

Potential of Tannins for Exterior Grade Plywood

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Abstract

Resins from *Uncaria gambier* and *Acacia catechu* tannins were prepared by copolymerization with phenol and formaldehyde at 100°C. Both tannins were used to substitute up to 50 percent of the phenol using 5, 8, and 11 percent alkali concentrations. Adhesive formulations and gluing conditions were tested by preparing three-ply *Shorea robusta* boards (53.34 by 53.34 cm). We found that *U. gambier* tannin can substitute up to 50 percent of the phenol, using 8 and 11 percent sodium hydroxide as a catalyst; *A. catechu* tannin can substitute up to 30 percent of the phenol, using 8 and 11 percent sodium hydroxide. The resultant boiling water resistance grade plywood meets the requirements laid down in Indian Standards (IS) 303-1989 for exterior grade plywood in all respects (i.e., glue shear strength in dry, water resistance, and mycological tests).

In most countries only phenolic adhesives are considered suitable for the manufacture of exterior grade wood products, particularly if exposure to extreme climatic conditions is anticipated (Pizzi et al. 1981). Due to the high cost of synthetic adhesives, there have been several attempts to replace a portion of the petroleum-derived compounds with phenolic-type compounds obtained from renewable resources. Principal among these efforts is the development of adhesives from tannin (Pizzi and Scharfetter 1978, Pizzi 1983). Tannin-based adhesives have in the past been heavily fortified with urea, urea-formaldehyde, phenol-formaldehyde (PF), and resorcinol-formaldehyde with encouraging results (Pizzi 1977, 1983, 2008; Pizzi and Roux 1978; Pizzi and Scharfetter 1978). However, very little work has been done with *Acacia catechu* and *Uncaria gambier* tannins. Tannins contained in vegetable extracts are polymers of flavonoid units or polyflavonoids fairly well diffused in various tree barks, wood, cones, and fruits. Tannins are broadly divided into hydrolyzable and condensed tannins. The former are simple mixtures of pyrogallols, gallic acid, and ellagic acid, all of which are simple phenols with low reactivity toward formaldehyde. However, they constitute only 5 to 10 percent of a total industrial production of tannin extracts manufactured in the world. The main tree species exploited to obtain these hydrolyzable or gallic tannins is chestnut (*Castanea*) (Pizzi 1980).

Condensed tannins are the polymerization of monomeric flavan-3-ol or flavan-3,4-diol precursors (Figs. 1 and 2). The

structure and formation of condensed tannins are the topic of many speculative theories that have been summarized and criticized by many researchers. The “catechin hypothesis” was introduced by Freudenberg and De Lama (1958) and suggests that the complex polymeric structures of many of the condensed tannins are primarily derived by polycondensation of precursors of a flavonoid type.

The generic term catechin was first used by Freudenberg and De Lama (1958) to describe the colorless crystalline substances commonly located in plant tissues in association with the condensed tannins. Since the catechins were readily converted in vitro to amorphous tannin-like materials, the researchers regarded them as direct precursors of the tannins in nature.

Later work showed that the catechins are derivatives of the basic flavan-3-ol structure, and these compounds are currently referred to as flavan-3-ols to avoid confusion with trivial names (Haslam 1966). The first and perhaps most widely distributed compounds of this class to be isolated

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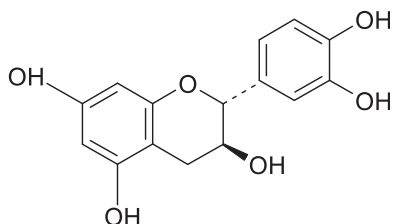


Figure 1.—5,7,3',4'-Tetrahydroxyflavan-3-ol.

from natural sources were (+)-catechin from *U. gambier* and (–)-epicatechin from *A. catechu*; these are diastereoisomers of the 5,7,3',4'-tetrahydroxyflavan-3-ol structure (Figs. 3 and 4)

The tannins of *U. gambier* and *A. catechu* belong to the phloroglucinolic type. These types of tannins are difficult to handle because of their high molecular weight and extremely high reactivity toward formaldehyde (Hemingway and McGraw 1976, Schroeder 1976, Rossouw 1978). This reactivity causes premature curing, and the residual active centers become too far apart for formaldehyde molecules to bridge, resulting in incomplete cross-linking. This shortcoming results in brittleness, poor wood penetration, and poor wet strength (Sowunmi et al. 1996). This also prevents the formation of tannin-resols, tannin resins carrying methylol reactive groups, because the methylol reactive groups will condense with other tannin phenolic nuclei in a very short time. Thus resol resins, which dominate synthetic PF technology, are not a feasible alternative for tannins. In short, tannin-resols are not stable, and their shelf life is far too short to be of industrial or practical significance. This leads to tannins being added to PF resins to overcome the short pot life of tannin-formaldehyde resins.

The aim of this study therefore was to improve the adhesive properties of *U. gambier* and *A. catechu* tannin adhesives. Specifically, the objective was to modify the resulting structure with resol-type PF resin to reduce the tendency for premature curing and encourage a high degree of cross-linking.

Materials and Methods

Materials

Uncaria gambier tannin (Stiasny value 74.5%, hide powder tannin content 59.49%, nontannins 20.08%, and total solubles 79.57%) is a commercial product obtained after the separation of katha and was supplied by Chemistry Division, Forest Research Institute, Dehradun (patent no. 1484/DEL/98, 1485/DEL/98, P981302/98, 9804614/98). *Acacia catechu* tannin (Stiasny value 72.2%, hide powder tannin content 55.89%, nontannins 22.04%, and total

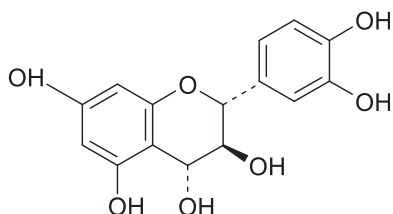


Figure 2.—5,7,3,4-Tetrahydroxyflavan-3,4-diol.

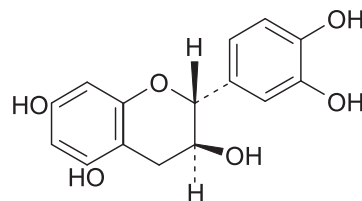


Figure 3.—(+)-Catechin from *Uncaria gambier*.

solubles 77.93%) was supplied by the Mantu Khair Industry, Rangia Assam.

Chemicals

The chemicals used in this study included phenol (Qualigens, laboratory reagent [LR] grade), formalin (37% to 41%; Ranbaxy, LR grade), sodium hydroxide pellets (Ranbaxy, LR grade), hide powder (E. Merck AG), chrome alum (s d fine-chem Limited, LR grade), kaolin (CDH, LR grade), hydrochloric acid (Ranbaxy, LR grade), and methanol (Ranbaxy, LR grade).

Preparation of PF resin, using 5, 8, and 11 percent alkali as the catalyst.—One hundred grams of molten phenol (60°C to 65°C) was charged into the 500-mL round-bottom flask followed by 120 g of formalin (37% to 41% concentration) and 5 g of sodium hydroxide dissolved in 10 mL of distilled water. The condensation reaction was carried out for 30 minutes at a refluxing temperature of approximately 100°C. When the viscosity of the resin syrup was about 100 cps and the water tolerance was about 1:5, the resin was discharged from the round bottom flask and cooled to room temperature by keeping the container in cold circulating water (George 1977).

The procedure for the manufacture of PF resin using 8 and 11 percent alkali concentration was similar to that described for the 5 percent alkali concentration, except for the increased amount of sodium hydroxide.

Preparation of phenol-tannin-formaldehyde (PTF) resin at 5, 8, and 11 percent alkali concentration.—The adhesive formulation was based on a constant molar ratio of phenol-tannin with formaldehyde. The molar ratio (P+T):F was 1:1.2. The replacement of phenol by tannin was successfully achieved up to 50 percent, above which gel formation of resins was observed.

Required amounts of molten phenol (grams) and formaldehyde (grams) were mixed together in a beaker. Tannins of *U. gambier* and *A. catechu* taken separately (grams, oven dry) were added into the phenol-formaldehyde mixture and stirred for 15 to 20 minutes at room temperature until the tannin was completely incorporated (Table 1). The reactants were transferred into a 500-mL round-bottom flask with aqueous sodium hydroxide (5%, 8%, and 11% to that of phenol and tannin) and experiments were carried out for 30 minutes at the refluxing temperature (100°C). The

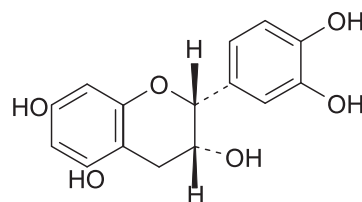


Figure 4.—(-)-Epicatechin from *Acacia catechu*.

Table 1.—Partial substitution of phenol with tannins of *Uncaria gambier* and *Acacia catechu* in phenol-formaldehyde resin.

Resin sample code	P:T:F molar ratio ^a
5% Catalyst	
U1, A1	90:10:120
U2, A2	80:20:120
U3, A3	70:30:120
U4, A4	60:40:120
U5, A5	50:50:120
8% Catalyst	
U6, A6	90:10:120
U7, A7	80:20:120
U8, A8	70:30:120
U9, A9	60:40:120
U10, A10	50:50:120
11% Catalyst	
U11, A11	90:10:120
U12, A12	80:20:120
U13, A13	70:30:120
U14, A14	60:40:120
U15, A15	50:50:120

^a P:T:F = phenol:tannin:formaldehyde; U = *Uncaria gambier*; A = *Acacia catechu*. Gelation of resin was observed at a molar ratio of 40:60:120.

physicochemical properties of PF resin prepared after substitution of phenol with tannins of *U. gambier* using 5, 8, and 11 percent sodium hydroxide as the catalyst are reported in Tables 2 and 3.

Testing

Eighteen test specimens of 2.54 by 15.24 cm were cut along the grain of face veneers from each plywood panel and used for glue shear strength testing (Anonymous 1983, 1989) in dry, water resistance, and mycological environments (Table 4). The results are shown in Tables 5 and 6.

In the water resistance test, the specimens were kept in boiling water for 8 hours. They were then cooled by submerging in cold water at room temperature and then tested for glue shear strength. For the mycological test, the specimens were kept in a porcelain dish filled with a 25-mm layer of sawdust obtained from the sapwood of a perishable timber like semul (*Bombax ceiba*) in its natural condition. The sawdust was moistened with 1 liter of water containing 15 g of sucrose (cane sugar was normally used), so that it was damp but not so wet that free water could be squeezed from it by hand pressure. To attain this condition with dry sawdust, it is generally necessary to add water at three times the mass of the sawdust. The dish was sealed against the glass with screws so that the atmosphere around the test ply samples remained saturated. The dish and contents were maintained at a temperature of 27°C ± 2°C for a period of 3 weeks, after which specimens were tested at room temperature for glue shear strength.

Results and Discussion

PTF adhesives

Properties of PTF adhesives prepared using different molar ratios of reactants and alkali concentrations are reported in Table 1; viscosity, pH, gelation time, and specific gravity of *U. gambier* and *A. catechu* tannins are reported in Tables 2 and 3, respectively.

Table 2.—Physicochemical properties of phenol-formaldehyde (PF) resin with phenol partially substituted with *Uncaria gambier* tannin.^a

Resin or resole	Viscosity		pH	Gelation time at 100°C (h:min:s)	Specific gravity
	Shear rate (s ⁻¹)	Viscosity (cps)			
5% Catalyst					
PF1	9.3	110	9.89	>10:0:0	1.15
U1	9.3	135	9.09	2:59:0	1.15
U2	9.3	175	9.05	2:07:0	1.16
U3	9.3	255	9.01	1:50:0	1.20
U4	3.4	300	8.95	1:05:0	1.20
U5	2.8	350	8.19	0:45:0	1.21
8% Catalyst					
PF2	9.3	145	10.75	>10:0:0	1.16
U6	9.3	190	10.6	1:18:0	1.18
U7	9.3	200	10.53	1:02:0	1.19
U8	9.3	210	10.52	0:48:04	1.20
U9	2.8	600	10.49	0:34:14	1.22
U10	2.5	7,700	9.22	0:17:0	1.24
11% Catalyst					
PF3	9.3	170	11.55	>10:0:0	1.17
U11	2.5	900	11.42	1:58:0	1.184
U12	2.5	1,200	11.39	1:30:0	1.19
U13	2.5	2,500	11.24	0:53:42	1.22
U14	2.5	3,800	10.78	0:23:46	1.23
U15	2.5	10,600	10.5	0:9:9	1.25

^a cps = counts per second; U = *Uncaria gambier*.

Table 3.—Physicochemical properties of phenol-formaldehyde (PF) resin with phenol partially substituted with *Acacia catechu* tannin.^a

Resin or resole	Viscosity		pH	Gelation time at 100°C (h:min:s)	Specific gravity
	Shear rate (s ⁻¹)	Viscosity (cps)			
5% Catalyst					
PF1	9.3	110	9.89	>10:0:0	1.15
A1	9.3	305	9.2	2:10:0	1.15
A2	9.3	400	9.08	1:56:0	1.16
A3	9.3	550	9.03	1:35:0	1.16
A4	3.4	775	8.99	0:55:0	1.18
A5	2.8	1,250	8.92	0:35:0	1.20
8% Catalyst					
PF2	9.3	145	10.75	>10:0:0	1.16
A6	9.3	510	10.65	1:05:0	1.18
A7	9.3	600	10.58	0:50:0	1.19
A8	9.3	630	10.55	0:39:01	1.20
A9	2.8	1,900	10.51	0:23:47	1.20
A10	2.5	15,400	9.41	0:7:38	1.22
11% Catalyst					
PF3	9.3	170	11.55	>10:0:0	1.17
A11	2.5	2,100	11.45	1:51:0	1.17
A12	2.5	3,400	11.40	1:25:0	1.18
A13	2.5	6,900	11.26	0:51:40	1.21
A14	2.5	9,100	10.06	0:20:36	1.22
A15	2.5	28,200	10.8	0:2:45	1.24

^a cps = counts per second; A = *Acacia catechu*.

Table 4.—Basic gluing conditions for different resins prepared with *Uncaria gambier* and *Acacia catechu* tannins.^a

Plywood parameters	Processing conditions
Veneer species	Sal (<i>Shorea robusta</i>)
Veneer thickness	1.5 mm
Veneer moisture content	7%–9%
Glue spread for:	
<i>U. gambier</i>	195–218 g/m ² , double glue line, solid basis
<i>A. catechu</i>	193–218 g/m ² , double glue line, solid basis
Panel assembly	3-ply
Pressing temperature	150°C ± 5°C
Pressing time	12 min
Pressing pressure	14 kg/cm ²

^a Plywood panels of 53.34 by 53.34 cm were made under the indicated laboratory conditions.

With an increasing molar ratio of tannin in PF resin, the viscosity of adhesives increased sharply as with a simultaneous increase of catalyst from 5 to 11 percent in both cases. Adhesives made from *A. catechu* tannin had greater viscosity than those made from *U. gambier* tannin (Figs. 5 and 6). This may have been due to *A. catechu* tannin extract having more nontannins (22.04%) compared with *U. gambier* tannin extract (20.08%). The presence of nontannin compounds such as hydrocolloid gums, which are hydrophilic and highly branched polysaccharides, in *A. catechu* tannin extract tends to promote high solution viscosities and affects the properties of tannin-based adhesives, particularly their moisture resistance (Sowunmi et al. 1996). The pH of the adhesives prepared using both tannins remained alkaline yet it decreased with increasing catalyst and molar ratio of tannin. This was due to the acidic nature of tannins used. The effect of viscosity was clearly reflected in the gelation

time of resin prepared from both of the tannins; the higher the viscosity, the lower the gelation time. Resins with more viscosity have higher polymerization because less time is required for complete polymerization during the determination of gelation time. The specific gravity of the resins prepared using both the tannins showed an increasing trend with an increase in molar ratio of tannins in PF as well as the catalyst. However, it was insignificant compared with the specific gravity of the control resin.

Glue shear strength

In IS 303 (Anonymous 1989), the average and the minimum values specified for boiling water resistance (BWR) grade plywood for glue shear strength are 135 and 110 kg in a dry state, 100 and 80 kg for the water resistance test, and 100 and 80 kg for the mycological test, respectively. Glue shear strength values of plywood prepared using different molar ratios of *U. gambier* and *A. catechu* tannins are reported in Tables 5 and 6.

Phenol-U. gambier tannin-formaldehyde resin.—Glue shear strength for dry, water resistance, and mycological tests of plywood samples using PF resin prepared by substituting phenol with 10 percent *U. gambier* tannin and 5 percent sodium hydroxide was found to be slightly lower (Table 5), except water resistance was slightly better compared with the average and minimum requirements for BWR grade plywood. Further, substitution of phenol with tannins not only lowered the glue bond in dry and mycological tests, but samples even delaminated in water resistance tests. These results may have been due to incomplete condensation of reactants, possibly due to the low concentration of the catalyst. With an increase in the catalyst from 5 percent to 8 and 11 percent (Table 5), glue bond improved considerably, to the extent that up to 50

Table 5.—Test results of glue shear strength of plywood made using phenol-formaldehyde (PF) and phenol-tannin-formaldehyde resins (*Uncaria gambier*).^a

Resin	Catalyst (%)	Glue shear strength failing load (kg)					
		Dry test		Water resistance test		Mycological test	
		Avg.	Min.	Avg.	Min.	Avg.	Min.
PF1	5	137	122	110	97	104	90
U1	5	125	106	108	100	95	85
U2	5	69	48	dl	dl	54	45
U3	5	99	95	dl	dl	85	85
U4	5	86	70	dl	dl	85	72
U5	5	83	60	dl	dl	83	72
PF2	8	141	132	112	97	105	97
U6	8	139	132	108	103	106	95
U7	8	136	130	115	95	112	97
U8	8	153	135	113	100	105	92
U9	8	138	130	118	109	107	100
U10	8	143	132	121	107	114	103
PF3	11	145	139	115	101	112	99
U11	11	138	128	117	107	105	102
U12	11	141	132	139	122	113	104
U13	11	137	127	102	95	97	92
U14	11	161	154	137	128	113	107
U15	11	158	151	110	92	107	102
IS 303 BWR grade		135	110	100	80	100	80

^a Avg. = average; Min. = minimum; U = *Uncaria gambier*; dl = delamination; BWR = boiling water resistance.

Table 6.—Test results of glue shear strength of plywood made using phenol-formaldehyde (PF) and phenol-tannin-formaldehyde resins (*Acacia catechu*).^a

Resin	Catalyst (%)	Glue shear strength failing load (kg)					
		Dry test		Water resistance test		Mycological test	
		Avg.	Min.	Avg.	Min.	Avg.	Min.
PF1	5	137	122	110	97	104	90
A1	5	106	82	95	90	95	85
A2	5	120	105	105	94	90	88
A3	5	110	95	103	85	101	98
A4	5	80	65	dl	dl	78	65
A5	5	85	72	dl	dl	79	72
PF2	8	141	132	112	97	105	97
A6	8	139	132	105	92	103	92
A7	8	136	129	104	93	100	92
A8	8	135	127	118	110	117	111
A9	8	123	100	88	82	87	75
A10	8	86	78	79	67	79	72
PF3	11	145	139	115	101	112	99
A11	11	141	134	112	98	107	100
A12	11	135	122	101	88	98	91
A13	11	139	122	116	92	100	89
A14	11	140	132	106	92	101	96
A15	11	123	117	96	89	94	86
IS 303 BWR grade		135	110	100	80	100	80

^a Avg. = average; Min. = minimum; A = *Acacia catechu*; dl = delamination; BWR = boiling water resistance.

percent phenol could be replaced with *U. gambier* tannin without any appreciable effect on glue bond.

Plywood prepared with a 50 percent substitution of phenol with *U. gambier* tannin also met the minimum and average requirements of glue shear strength specified for BWR grade of plywood in all respects.

Phenol-A. catechu tannin-formaldehyde resin.—Table 6 shows the results for glue shear strength in dry, water resistance, and mycological tests of plywood samples using PF resin prepared by substituting phenol with *A. catechu* tannin and 5 percent sodium hydroxide as the catalyst. The glue shear strength values were lower compared with the control, particularly in the dry state. Further, it was also observed that in the water resistance tests the values of glue shear strength met the requirements for BWR grade plywood made after 20 and 30 percent replacement of phenol with *A. catechu* tannin. Further, the replacement of

phenol with tannin resulted in delamination of the plywood during testing. However, with 30 percent replacement of phenol with tannin, only in the mycological tests did glue shear strength meet the requirements for BWR grade plywood.

Test results reported in Table 6 for glue shear strength in dry, water resistance, and mycological tests of plywood samples using PF resin with up to 30 percent of the phenol substituted with tannin and using 8 percent alkali as the catalyst indicate that the samples met the requirements for BWR grade plywood in all aspects.

Further, by increasing the concentration of alkali (the catalyst) to 11 percent, up to 40 percent of the phenol can be substituted with tannin without affecting the glue bond quality; this plywood meets the requirements for BWR grade plywood (i.e., minimum and average specified for

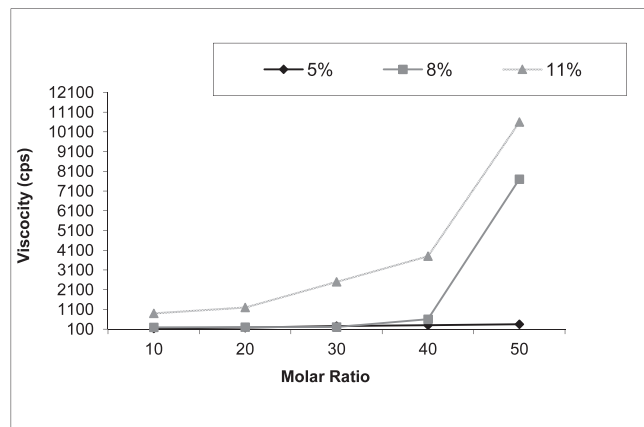


Figure 5.—Viscosity with respect to molar ratio of *Uncaria gambier* tannin.

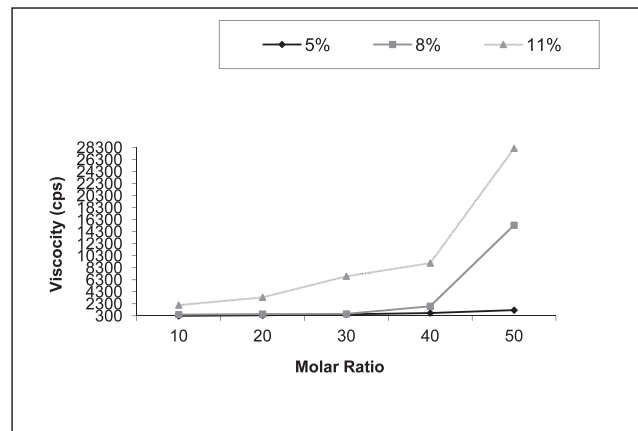


Figure 6.—Viscosity with respect to molar ratio of *Acacia catechu* tannin.

Table 7.—Mean values for comparison between control and treated samples.^a

Sample	5% Catalyst			8% Catalyst			11% Catalyst		
	DFTL	BWRFL	MTFL	DFTL	BWRFL	MTFL	DFTL	BWRFL	MTFL
Control	136.50	110.17	104.17	140.83	112.00	104.50	144.00	115.00	111.67
Treated	96.32	41.08	84.50	132.82	106.7	102.92	141.07	113.18	103.47

^a DFTL = dry testing failing load; BWRFL = boiling water resistance failing load; MTFL = mycological testing failing load.

glue shear strength in dry, water resistance, and mycological tests).

The substitution of phenol with tannin beyond 30 percent with 8 percent catalyst and 40 percent with 11 percent catalyst affected the glue bond adversely. It was also evident that an increase in catalyst from 5 to 11 percent in partially substituted PTF resin helped in the completion of the condensation reaction to a great extent. Further, the glue bond quality also improved with an increase in partial substitution of phenol with tannin and also with an increase in the catalyst concentration as with the *U. gambier* tannin-based adhesives.

Statistical analysis

The data of various parameters, dry testing failing load (DFTL), boiling water resistance failing load (BWRFL), and mycological testing failing load (MTFL), were subjected to analysis of variance (ANOVA) for 5, 8, and 11 percent alkali concentrations. From this analysis, we found a significant difference for 5 and 8 percent alkali concentrations from the standard (control) for all parameters in all effects. However, for 11 percent alkali concentration, the glue bond quality of treated plywood was on par with the standard for DFTL and BWRFL; for MTFL it was significantly different from the standard (Table 7). To evaluate the differences among alkali concentrations, all data were pooled excluding the performance of standard and analyzed. From this analysis it was observed that all major effects (i.e., alkali concentration, species, molar ratio), all possible two-factor interactions, and three-factor interactions were significantly different for all three parameters except the main effect of species for the BWR test (Table 8).

Conclusions

We observed that *U. gambier* tannin can be substituted for up to 50 percent of the phenol using 8 and 11 percent

sodium hydroxide as catalyst, and in the case of *A. catechu*, tannin can be substituted for up to 30 percent of the phenol using 8 and 11 percent sodium hydroxide as the catalyst for making BWR grade plywood meeting the requirements of IS 303 (Anonymous 1989) in all respects (i.e., glue shear strength in dry, water resistance, and mycological tests). We prepared PTF resin at 5, 8, and 11 percent alkali concentrations. The effect of pH on the rate of curing and polymerization of phenolic resin is well known. It is also widely accepted that at alkaline pH, the curing rate of phenolic nuclei as nucleophiles is strengthened by ionization of the phenol to form phenolate ions. PF resins are used as thermosetting wood adhesives, an application for which only PF resins of very high alkalinity, generally at pH values between 10 and 13, are used to impart faster reactivity and shorter pressing time to the adhesive. Further, it is also observed that *U. gambier* tannin is a better partial substitute of phenol compared with *A. catechu* tannin. This may be because of the presence of more nontannin compounds in *A. catechu* such as hydrocolloid gums that promote high solution viscosity and poor moisture resistance of tannin-based adhesives (Sowunmi et al. 1996).

Resin from both of these tannins with 8 percent alkali used as the catalyst results in glue bond quality of the plywood meeting the Indian Standard; thus, these tannins can be used for making resin. The use of 11 percent sodium hydroxide as the catalyst will increase the cost of resin; however, the statistical analysis of the results showed that 8 and 11 percent sodium hydroxide can be used as the catalyst. In the case of *U. gambier* tannin, up to 50 percent of the phenol can be replaced, and in the case of *A. catechu* tannin, up to 30 percent of the phenol can be replaced. Both yield comparable results for plywood meeting the IS 300 requirement. However, if 11 percent sodium hydroxide is used as the catalyst (with both tannins), results are comparable to the control and better than those with resin prepared using 8 percent sodium hydroxide as the catalyst.

Table 8.—ANOVA for different parameters.^a

Source	df	MSS ^b		
		DFTL	BWRFL	MTFL
Replication	5	149.72	190.25	392.51
All treatments	29			
Catalyst	2	34,028.75*	95,538.84*	6,992.11*
Species	1	2,304.09*	259.20	579.61*
Molar ratio	4	1,829.61*	9,174.79*	612.41*
Catalyst × species	2	2,540.91*	15,101.02*	1,611.17*
Species × molar ratio	4	2,423.45*	6,312.60*	1,199.91*
Catalyst × molar ratio × species	8	1,037.81*	3,368.15*	484.99*
Error	145	108.26	77.66	50.34

^a MSS = mean sum of squares; DFTL = dry testing failing load; BWRFL = boiling water resistance failing load; MTFL = mycological testing failing load.

^b * Significant at 5 percent.

As shown in Table 7, results of treated plywood (both tannins) are comparable to those of the control at 8 and 11 percent sodium hydroxide using all parameters. Consequently, tannins of *U. gambier* and *A. catechu* are successful partial substitutes for phenol in PF resin for making three-ply *S. robusta* boards.

Literature Cited

- Anonymous. 1983. Methods of test for plywood. IS 1734 (Parts I–XX). Bureau of Indian Standards, New Delhi. pp. 1–5.
- Anonymous. 1989. Specification for plywood for general purposes. IS 303. Bureau of Indian Standards, New Delhi. pp. 1–7.
- Freudenberg, K. and J. M. A. De Lama. 1958. Tannin catechins. *Annalen* 612:78–80.
- George, J. 1977. Economics of production of synthetic resin adhesives. *IPIRI J. Indian Plywood Ind. Res. Inst.* 7(2):48–71.
- Haslam, E. 1966. Condensed tannins analysis of extracts. In: *Chemistry of Vegetable Tannins*. Academic Press Inc., London. pp. 14–64.
- Hemingway, R. W. and G. W. McGraw. 1976. Southern pine bark polyflavonoids: Structure, reactivity and use in wood adhesives. *Appl. Polym. Symp.* 28:1349–1364.
- Pizzi, A. 1977. Hot-setting tannin-urea-formaldehyde exterior wood adhesives. *Adhes. Age* 20(12):27–35.
- Pizzi, A. 1980. Tannin-based adhesives. *J. Macromol. Sci. C* 18(2):247–315.
- Pizzi, A. (Ed.). 1983. *Wood Adhesives: Chemistry and Technology*. Marcel Dekker Inc., New York. pp. 105–178.
- Pizzi, A. 2008. Tannins: Major sources, properties and applications. In: *Monomers, Polymers and Composites from Renewable Resources*. M. N. Belgacem and A. Gandini (Eds.). Elsevier, Amsterdam. pp. 179–199.
- Pizzi, A. and D. G. Roux. 1978. The chemistry and development of tannin-based weather- and boil-proof cold-setting and fast-setting adhesives for wood. *J. Appl. Polym. Sci.* 22:1945–1954.
- Pizzi, A. and H. O. Scharfetter. 1978. The chemistry and development of tannin-based adhesives for exterior plywood. *J. Appl. Polym. Sci.* 22:1745.
- Pizzi, A., H. Scharfetter, and E. W. Kes. 1981. Adhesives and techniques open new possibilities for the wood processing industry. *Holz Roh-Werkst.* 39:85–89.
- Rossouw, D. du T. 1978. *Outwikkeling van denneloostoffe*. Special Report Hout 137. CSIR, Pretoria, South Africa.
- Schroeder, H. 1976. *Pine tannin adhesives*. Special Report Hout 120. CSIR, Pretoria, South Africa.
- Sowunmi, R., O. Ebebele, A. H. Conner, and H. River. 1996. Fortified mangrove tannin-based plywood adhesives. *J. Appl. Polymer Sci.* 62:577–584.