	7109	90	3551	42
49	No. 4	2	2	8894	79	3084	75
50	No. 4	4	2	6419	94	3372	78
51	No. 4	6	2	7651	95	3489	71
58	No. 5	2	2	7201	55	5052	10
59	No. 5	4	4	7886	45	5256	20
64	No. 6	2	2	6088	43	6088	21
65	No. 6	4	4	5757	72	2461	23

Table 7. Properties of glue bonds of modified tannin-based adhesived No. 1, No. 2, No. 3 and No. 4 (12,24 g solid content of tannin-based resin, 10,28 g solid content of pecan tannin), tannin-based resin No. 5 and No. 6 (11,26 g solid content of tannin-based resin, 11,26 g solid content of pecan tannin) – bonding wood of spruce
Tabelle 7. Eigenschaften der Klebverbindungen mit den modifizierten Gerbstoff-Klebstoffen Nr. 1, Nr. 2, Nr. 3 und Nr. 4 (12,24 g Trockensubstanz des Gerbstoff-Harzes, 10,28 g Trockensubstanz des Gerbstoffes) und den modifizierten Gerbstoff-Klebstoffen Nr. 5 and Nr. 6 (11.26 g Trockensubstanz des Gerbstoff-Harzes; 11,26 g Trockensubstanz des Gerbstoff-Harzes) beim Kleben von Fichtenholz

Sample no.	Tannin resin used	Para-form. (g)	NaOH (g)	DRY samples		VPS samples	
				Shear strength (kPa)	Wood failure %	Shear strength (kPa)	Wood failure %
38	No. 1	2	2	6288	48	3399	22
47	No. 3	2	4	7757	83	2289	55
48	No. 3	2	2	9240	83	3565	62
55	No. 4	2	2	7557	75	1296	62
56	No. 4	4	2	8260	88	1627	57
57	No. 4	6	2	7026	91	3245	60
62	No. 5	2	2	6269	70	3163	60
63	No. 5	4	4	7858	87	3714	85
69	No. 6	2	2	7651	62	3036	44
70	No. 6	4	4	6355	75	1880	20

Table 8. Properties of glue bonds of modified tannin-based adhesived No. 1, No. 2, No. 3 and No. 4 (12,24 g solid content of tannin-based resin, 10,28 g solid content of pecan tannin), tannin-based resin No. 5 in No. 6 (11,26 g solid content of tannin-based resin, 11,26 g solid content of pecan tannin) – bonding wood of southern pine
Tabelle 8. Eigenschaften der Klebverbindungen mit den modifizierten Gerbstoff-Klebstoffen Nr. 1, Nr. 2, Nr. 3 und Nr. 4 (12,24 g Trockensubstanz des Gerbstoff-Harzes, 10,28 g Trockensubstanz des Gerbstoffes) und den modifizierten Gerbstoff-Klebstoffen Nr. 5 and Nr. 6 (11.26 g Trockensubstanz des Gerbstoff-Harzes; 11,26 g Trockensubstanz des Gerbstoff-Harzes) beim Kleben von Kiefernholz

Sample no.	Tannin resin used	Para-form. (g)	NaOH (g)	DRY samples		VPS samples	
				Shear strength (kPa)	Wood failure %	Shear strength (kPa)	Wood failure %
37	No. 1	2	2	7591	72	3103	15
40	No. 2	2	2	8963	75	3937	13
42	No. 2	4	4	11590	80	4461	52
43	No. 3	2	2	10074	62	3551	18
44	No. 3	2	4	10974	40	4102	10
45	No. 3	2	6	8508	88	3965	15
46	No. 3	4	2	8453	80	3620	42
52	No. 4	2	2	8756	60	3558	23
53	No. 4	4	2	7460	86	3482	50
54	No. 4	6	2	7998	90	3937	43
60	No. 5	2	2	7237	93	2857	75
61	No. 5	4	4	7458	95	3441	47
66	No. 6	2	2	7784	77	4012	35
67	No. 6	2	4	6196	95	2901	33
68	No. 6	4	4	8046	82	2509	37

3.1 Characteristic of adhesive bonds with tannin-based adhesives

Results in Tables 3–5 and Fig. 4 reveal a definite influence of substrate on adhesive bond characteristics. In this connection, attention should be drawn to the difficulty in bonding of southern pine wood. The wood of this type of pine is the hardest and has the highest density (0.51–0.61 g/cm^3) among the commercially important softwoods. The problems encountered in reference with the bonding of southern pine wood, due to great differences in the structure of early and late wood (density of early wood is approx. 0.30 g/cm^3 and of late wood approx. 0.85 g/cm^3), were pointed out previously by Kollmann (1975) and Hse (1968). Because of the highly non-uniform wood structure, in bonding, there is the problem of excessive penetration of adhesive into porous early wood and of its inadequate penetration into late wood. In the early wood/early wood areas there was excessive penetration of wood by adhesive and the adhesive bond was consequently dry. In the case of late wood/late wood area, adhesive penetration was minimal. Non-uniform penetration is not such a problem in the case of bonding spruce and Douglas fir wood.

These tannin-based adhesives are characterized by relatively long gel times (~20 min), which can be a desirable property in this application (McGraw, 1992). However, after 60 min the adhesives were still not completely cured. The short time under pressure has an effect on properties exhibited by adhesive bonds. This was most evident in bonded specimens of southern pine. Adhesive bonds of southern pine wood specimens did not give acceptable wood failure (Table 5). Increasing the press time would undoubtedly have positive effect on the characteristics of adhesive bonds. Characteristics of tannin-based adhesive

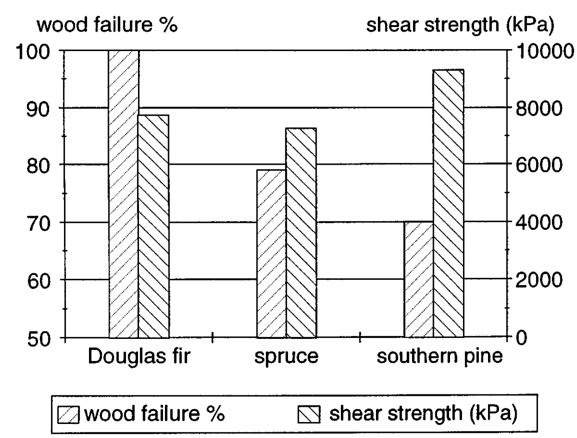

Fig. 4. Characteristics of adhesive bonds in the case of bonding wood of different wood species (tannin-based resin No. 1, 2 g paraformaldehyde, 2 g NaOH)
Bild 4. Eigenschaften der Klebverbindungen beim Kleben von verschiedenen Holzarten (Gerbstoff-Harz Nr. 1; 2 g paraformaldehyde, 2 g NaOH)

bonds in Table 3 and 4 show that some tannin-based adhesives comply with the requirements of the standards applicable to wood lamination adhesive bond properties.

Tannin-based resin No1, which was cured using 2 g of paraformaldehyde and catalysed by 2 g of NaOH, fully complies with applicable standards in the case of bonding the wood of Douglas-fir (Table 3).

Bonding spruce wood in the case of using tannin-based resin No. 5 (Table 4) complied with the requirements of applicable standards. Relatively high shear strength values of adhesive bonds using identical tannin-based adhesives in the case of Douglas-fir specimens (Table 3) caused a lower percentage of wood failure than is allowed according to standard.

Tannin-based adhesives in the case of bonding spruce wood (Table 4) using resin No. 6, where the adhesive was cured using 4 g of paraformaldehyde and 4 g of NaOH exhibited excellent adhesive bond characteristics.

Results of analysing tannin-based adhesives based on phenol-resorcinol-formaldehyde resin in which tannin added as a substitute for resorcinol during the resin synthesis justify, as far as shear strength requirements are concerned, the use of these for wood lamination purposes. The advantage of using tannin-based adhesives are the relatively long gel times and open assembly times that can be obtained while substantially reducing the cost of the adhesive. It is assumed that, with longer press times, adhesive bonds would comply with the requirements of standards applicable to the more difficult bonding of wood of southern pine, even under the rigorous testing conditions specified by AITC-110 standard. It would be reasonable to increase the press time of 180 min, and this would not be a problem for existing bonding technology, for adhesives used in this type of bonding require press times between 4 and 10 h at the temperature of 20 °C.

3.2 Characteristics of adhesive bonds with modified tannin-based adhesives

Parallel to experiments where tannin-based adhesives were used, bonding was also carried out by using modified tannin-based adhesives. Modified tannin-based adhesives (modification is described in subsection 2.4) were tested in the same way and under the same conditions as tannin-based adhesives. Tables 6–8 show the strength of adhesive bonds of modified tannin-based adhesives and wood failure percentage.

Modified tannin-based adhesives have a shorter gel time, because modification was carried out by means of addition of further amounts of tannin which reacts very quickly in the presence of formaldehyde. This had to be taken into consideration in particular in the case of tannin-based adhesives with greater amounts of NaOH catalyst.

The influence of the quantity of the curing agent on wood failure of dry specimens is shown in Fig. 5. With adhesives with a greater amount of curing agent, higher percentage of wood failure was observed.

Also, in the case of using modified tannin-based adhesives, the morphology of the substrate has an important effect, and tannin-based adhesives with identical composition produce adhesive bonds of quite different characteristics when used for bonding wood of different tree species. Bonding of southern pine wood is more difficult. Adhesive bonds of dry specimens, as a rule, provided adequate shear strength and acceptable wood failure but water resistance was not adequate to meet AITC-110 standards for wood failure on southern pine.

Modified tannin-based adhesives using tannin-based resin No. 1 and tannin-based resin No. 2, which were cured by 2 g of paraformaldehyde and 2 g of NaOH (Table 6, specimens No. 35 and No. 39), were found to be satisfactory and to comply with the requirements of ap-

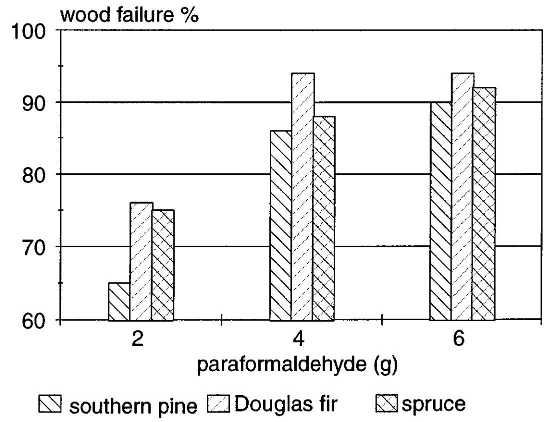

Fig. 5. Influence of curing agent on wood failure (modified tannin-based and No. 4; 2 g NaOH, press time 60 min, dry specimens)

Bild 5. Einfluß des Vernetzers auf den Holzbruchanteil (modifiziertes Gerbstoff-Harz Nr. 4; 2 g NaOH, Preßzeit 60 Min., trockene Prüfstücke)

plicable standard in the case of bonding wood of Douglas-fir.

Modified tannin-based adhesives using tannin-based resin No. 4 complied with the requirements of applicable standard in the case of bonding wood of Douglas-fir.

Modified tannin-based adhesive using tannin-based resin No. 5 (Table 4) was less suitable for bonding wood of Douglas fir, because very marked loss of shear strength in the case of VPS specimens.

The adhesive bond of specimen No. 63 (Table 7) exhibited excellent characteristics and complied with the requirements of applicable standard for bonding spruce wood.

Modified tannin-based adhesive using tannin-based resin No. 5 (Table 7, specimen No. 60) where the adhesive was cured using 2 g of paraformaldehyde and 2 g of NaOH exhibited excellent adhesive bond characteristics in the case of bonding southern pine wood.

4 Conclusions

The aim of this research work was to examine the possibility of using pecan tannin as substitute for resorcinol in adhesives used for cold-setting wood lamination. Phenol-resorcinol-formaldehyde resins were synthesized with pecan tannin added to replace resorcinol and the characteristics of these tannin-based resins were found to be suitable for cold-setting wood lamination of Douglas-fir and spruce. Differences in surface morphology of the wood species have a major influence on bonding process and shear strength of adhesive bonds. By modifying southern pine using a dilute sodium hydroxide solution, a satisfactory solution was provided for problems encountered in bonding that wood.

Tannin-based resins in which 50 percent or more of resorcinol was substituted during synthesis by pecan tannin can be used for cold-setting wood lamination. One should point out that in this research, bonding by tannin-based resins lasted 60 min only, which is too short a period for the majority of adhesives to reach a cross-linked structure. Undoubtedly, increased gluing time would have positive effect on properties of adhesive bond. Nevertheless, some tannin-based adhesive mixtures gave bond strength and water resistance required in applicable standards.

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