Polyphenolic Extracts of *Pinus radiata* Bark and Networking Mechanisms of Additive-Accelerated Polycondensates

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ABSTRACT: The use of various chemicals for extracting polyphenolic fractions (tannins) from *Pinus radiata* bark was examined with the aim of obtaining high yields of high-quality tannins to be used as wood adhesives. Extractions carried out under very highly alkaline conditions (pH > 10.5) gave relatively high yields but also excessive viscosity values even in 30% (w/w) solutions, and this demonstrated their inability to function as wood adhesives. Solutions (30% w/w) of mildly extracted (pH < 8.3) fractions gave workable viscosity values and were used in a subsequent study. A rapid acceleration effect was observed in these fractions when ammonia was used as a catalyst. Solid-state, cross-polarization/magic-angle-spinning ^{13}C-NMR of the cured samples showed evidence proving the existence of benzyl amine bridging networks in their hardened state. Simultaneously accelerated copolymerization could be observed in phenol–resorcinol–formaldehyde/*P. radiata* bark tannin mixtures with the addition of ammonia, as indicated by viscosity measurements. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2487–2493, 2007

Key words: adhesives; gelation; gels; NMR; renewable resources

INTRODUCTION

Because of its high reactivity and slow solubility, the processing of *Pinus radiata* tannin for commercialization has been a slow process. *P. radiata* tannins[1] are considerably more reactive toward hardeners than mimosa or quebracho because of their more reactive phoroglucinolic A-ring in their monomeric flavonoid structure. *P. radiata* tannins have a much higher average degree of polymerization than mimosa tannins, that is, 11 versus 4–5 (a molecular weight of 3200 vs a molecular weight of 1250). *P. radiata* tannins[1] have a much lower extraction yield than mimosa, that is, 13–15 versus 30–33%. The reaction parameters that affect the extraction process with respect to the quality and quantity of *P. radiata* bark tannins and tannin fractions have been investigated in detail and are reported in this article. Furthermore, an attempt has been made to quantify its hardening mechanisms with commonly used accelerators by rheological measurements as *P. radiata* tannin adhesives can be used as very good substitutes for phenol–resorcinol–formaldehyde (PRF) resins in glulam and finger-jointing applications; the results are reported here.

PRF resins have been used in the manufacture of cold-setting wood adhesives for many decades.[2–4] Resorcinol-based adhesives have excellent properties, such as high bond strength, high water resistance, and long-term durability.[5–8] Resorcinol is a synthetic chemical species that imparts to a PRF system its characteristic uniform performance and accelerated and improved crosslinking at the ambient temperature upon the addition of a hardener. However, resorcinol is an expensive chemical, and as a result, the majority of the cost of the wood-bonded product is associated with the resin component rather than the accelerator. If renewable polyphenolic substances, such as tannins, could effectively partially or fully replace resorcinol in a system, there could be economic advantages; therefore, tannins have been subjected to study in this project.

EXPERIMENTAL

Tannin extraction

An air-dried and finely ground 2-mm-mesh powder of *P. radiata* bark (200 g) was transferred to a 2-L, round-bottle flask. Distilled water (1.4 L) and various chemicals or combinations of chemicals (as listed) were charged. A water condenser was connected to the flask, and the suspension was heated gently just below 100°C for 1 h and then refluxed for another 2 h. After heating, the extract was cooled, centrifuged, and filtered through glass wool or filter paper. Water

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TABLE I
Effects of Chemicals on the Extraction Yield of *P. radiata* Tannins Obtained by UV Absorption Measurements

Chemical	pH of the medium	Theoretical yield on a dry bark basis (%)
Water	6.5	11.1
Na_2SO_3 (2.2%)/urea (2.2%)	6.8	18.1
Na_2SO_3 (4%)/Na_2CO_3 (0.4%)	8.3	23
Na_2CO_3 (4.4%)	10.5	26.08
NH_4OH (4.4%)	11	29.4
NaOH (4.4%)	14	35.2

evaporated at a moderate temperature, and a dry powder was prepared and used for the subsequent analysis. The following chemicals and percentages were used in the extraction process: (1) Na_2SO_3 (4%)/Na_2CO_3 (0.4%), (2) Na_2SO_3 (2.2%)/urea (2.2%), (3) Na_2CO_3 (4.4%), (4) NH_4OH (4.4%), (5) NaOH (4.4%), and (6) water.

Ultraviolet–visible (UV–vis) spectroscopy

A standard curve was prepared with the aid of a Varian 634 UV–vis scanning spectrophotometer (Varian Inc., Palo Alto, CA) by the measurement of the absorbency (at 330 nm) of a series of *P. radiata* tannin solutions of known concentrations. The resultant curve obeyed the Beer–Lambert law, and this method was extended to determine the polyphenolic matter content after successive dilution of the extracted *P. radiata* tannin solutions.

Gel-time measurements

About 10 g of a 30% (w/w) *P. radiata* tannin solution was studied. A 10%, finely powdered form of *para*-formaldehyde and/or 2% (w/w) ammonia on a dry and solid tannin matter content basis was added to a test tube and placed in a water bath, which was maintained at boiling (just below 100°C) at normal atmospheric pressure. The time taken to reach the gel point was recorded during constant stirring with the aid of a wire spring and a stopwatch. The test was duplicated, and the average value was reported.

Viscosity measurements

To investigate the acceleration effect of ammonia on *P. radiata* tannins, the viscosity of *P. radiata* tannin/NH_3/HCHO adhesive resin mixtures and the pot life of the blends were measured with the aid of a Brookfield viscometer (Brookfield Engineering Laboratories, Middleboro, MA) with LV-1, LV-2, and LV-3 spindles. Here a 10% (w/w), finely powdered form of *para*-formaldehyde and/or 1 or 2% (w/w) ammonia was added to about 5 g of a 30% *P. radiata* tannin solution.

After vigorous stirring, this homogeneous adhesive resin mixture was immediately transferred into the viscometer, and the viscosity-advancement data collection was initiated. The time gap between the ammonia addition and data collection (in seconds) was noted and taken into account for data correction. All viscosity measurements were performed at the ambient temperature of approximately 24°C.

Stiasny number measurement test

After the gravimetric measurement of the moisture content, about 100 mg of a solid *P. radiata* tannin sample, 1 mL of 10*M* HCl, and 2 mL of 36–38% formaldehyde were mixed together and refluxed for 30 min. The reaction mixture was filtered while hot through a sintered glass (filter no. 3). The precipitate was washed with hot water (5 × 10 mL) and dried at 100°C for 2 h. The yield was expressed as a percentage of the weight of the starting sample.

^{13}C-NMR spectra

Solid-state, cross-polarization/magic-angle-spinning (CP–MAS) ^{13}C-NMR spectra of each sample were obtained on a Bruker MSL 300 Fourier transform NMR spectrometer (Bruker Bio Spin GmbH, Rheinstetten, Germany) at a frequency of 75.47 MHz with a sample spin at 4.0 kHz. The chemical shifts were calculated with respect to $(CH_3)_3Si(CH_2)_3SO_3Na$ for NMR control. The acquisition time was 0.026 s, and the number of transitions was about 5000. All spectra were run with a relaxation delay of 5 s and were accurate to 1 ppm with a cross-polarization time of 1 ms and a spectral with of 20,000 Hz.

DISCUSSION

The extraction yields of tannins from bark depend on the time that elapses between the removal of the bark from the tree and its use in the extraction process (freshness). The age of the tree also plays a major role. Barks from different locations and after different periods of storage also affect the yield; therefore, all these factors have been kept constant. The extraction yield mainly depends on a number of factors,[9,10] such as the solvent, duration of extraction, particle size of the bark fraction, and pH. A multiple-step squeeze-extraction process with hot water and aqueous NaOH

TABLE II
Stiasny Values of Selected Tannin Extracts from *P. radiata* Bark

Bark extract	Stiasny value
Water	63.85
Na_2SO_3 (4.0%)/Na_2CO_3 (0.4%)	60.1
Na_2SO_3 (2.2%)/urea (2.2%)	59.72

TABLE III
Gel Times of 30% (w/w) *P. radiata* Tannin Solutions Measured at 94°C
with Various Reagents

Extraction solvent	pH of a 30% solution	Gel time (s)	
		10% HCHO	10% HCHO/2% NH$_3$
Na$_2$SO$_3$ (4%)/Na$_2$CO$_3$ (0.4%)	6.95	52	32
Na$_2$SO$_3$ (2.2 4%)/urea (2.2%)	5.4	170	56
Water	3.7	175	68

has resulted in high-yield but low-adhesive-property products.[11] Therefore, the use of these chemicals should be minimized if not much smaller proportions have to be used to obtain productive results. It has been postulated that the major components of these extracts (procyanidin polymers) change during the extraction process and lose their reactivity. Furthermore, it has been suggested that the use of highly alkaline conditions leads to solubilized bark lignin fractions as well.[11,12] Even mildly alkaline conditions during extraction promote the hydrolysis of waxes and fats to produce soaps that cause adverse effects in end-use applications.[13]

The introduction of a —SO$_3$H group to tannin has some advantages.[14] The introduction of urea also has some advantages, such as an increase in the extraction yield of pine tannins. Pine tannins are highly sensitive to autocondensation even under mildly acidic conditions and at mild temperatures. The formation and precipitation of phobaphenes during the sulfite/water extraction of pine tannins from pine bark has therefore been minimized by the blocking of tannin self-condensation by the addition of low-cost nucleophiles such as urea.[14]

The absorption values of diluted fractions of tannin solutions were measured at 330 nm, and the concentrations of the original solutions were calculated and are reported in Table I. The results indicate that with an increase in the pH of the medium used for the extraction, there was a gradual increase in the extraction. Hot-water extraction produced the lowest yield. However, even 30% (w/w) solutions extracted under very highly alkaline conditions (pH > 10.5) were very thick pastes, and so it was not possible to do any work with these fractions. However, a comparative analysis could be made for the yields, so the results are reported here. It has therefore been demonstrated that the use of chemicals in high proportions causes a high pH in the medium, and this is not good enough for any further experimental work.

Most of the reagents used in this study have been used to extract tannins in the past by some other researchers, but in much lower proportions, such as NaOH in the range of 0.01–1.0% and in some cases up to a maximum of 1.78%, with very poor adhesive properties.[8,10] NH$_4$OH has been used[12] in the range of 0.02–0.4%, and Na$_2$CO$_3$ has typically been used at a concentration of approximately 1% (w/w).
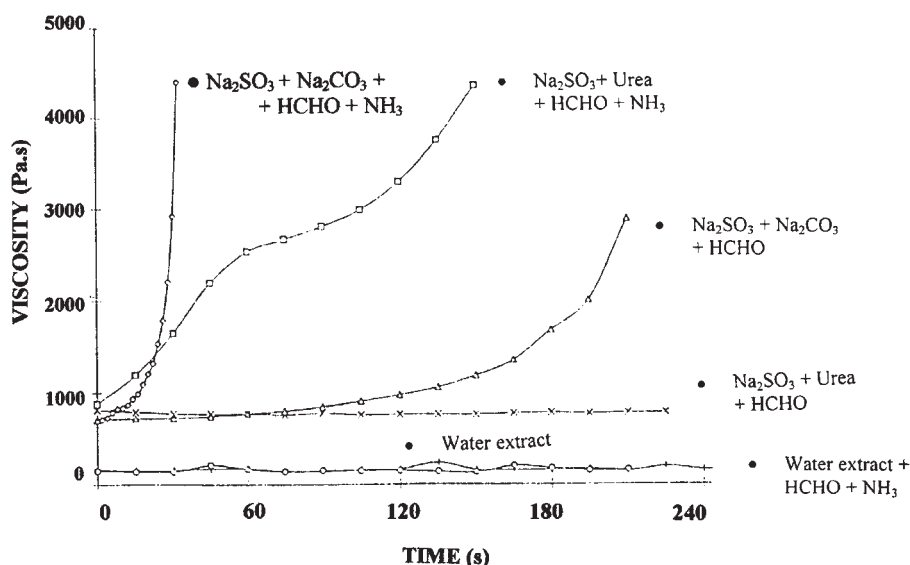

Figure 1 Gradual increase in the viscosity patterns of 30% (w/w) tannin solutions with the addition of either 10% HCHO or 10% *para*-formaldehyde/2% NH$_3$ at the natural pH values and the ambient temperature.

The adhesive property of a polyphenolic compound depends on the active functional groups present. The higher the number is of active phenolic groups, the greater the crosslinking capacity is and therefore the greater the strength is of the cured glue line. The Stiasny number can be used for comparison. The determination of the active polyphenolic component has indicated that there is no greater difference in this value for all the extracts (Table II).

Gelation is defined as the point at which the polycondensates formed by the reaction of a tannin extract and accelerators form a viscous liquid and become a soft, elastic, rubbery solid. This is an indication of the reactivity of the sites of a tannin molecule and can be used for structural characterization for the adhesive. The gradual increase in the pH of the medium causes a gradual decrease in the gel time as long as constant proportions of the accelerators are used. The results in Table III indicate that there is a drastic reduction in the gel time when ammonia is present as a catalyst, indicating the vast acceleration potential of NH_3 for tannins.

By studying the viscosity patterns in Figures 1 and 2 and the differences in the solid-state, CP–MAS ^{13}C-NMR tannin spectra (Figs. 3–6), it is possible to make the following observations:

1. Water-extracted pine tannin shows no ambient-temperature curing properties with either *para*-formaldehyde or a mixture of *para*-formaldehyde and ammonia. Its low pH and hence low reactivity might be the reason (Fig. 1).
2. There is no reaction whatsoever between tannin and NH_3 when HCHO is not present (Figs. 3 and 4; that does not mean that there is no reaction).
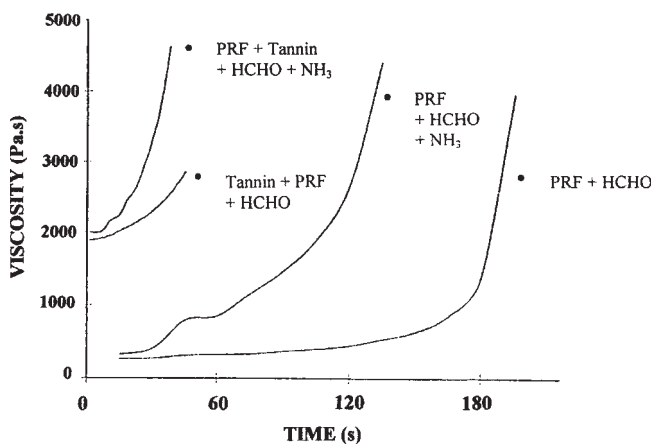

Figure 2 Gradual increase in the viscosity patterns of a commercial PRF resin (50% w/w) and a 1:1 (w/w) PRF resin (50% w/w)/pine-tannin extract (40% w/w) mixture measured with the addition of either 10% *para*-formaldehyde or 10% *para*-formaldehyde/1% NH_3 at the natural pH values and the ambient temperature.
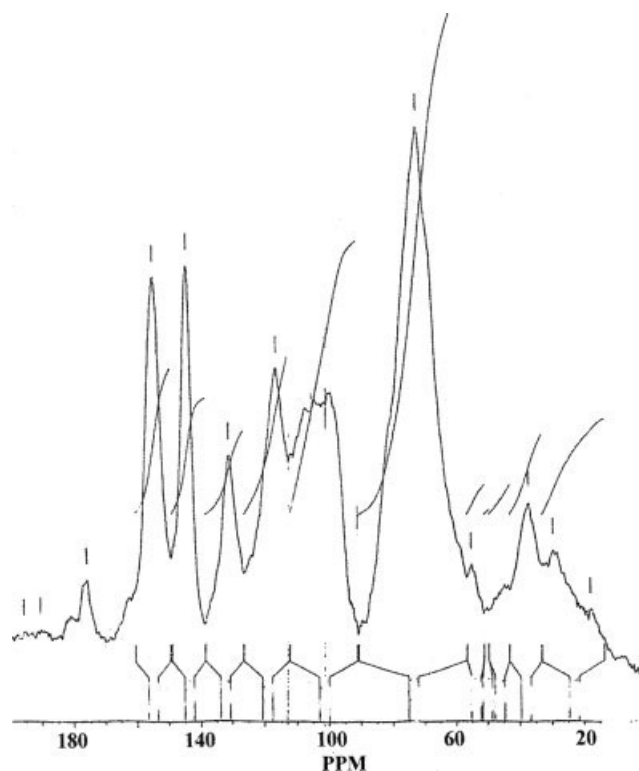
Figure 3 Solid-state, CP–MAS ^{13}C-NMR spectrum of a 30% Na_2SO_3 (4%)/Na_2CO_3 (0.4%) extracted pine-tannin solution (at its natural pH value of 6.95) hardened by the addition of 10% *para*-formaldehyde/6.5% ammonia at the ambient temperature (after the gelation product was dried for several days at the ambient temperature).

3. The Na_2SO_3 (2.2% w/w)/urea (2.2% w/w) extract has not shown any ambient-temperature curing properties with *para*-formaldehyde (Fig. 1). However, after the addition of 2% (w/w) ammonia, a relatively slow advancement of the viscosity has been found (Fig. 1). The presence of an already chemically bonded N atom in the tannin molecule might retard the acceleration effect to a substantial extent, as observed. Here NMR spectra clearly indicate the formation of benzyl amine bridges by the peaks in the range of 100–120 ppm (Fig. 5).
4. The Na_2SO_3 (4.0%)/Na_2CO_3 (0.4%) extract is the only pine-tannin formulation that has demonstrated ambient-temperature curing properties solely with *para*-formaldehyde (Fig. 1). In this case, after the addition of 2% (w/w) ammonia causes a rapid advancement in the viscosity, no chemically bonded N atoms are present in the tannin molecule; hence, it might cause the rapid acceleration effect observed (Fig. 1). In addition, there is a gradual increase in the pH of the medium as well.

The acceleration of any phenolic-type resin by ammonia (and amines) is not new but is well known. The
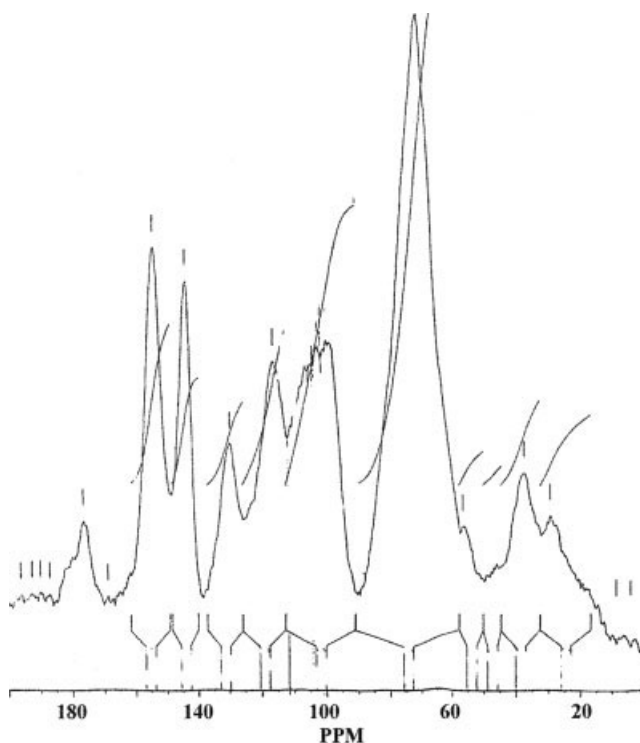
Figure 4 Solid-state, CP–MAS ^{13}C-NMR spectrum of a 30% Na$_2$SO$_3$ (4%)/Na$_2$CO$_3$ (0.4%) extracted pine-tannin solution (at its natural pH value of 6.95) hardened by the addition of 6.5% ammonia (only) at the ambient temperature (after the gelation product was dried for several days at the ambient temperature).
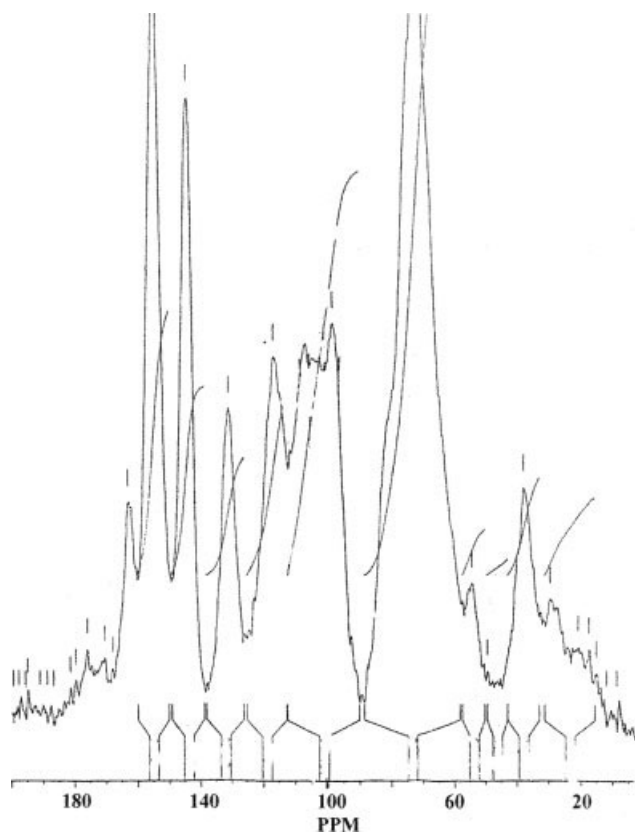

Figure 5 Solid-state, CP–MAS ^{13}C-NMR spectrum of Na$_2$SO$_3$ (2.2%)/urea (2.2%) extracted pine tannin (at its natural pH value of 5.4).

observed acceleration is due to the simultaneous formation of HO—CH$_2$—NH—CH$_2$—OH and $^+$CH$_2$—NH—CH$_2$$^+$ before the formation of hexamethylenetetramine leading to benzyl amine bridges, and further acceleration is caused by the increase in the pH due to the addition of ammonia.

With the addition of *para*-formaldehyde or *para*-formaldehyde and ammonia simultaneously to a tannin solution mixture, it is possible that either HCHO or ammonia can preferably add to any of the macromolecules, and this is followed by secondary reactions. A classical mechanism for the process is given in Figure 7.

The Na$_2$SO$_3$ (4.0%)/Na$_2$CO$_3$ (0.4%) extract was the only extract that demonstrated ambient-temperature curing properties with *para*-formaldehyde and therefore was chosen for further study. The tannin/PRF resin (1 : 1 w/w) solid content was maintained and used for subsequent analysis because this could lead to a recipe for the formation of a tannin–resorcinol–formaldehyde copolymer. The initial differences in the viscosity values of the two mixtures are clearly visible in Figure 2. Pine tannins extracted with Na$_2$SO$_3$ (4.0%)/Na$_2$CO$_3$ (0.4%) had higher reactive properties than PRF resins, and this may have been due to the
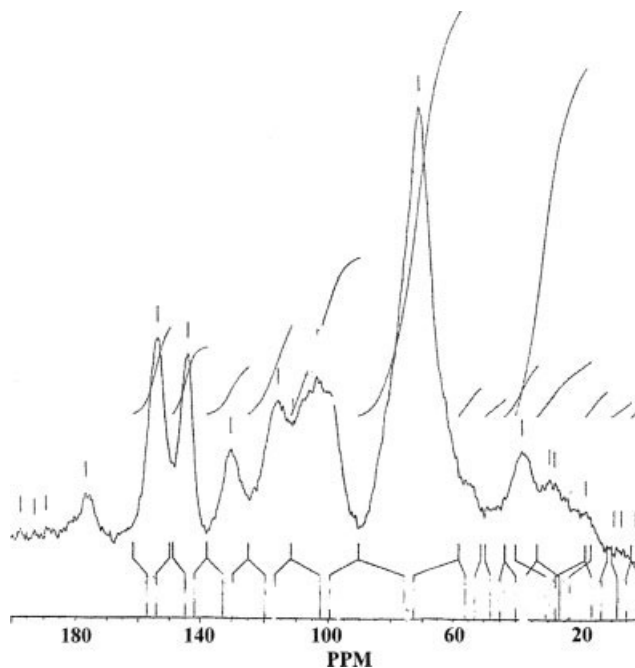

Figure 6 Solid-state, CP–MAS ^{13}C-NMR spectrum of a 30% Na$_2$SO$_3$ (4%)/Na$_2$CO$_3$ (0.4%) extracted pine-tannin solution (at its natural pH value of 6.95) hardened by the addition of 10% hexamine (only) at the ambient temperature (after the gelation product was dried for several days at the ambient temperature).
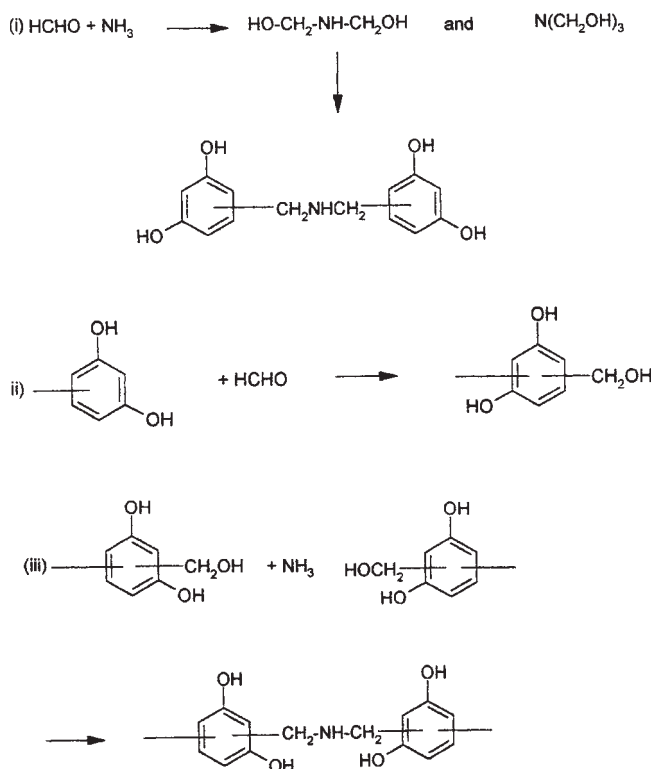
Figure 7 Classical mechanism for the addition of ammonia/formaldehyde to polyphenolic molecular fragments.

presence of a phoroglucinolic A-ring in the tannin molecule (Fig. 2).

The addition of ammonia to a tannin molecule is most likely to take place via interflavonoid bond cleavages, which prodelphinidin-type tannins undergo in acidic or alkaline environments; they are thus present in pine-bark tannins. A mechanism has been suggested[14] for the addition of urea to a tannin molecule, and the same could be extended here as well. However, urea is a weaker base than ammonia, so when urea reacts with a carbocation center, only one H atom is eliminated, and a tannin–NH—CO—NH$_2$ product is produced. This reduces the self-condensation possibility of the tannin molecule and improves the extraction yield. After the first step, the reactivity

of the urea molecule is greatly reduced because of the alternation of its electronic environment.

Amazingly, urea instead appeared to have reacted, though to a small extent: the $\delta = 107–102$ ppm peaks appear to be much bigger, and the urea peak is at $\delta = 162.8$ ppm, which might indicate that this is at best a monosubstituted urea (Fig. 5). For confirmation, CP–MAS ^{13}C-NMR of solid urea was run separately, and urea gave a single, sharp peak between 163 and 165 ppm. This confirmed that urea reacted to a —C$_2$ position of the tannin molecule.

Ammonia, being a strong base with a single, lone pair of electrons, can react with a carbocation atom on a tannin molecule. At high pH values, the reactivity of the nitrogen center in the resultant tannin–NH$_2$ complex cannot be altered to a great extent. Thus, the reactivity of the tannin–NH$_2$ molecule can be almost as high as that of ammonia. Therefore, there may be a high possibility that a second tannin molecule can react with the complex to form tannin–NH–tannin complexes. This might proceed up to three tannin molecules bonded to a single ammonia molecule [(tannin)$_3$N]. The steric hindrance effect also must be considered here in this respect.

It can be suggested that a pholoroglucinolic-type A-ring couple with cold, aqueous ammonia gives 5-amino-resorcinol and a 3,5-diamino phenolic A-ring. Therefore, there is a strong possibility that this reaction proceeds here as well. If so, ammonia might directly add to the pholoroglucinolic A-ring of the pine tannin, giving mono- and diamino products, followed by secondary reactions.

Hexamethylenetetramine appears to not react with tannins at room temperature (Fig. 6) as the decomposition of hexamethylenetetramine[15] to methylene bases ($^+$CH$_2$—NH—CH$_2^+$) starts only at $\pm65°$C. After this temperature, massive amounts of benzyl amine bridges are formed, as shown in Figure 6.

The simultaneous addition of ammonia and *para*-formaldehyde is also known to result in the formation of hexamethylenetetramine and is believed to proceed via a transient methylene intermediate. However, at the ambient temperature, this reaction is not favor-

TABLE IV
Strength and Wood Failure of Green-Wood/Wood Joints Bonded with
PRF/Pine-Tannin Separate-Application Adhesives

Green-wood/wood joints	Mechanical strength of component B (*P. radiata* tannin solution) at pH 12	
	NaOH	NaOH/NH$_3$
Dry (N/mm^2)	3770 (90)	3800 (100)
After 24 h of soaking in cool water, tested wet (N/mm^2)	2232 (78)	2800 (87)
After 2 h of boiling, tested wet (N/mm2)	2712 (85)	2715 (86)

The *P. radiata* tannin was extracted with Na$_2$SO$_3$ (4%)/Na$_2$CO$_3$ (0.4%). The percentages of wood failure are indicated in parentheses.

able. In addition to the three proposed mechanisms, the slow, traditional methylolation of the A-ring with the addition of *para*-formaldehyde, followed by secondary reactions, is present all the time, even at the ambient temperature.

The results in Table IV show laboratory-scale beech-strip trial results for green-wood/wood joints bonded with PRF (component A)/pine-tannin (component B) honeymoon adhesive systems for separate applications. The pine tannin extracted with Na_2SO_3 (4.0%)/Na_2CO_3 (0.4%) was selected for this study. A comparison of the mechanical strength and wood failure indicates an improvement with this new system.

CONCLUSIONS

A *P. radiata* bark tannin extraction process has been studied with various chemicals. The theoretical yields have been calculated with UV absorption measurements. The use of highly alkaline conditions for the extraction process produces extracts of poor quality. Ambient-temperature viscosity-advancement measurements of the extracts indicate a rapid acceleration effect with ammonia. There can be mechanical and economic advantages when ammonia is incorporated as component B of PRF/pine-tannin honeymoon adhesive systems.

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