

Pyrogallol–Formaldehyde Thermosetting Adhesives

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ABSTRACT: A new thermosetting wood adhesive system from pyrogallol has been developed. Pyrogallol can be easily obtained from tara pods (*Caesalpinia spinosa*) a native leguminosae of low cost widely distributed in Peru. In this work, polymerization of formaldehyde with pyrogallol was carried out at different pH values and optimal conditions were determined to establish the adhesive formulation. The reactivity of this resin was characterized by differential scanning calorimetry (DSC) and the results were compared with those obtained with resins made with tara tannin, gallic acid, and phenol. The results show that tara tannin and gallic acid are less reactive due to the presence of deactivating groups (i.e., carboxylates) in the phenolic moieties while their polymerization is limited to that of a bidimensional network upon curing. In contrast, pyrogallol–formaldehyde kinetic parameters (E_a and ΔH) were determined and they are comparable with those of phenol–formaldehyde adhesives. In addition, mechanical property values (MOR, MOE, and IB) of particleboards prepared with pyrogallol–formaldehyde compare favorably to those of Canadian standard requirements (CSA). Main assets of the new thermosetting adhesive is lower pressing times and temperatures than those currently used in the industry. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 399–408, 1997

Key words: tara tannin; gallic acid; pyrogallol; differential scanning calorimetry; particleboards

INTRODUCTION

The cost of phenolic adhesives has increased by 35% since the beginning of 1994. The principal factor responsible for this major increase is the high demand for Bisphenol A, a basic feedstock for polycarbonates used in computers and compact disks.¹

Phenolic resins can be synthesized both in acidic and alkaline conditions.² Acid-catalyzed resins are called novolacs. Their formaldehyde/phenol (F/P) ratios are 0.75 to 0.85 and all their chains are phenol-terminated. Before crosslinking

takes place, they behave like thermoplastics. Addition of formaldehyde to novolacs initiates cure and crosslinking. Alkaline-catalyzed phenolic resins are called resoles. Their F/P ratio is larger than 1, and they can cure by themselves. Phenol–formaldehyde resole resins are considered to be thermosetting resins.

There are two steps leading to formation of PF resole resins: methylation and condensation reactions.

The first step, methylation, is an electrophilic aromatic substitution reaction and, consequently, the products obtained will be substituted in *ortho* and *para* positions. The presence of a second or third activating group as in the case of resorcinol or phloroglucinol [Fig. 1(b) and 1(c)] will activate even more the original phenol [Fig. 1(a)]. The second step is a condensation reaction, where a methylol group of one molecule reacts with a sec-

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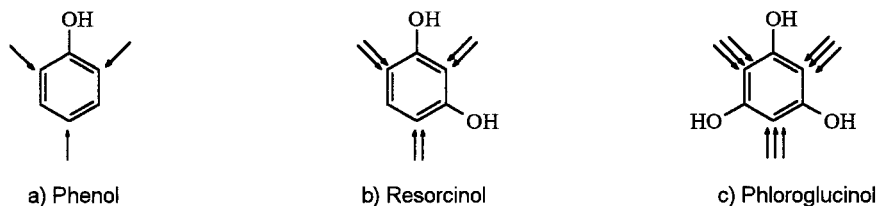


Figure 1 Directing and activating effects in (a) phenol, (b) resorcinol, and (c) phloroglucinol.

ond phenol, releasing a water molecule, thus forming a methylene linkage. Further condensations result in polymerization to obtain the thermosetting resol.

The most important renewable resource to replace phenol in wood adhesives are tannins.³ Formulations used in the industry are based on condensed tannins of resorcinolic type [Fig. 2(a)]: wattle^{4,5} and quebracho⁶ or phloroglucinolic type [Fig. 2(b)]: pine⁷⁻⁹ and pecan.^{10,11} They have, respectively, two and three activating oxygenated groups, and it is well known that pine and pecan tannins are among the most reactive of all tannins.⁷

The resorcinolic or phloroglucinolic moiety determines the reactivity towards formaldehyde and, consequently, their potential to crosslink. The rate of this reaction is enhanced 8- to 35-fold compared to that of phenol-formaldehyde reaction.¹⁰ This limits the formation of methylol groups, as these will condense with other tannin phenolic nuclei in a very short time. As such, methylolated intermediates are not stable and their shelf life is far too short, which represents a problem in industrial applications.

Previous work on hydrolyzable tannins¹² showed that even though these tannins are not really as reactive as condensed tannins, they form an interesting starting material for pyrogallol synthesis and thus could replace phenol in phenol-formaldehyde adhesives or work as cure accelerator for these adhesives.

Pyrogallol is obtained easily from hydrolyzable

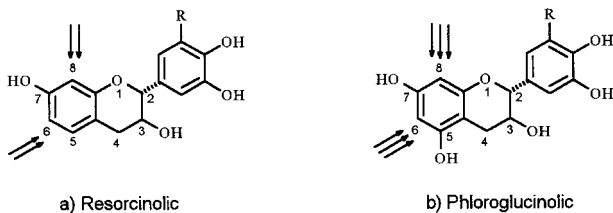
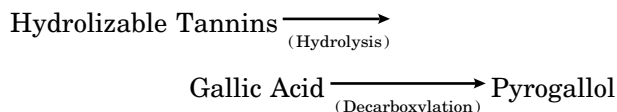


Figure 2 Resorcinolic and phloroglucinolic moieties.

tannins by two consecutive transformations, as follows:



Gallic acid was obtained in 25% yield (anhydrous base) by alkaline hydrolysis of tara pods (*Caesalpinia spinosa*), a native leguminosae widely distributed in Peru.¹² Decarboxylation of gallic acid to pyrogallol (not included in the present work) can be achieved by chemical¹³ or enzymatic methods,¹⁴ the latter with 98.5% conversion.

Gallic acid [Fig. 3(a)] consists of an aromatic ring bearing a carboxyl group (position 1) and three adjacent hydroxyl groups (positions 3, 4, and 5), leaving two free sites on the ring. Reactivity considerations show that the hydroxyl functions in 3 and 5 activate the free positions while the remaining groups deactivate them. The overall effect is that gallic acid possesses an enhanced reactivity toward electrophilic aromatic substitution, compared to phenol, while not being as reactive as phloroglucinol. The carboxylic group, besides deactivating the molecule towards formaldehyde, limits the amount of methylol formations to two per molecule, which leads to linear macromolecules.

In the case of pyrogallol [Fig. 3(b)], there are

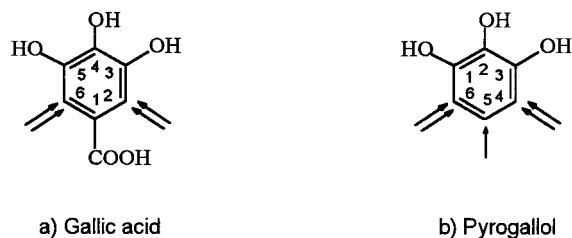


Figure 3 Directing and activating effects in (a) gallic acid and (b) pyrogallol.

three hydroxyl groups (positions 1, 2, and 3) that enhance the reactivity of positions 4 and 6. The remaining position (5) would have the same degree of activation as phenol. These three possible reactive sites permit the eventual formation of a tridimensional network during polymerization as in the case of phenol. Following this approach, the reactivity of pyrogallol should be intermediate between those of resorcinolic and phloroglucinolic moieties,¹⁵ i.e., between that of tannins that work well and tannins that do not work as well in the manufacture of wood adhesives. Thus, we decided to study the reactivity of pyrogallol in the synthesis of pyrogallol-formaldehyde adhesives.

The following presents polymerization of formaldehyde with pyrogallol at different pH values and kinetic parameters obtained by differential scanning calorimetry (DSC). Optimal conditions (pH = 7.31, solid contents = 49%) were determined and compared with those of tara tannin, gallic acid, and phenol, previously determined.¹² Particleboards were prepared in current conditions applied in industry and mechanical properties obtained are comparable to those obtained with phenol-formaldehyde adhesives.

EXPERIMENTAL

Materials

Plant material and chemical were commercially available: fruits pods of *Caesalpia spinosa* (tara) from a local market (Ayacucho, Peru); phenol (90% in water), Anachemia; para-formaldehyde, BDH; pyrogallol, Anachemia, and gallic acid (97% purity; 1.44% moisture), Sigma. All the chemicals were reagent grade and were used without any further purification.

Moisture Content (Karl-Fischer Method)

The samples of tara powder, tara tannin, and extracted gallic acid were analyzed with a Metrohm E 547 automatic Karl-Fischer titrator utilizing a dead stop endpoint method. The titrator had an attached E 415 Multi Dosimat motor-driven piston burette with drum counter indicator. Samples (200 mg) were introduced into the titration vessel and dispensed into the middle of the vessel solution, taking care not to allow the sample to cling to the walls of the vessel. The titration was monitored by the continuous measurement of current flow in the solution and was terminated when the

current reading was greater than 15 mA for 30 s. The volume of titrant V displayed in milliliters was used to calculate the water content in the analyzed sample as follows:

$$\% \text{H}_2\text{O} = 100 \times V \times \text{titer/sample wt (mg)}$$

where titer is the weight (mg) of water that reacts with 1 mL of Karl-Fischer reagent.

Tara Tannin from Tara Pods¹²

The tara pods were air dried and ground to a powder in a Wiley mill (60-mm screen). The powder was then extracted for 1 h with water (1 : 4 w/v) at 65°C. The extract was vacuum filtered through celite and spray dried to obtain tara tannin (53.1% gallic acid and 9.7% moisture).

Extraction of Gallic Acid from Tara Powder¹²

Tara powder (40 kg; 9% moisture) was extracted for 6 h with demineralized water (1 : 10 w/v) at 60°C. The extract was vacuum filtered through celite and concentrated under vacuum at 60°C to one-tenth of its original volume. Hydrolysis was carried out with 48% NaOH (1 : 1.5 v/v) for 6 h at 102°C. The solution was cooled at 30°C and neutralized with 60% H₂SO₄. Adjusting pH at 2 and cooling to 10°C initiated crystallization of crude gallic acid (11 kg). Recrystallization from demineralized water with activated carbon (3 : 11 w/w) yielded pure gallic acid (8.9 kg; 97% HPLC purity; 1.48% moisture and 25% yield from tara pods, anhydrous base).

Tara Tannin-Formaldehyde: Resin a

A solution of tara tannin (50 g equivalent to 23.98 g of gallic acid; 0.141 mol), demineralized water (40 mL) and NaOH solution (50% w/w; 15 mL) were mixed with stirring and allowed to react for 15 min. Then (9.26 g; 0.308 mol) were added (temperature raised to 35–40°C) and the pH was adjusted to 8.86. In this preparation a molar ratio of 2.2 : 1 (formaldehyde : equivalents of gallic acid) was maintained and reaction time was fixed at 10 min. After cooling to room temperature, samples were taken for analysis.

Gallic Acid-Formaldehyde: Resin b

A solution of gallic acid (25 g; 0.140 mol) in demineralized water (35 mL) and NaOH solution (50%

w/w; 12 mL) was heated to 60°C with mechanical stirring. Then paraformaldehyde (9.26 g; 0.308 mol) were added and the reaction mixture was heated at this temperature for 15 min. After cooling to room temperature, samples (pH = 8.1, $T = 22^{\circ}\text{C}$) were taken for analysis.

Pyrogallol-Formaldehyde: Resin c

A stirred solution of pyrogallol (40 g; 0.317 mol) in demineralized water (44 mL) was heated to 30°C. The appropriate amount of NaOH solution (50% w/w) was added to adjust the pH at different values. When the reaction mixture was completely solubilized, paraformaldehyde (19 g, 0.633 mol) were added. Solutions at different pH were reacted for 10 min at 60°C. The reaction mixture was cooled to room temperature and samples were taken for analysis.

Phenol-Formaldehyde: Resin d

Phenol-formaldehyde was prepared by combining (1 : 1) a low molecular weight resin and a high molecular weight resin according to the procedure described by Chiu.¹⁶

Low Molecular Weight Resin

Aqueous phenol solution (90% w/v; 240 g, 2.39 mol), para-formaldehyde (151.8 g, 5.06 mol) and water (202.4 mL), were mixed with mechanical stirring and heated. Sodium hydroxide (15.75 g) was added as an aqueous solution (50% w/v) in a 10-min period, while the temperature reached 100°C. After 3 min reaction time, the mixture was cooled to 65°C and maintained at this temperature until viscosity A-B in the Gardner-Holdt scale (ca. 0.53 stokes) was obtained (approx. 60 min). Then it was cooled down to 30–40°C and more NaOH were added as an aqueous solution (50% w/v; 10.65 g). Finally, the mixture was cooled to room temperature and aqueous NH_4OH (50% w/w; 14.1 g) were added.

High Molecular Weight Resin

Aqueous phenol solution (90% w/v; 234.8 g, 2.24 mol), para-formaldehyde (150.3 g, 5.01 mol), water (374 mL) and sodium hydroxide (31.3 g) as an aqueous solution (50% w/v) were mixed and heated. The temperature increased up to 100°C. After 2 min, the reaction mixture was cooled to 95°C and maintained at this temperature until an A-B viscosity in the Gardner-Holdt scale (ca. 0.53

stokes) was obtained (approx. 30 min). The mixture was cooled again to 80°C and the temperature maintained until viscosity K-L (ca. 2.9 stokes) was reached (approx. 15 min). After an additional 15 min at 80°C, the mixture was cooled to 65°C for 65 min. Finally, it was cooled to room temperature. When temperature was between 30–40°C, additional NaOH was added as an aqueous solution (50% w/v; 2.3 g). Finally, when at room temperature, aqueous NH_4OH (50% w/w; 14.1 g) was added.

Kinetic Parameters Measurements

Thermoanalytical measurements were carried out in a Mettler TA 400 thermal analysis system with DSC 20 microcalorimeter. Data analysis was performed with the software furnished by Mettler, which contained the Borchardt and Daniels (BD) kinetic model as well as Avrami and most usually encountered kinetic models used in thermal analysis. A sample (20 to 30 mg; anhydrous weight of the liquid sample) was sealed in a high pressure capsule pan that can withstand up to 20 bars, and was transferred, along with a reference capsule, into the DSC sample holder assembly, set at 25°C. A heating rate of 10.0°C/min was used, up to the final temperature of 250°C. Temperature and enthalpy calibrations were performed with Indium. Dynamic cure kinetics data were analyzed by BD technique.¹⁷

Viscosity Determination

Viscosities of all resins were measured according to the American Society for Testing Materials (ASTM) Method D-1084,¹⁸ with a Brookfield Digital Viscometer Model DV-I+ (Brookfield Engineering Laboratory, Inc., Stoughton, MA) using RVDV-I+ Spindle 1 at a rotation speed of 50 rpm, and a RVDV-I+ Spindle 2 at rotation speed of 20 rpm.

Gel Time Determination

Gelation is defined as the point at which resins cease to be a viscous liquid and become soft, elastic, rubbery solids. The gel time was measured with a Sunshine Gel-Meter in which a test tube with the resin sample was heated in an ethylene glycol bath (120°C). A wire spring was placed in the test tube and the system made it turn at a constant speed. At gel time, the wire stopped

turning and the time was automatically measured by an stopwatch.

Particleboards Preparation and Testing

Three single-layer laboratory particleboards (560 × 460 × 11.1 mm) were prepared with each adhesive at 700 kg/m³ target density and 10% target moisture content. Wood particles (chips; < 3% moisture), mostly from white spruce (*Picea glauca*) were supplied by TAFISA Canada, a local particleboard mill. Boards were manufactured under conditions shown in Table IV.

All board samples, after pressing and cutting, were conditioned in an atmosphere maintained at 65% relative humidity and 20°C for at least 7 days prior to testing.

Panels were tested for modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond strength (IB). These were evaluated according to the Canadian Standards Association (CSA).¹⁹

RESULTS AND DISCUSSION

Production of Pyrogallol from Gallic Acid

Careful review on the literature suggests that commercial production of pyrogallol from gallic acid could be achieved by several methods. Following are the most relevant examples for the production of pyrogallol from gallic acid.

In chemical methods,¹³ pyrogallol is produced from controlled decarboxylation of gallic acid. Gallic acid is heated in presence of different catalysts at 180°C for 2 h to obtain 72% pure pyrogallol.

In enzymatic methods,¹⁴ a bacterium identified as *Citrobacter freundii* TB3 immobilized in k-carrageenan was used for the bioconversion of gallic acid into pyrogallol. In a continuous system operation with a flow rate of 0.5 mL/min, production of 98.5% pyrogallol may be attained.

Differential Scanning Calorimetry Results

Differential scanning calorimetry has been extensively used to determine kinetic parameters of polymerization reaction during the thermosetting cure of adhesives.^{20,21} In this study, the enthalpic analysis of pyrogallol-formaldehyde reaction were analyzed by software containing the BD kinetic model. This kinetic model describes the time and temperature dependence of material reactivity and a program calculates the activation en-

ergy, preexponential factor, reaction order, and rate constant in a single temperature programmed experiment. The method assumes that the reaction follows *n*th order kinetics and the temperature dependence of the reaction rate follows an Arrhenius-type expression.

The reaction rate (da/dt) is directly proportional to the rate of heat generation (dH/dt) following the equation $da/dt = (dH/dt)/\Delta H$, where ΔH is the total area under the curve corresponding to the exothermic heat, which is well known and can be used to quantify the extent of the reaction.¹⁷ On the basis of the information furnished by DSC, the parameters of the reaction were calculated from the following equation:

$$da/dt = ko \exp(-Ea/RT)(1 - \alpha)^n$$

where ko is the preexponential factor (S⁻¹), Ea the activation energy (kJ/mol), R the gas constant (8.31 J/mol · K), T the absolute temperature (K), α the extent of the reaction, and n the order of the reaction.

Synthesis of pyrogallol-formaldehyde resins was carried out for 10 min at 60°C, keeping a constant molar ratio of formaldehyde/pyrogallol (F/Py) equal to 2.1. The pH was adjusted with 50% (w/w) NaOH in order to not change the solid content (~ 50%) of the final resin.

Thermograms for the cure of pyrogallol-formaldehyde resins were recorded as function of pH values (7–8). Attempts to carry out the synthesis at higher pH values only resulted in gelation of the resin in the reaction vessel. All thermograms presented only one exotherm and kinetic parameters could be easily obtained from the BD method. Information about the nature of the curing reaction is presented in Table I. The trend for Ea in terms of pH (Fig. 4) has a minimum value (124.5 Kj/mol) at pH 7.30, to which corresponds to a maximum value of the enthalpy of reaction (397.71 J/g). This means that the minimum energy required to produce a maximum amount of reaction takes place at pH 7.30 and the peak temperature for this optimal condition is 106°C. This is the pH and formulation retained in the present study (resin c).

In order to compare thermal analysis results of the cure of pyrogallol-formaldehyde resin with those of resins elaborated from its precursors and based on previous works,^{12,22} tara tannin-formaldehyde (resin a), gallic acid-formaldehyde (resin b), and phenol-formaldehyde (resin d) were pre-

Table I Kinetic Analysis of the DSC Data for Pyrogallol-Formaldehyde Reaction Products as a Function of pH Carried out by Borchardt-Daniels Method

Kinetic Parameters	pH [Solids (%)]							
	7.00 [42 ± 1]	7.15 [50 ± 1]	7.30 [49 ± 1]	7.45 [51 ± 1]	7.55 [48 ± 1]	7.65 [45 ± 1]	7.80 [49 ± 1]	8.00 [42 ± 1]
Ea (Kj/mol)	135 ± 1	132 ± 1	124 ± 1	135 ± 1	135 ± 1	137 ± 1	152 ± 1	159 ± 1
ΔH (J/g)	153.6	256.6	397.7	274.5	269.6	259.9	114.1	96.1
Peak Temp (°C)	104	100	106	97	98	99	95	106
ln K (S ⁻¹)	39 ± 0.2	38 ± 0.3	35 ± 0.2	40 ± 1.4	39 ± 0.3	40 ± 0.4	46 ± 0.2	46 ± 0.2
n	1.8	1.7	1.7	1.7	1.7	1.8	1.7	1.7

Reaction conditions: F/Py = 2.1; t = 10 min, T = 60°C.

pared as described in the Experimental Section. Thermograms for all the systems were carried out at 10°C/min (Fig. 5) and kinetic parameters are summarized in Table II. Properties of these adhesive systems are shown in Table III.

Comparison of the gel times (Table III) and peak temperatures of the thermograms (Fig. 5) show no evident relationship. This is not surprising, because gel times are done in isothermal mode and are strongly affected by rheology and molecular weight, while DSC thermograms are done in scanning (nonisothermal) mode. The long gel times observed for tara tannins and gallic acid are probably due to the bifunctional nature of the monomers, which can lead only to linear polymers, while pyrogallol and phenol are trifunc-

tional and are liable to form, upon cure, a three-dimensional gelled network.

Gel time could be considered a measurement of the reactivity of phenolic compounds toward formaldehyde. As a matter of fact, the lower the gel time, the most reactive the compounds are. A gel time of 2 min for pyrogallol is shorter than those for mimosa and quebracho extracts (9–2 min; pH = 6–8) and longer than those for pine and pecan extracts (<1 min; pH = 5–8),¹⁰ confirming our hypothesis that reactivity of pyrogallol is intermediate between those of resorcinolic tannins (mimosa and quebracho) and of phloroglucinolic tannins (pine and pecan).

Commercial phenolic resins viscosities vary between 200 and 400 mPa·s at room temperature. Within this viscosity range, the resin could be stored, mixed, pumped, and sprayed with reasonable efficiency, even when cold. Tara tannin was the only tannin whose viscosity compared with that of phenol (Table III). As it is well known, flavonoid tannin-based adhesives have high viscosity values (more than 500 mPa·s), which cause short pot life and weak crosslinking. Generally hydrolysis of the hydrocolloid gums,¹⁰ sulfonation,^{23–25} and addition of phenolic resins must be done in order to decrease the viscosity and to bridge the distance between reactive sites for an increase in intermolecular crosslinking. Tara tannin, an hydrolyzable tannin mainly constituted by oligomers of a galloylated quinic acid structure²⁶ with high contents of gallic acid,¹² leads to a lower viscosity resin than that of commercial phenolic adhesives as it can be found in the particular case of pure gallic acid (Table III). Pyrogallol-formaldehyde adhesive viscosity remained at the lowest value of the series because attempts to increase viscosity by heating for more than 10 min or in-

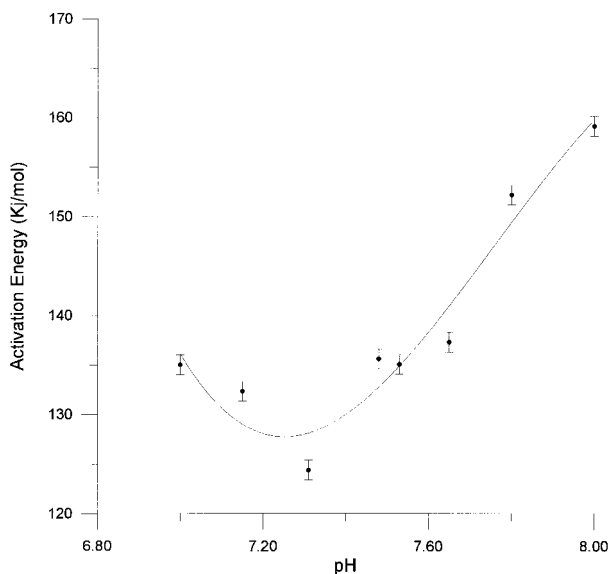


Figure 4 Activation energy (E_a) of pyrogallol-formaldehyde condensation reaction as a function of pH using the Borchardt-Daniels method.

Table II Kinetic Parameters of Adhesives Systems Evaluated by Borchardt–Daniels Method at 10°C/min

Kinetic Parameters	Adhesives			
	Tara Tannin ¹² (Resin a)	Gallic Acid ²² (Resin b)	Pyrogallol (Resin c)	Phenol (Resin d)
Ea (Kj/mol)	67 ^a	64 ^a	124 ± 1	121 ± 2
ΔH (J/g)	55.3	192.2	397.7	284.3
Peak Temp (°C)	107	152	106	152
ln k (S ⁻¹)	29 ± 1	18 ± 1	35 ± 1	30 ± 1
n	1.4	1.2	1.7	1.7

^a Evaluated by ASTM-689 method.

crease the pH to higher values than 8 result in gelation of the resin.

Even though pyrogallol and tara tannin thermograms show approximately the same peak temperatures (~106°C), the heat of reaction for pyrogallol (397.7 J/g) is much larger than that of tara tannin (55.3 J/g), probably because tannins themselves are composed of low molecular weight polymers (oligomers), which may not require extensive crosslinking for polymerization. Similarly, phenol and gallic acid have the same peak temperature (152°C), but once again, the heat of reaction for phenol (284.3 J/g) is larger than that for gallic acid (192.2 J/g). In this case, even though both are monomers of approximately the same molecular weight, the presence of a deactivating group,

in the form of a carboxylic group in gallic acid, certainly reduces its reactivity towards formaldehyde.

Comparison between pyrogallol–formaldehyde (resin c) and phenol–formaldehyde (resin d), shows very similar values for kinetic parameters: activation energy (*Ea*), Arrhenius parameter (ln *k*), and order of the reaction (*n*), but a major difference in the peak temperature, which is significantly lower (*T_p*: 105.6 vs. 151.8°C) for a higher degree of reactivity or crosslinking (Δ*H*: 397.71 J/g vs. 284.3 J/g). The fact that pyrogallol–formaldehyde cures 50° below the cure temperature of phenol–formaldehyde adhesives, as shown in thermograms, could result in significantly shorter press cycle times and lower temperatures in the manufacture of the boards.

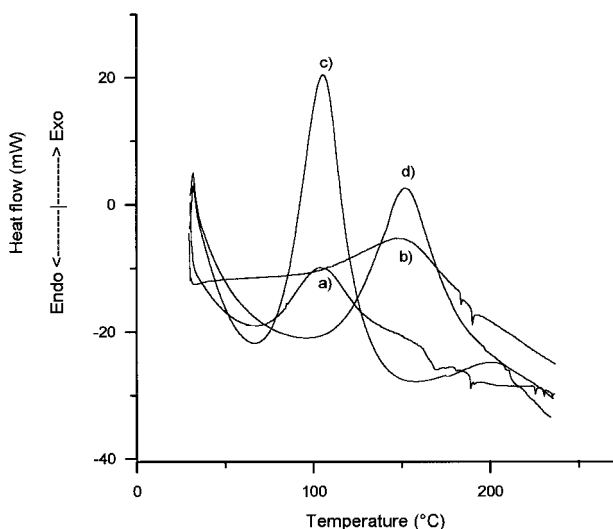


Figure 5 DSC thermograms of different resins recorded at 10°C/min. (a) Tara tannin formaldehyde; (b) gallic acid–formaldehyde; (c) pyrogallol–formaldehyde; and (d) phenol–formaldehyde.

Particleboard Test Results

During particleboard manufacture, similar conditions were maintained. In this way, the difference in mechanical properties of final boards are related to the quality of adhesives used only. Three homogeneous single layer laboratory particleboards (560 × 460 × 11.1 mm) were prepared for each adhesive at 700 kg/m³ target density and 10% target moisture content. Wood particles (2 mm screen) with 2.5% moisture were sprayed with the proper amount of resin. The boards were prepared by hot pressing for total pressing time of 4.5 min, with a cycle of 0.5 min for mat compression, 3 min for mat pressing, and 1 min for final decompression [Fig. 6(a)].

The first series of boards were prepared with phenol–formaldehyde (resin d) of known commercial formula,¹⁶ keeping constant press temperature (200°C) and press time (4.5 min) and changing the

Table III Properties of Adhesives Systems

Properties	Adhesives			
	Tara Tannin (Resin a)	Gallic Acid (Resin b)	Pyrogallol (Resin c)	Phenol (Resin d)
pH	8.8	8.1	7.3	10.8
Solids (%)	48 ± 1	47 ± 1	49 ± 1	50 ± 1
Viscosity (mPa · s)	160 ± 40 ^b	100 ± 25 ^a	36 ± 9 ^a	200 ± 50 ^b
Gel time ^c (min)	>60	>60	2 ± 0.5	16 ± 2

^a Brookfield RVDV-I+ Spindle 1 : 50 rpm/25°C.

^b Brookfield RVDV-I+ Spindle 2 : 20 rpm/25°C.

^c $T = 120^{\circ}\text{C}$.

anhydrous resin content (4, 8, and 12%). As can be noted from Table IV, mechanical properties increase with increasing content of adhesive.

For the next series of particleboards (pyrogallol–formaldehyde, resin c), the anhydrous content of resin solids was fixed at 8%. Because DSC thermogram of pyrogallol–formaldehyde showed that polymerization occurs at low temperature (106°C) we decided to change the pressing temperature from 180 to 110°C to verify the influence of this parameter on the mechanical properties of the final boards. Results show a clear trend towards improved mechanical properties with decreasing temperatures. As is well known, mechanical properties are closely related to density of

boards.²⁷ The higher the density of the boards, the better the mechanical properties obtained.

During the internal bond (IB) test, we observed that samples pressed at higher temperatures (180 and 160°C) showed surface failure instead of core failure, as normally happens. This problem arises from the low-density surface layer of the board, as can be seen in from its density profile [Fig. 7(a) and (b)]. It is fairly evident that at 180°C density in the surface layers was lower than that inside the core [Fig. 7(b)], suggesting an explanation to the fact that the sample failed at the surface. To verify this possibility, surfaces were sanded and a new density profile was obtained [Fig. 7(c)]. This resulted in samples breaking in the core. As can also be seen in the figure, pressing at lower temperature does seem to flatten the density profile, which is a good thing.

As revealed by the thermograms, pyrogallol–formaldehyde adhesive achieved complete cure at lower temperatures. In such cases, at earlier stages of pressing, cure progresses rapidly at the surface layer (surface precure) and pressing can only destroy the crosslinked network already built up in the surface of the board, resulting in a reduction of the density and the correspondent mechanical properties.

As the mat is heated in the press, the moisture changes to vapor and migrates from hottest areas (surface) to cooler areas (core). After the press is closed a temperature gradient is set up between the faces and the core, and also between the center of the panel and the edges. Corners are the coldest sections of the board because of their exposure to atmosphere on two edges. Consequently, these are the last areas to heat above the boiling point of water, and thus the last areas in which the resin is cured.

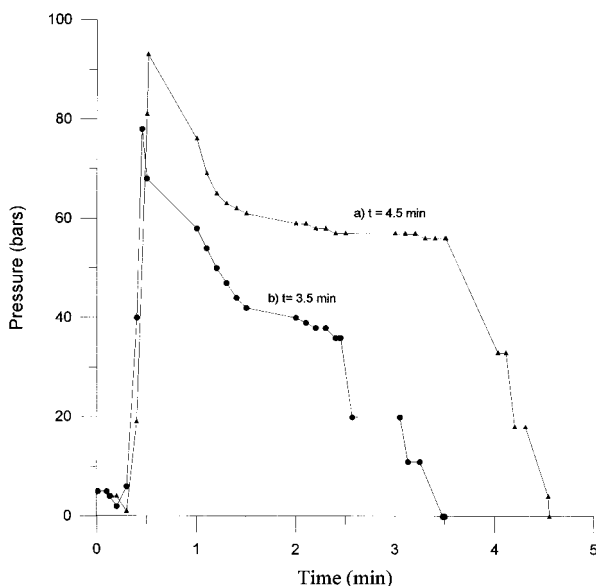


Figure 6 Press cycles that produce 11.1 mm-thick particleboards of 700 gr/cc density at 10% moisture content. (a) 4.5-min cycle, and (b) 3.5-min cycle.

Table IV Comparison between Tara Tannin, Gallic Acid, Pyrogallol, and Phenol-Formaldehyde Adhesives in Particleboard Manufacture (Laboratory Test Results)

	Particleboard Pressing Conditions			Panel Test Results				
	Resin Content (%)	Temp. (°C)	Cycle (min)	Thickness (mm)	Density (kg/m ³)	MOR (MPa)	MOE (GPa)	IB (KPa)
Resin d	4	200	4.5	11.6 ± 0.2	651 ± 20	7.3 ± 0.4	0.8 ± 0.2	556 ± 37
	8	200	4.5	11.1 ± 0.1	729 ± 29	16.7 ± 0.6	1.8 ± 0.2	717 ± 27
	12	200	4.5	11.1 ± 0.2	700 ± 27	17.8 ± 0.5	2.0 ± 0.2	928 ± 31
Resin c	8	180	4.5	10.9 ± 0.0	712 ± 27	9.7 ± 0.8	1.2 ± 0.2	—
	8	160	4.5	11.1 ± 0.1	685 ± 27	7.4 ± 0.6	1.0 ± 0.3	—
	8	140	4.5	10.9 ± 0.0	717 ± 21	9.4 ± 0.7	1.3 ± 0.2	662 ± 39
	8	130	4.5	10.9 ± 0.0	743 ± 20	12.4 ± 0.9	1.5 ± 0.1	1081 ± 29
	8	120	4.5	10.8 ± 0.0	733 ± 26	13.4 ± 1.0	1.7 ± 0.1	1108 ± 24
	8	120	3.5	11.5 ± 0.1	710 ± 22	11.7 ± 0.8	1.7 ± 0.2	1065 ± 15
	8	110	4.5	11.1 ± 0.1	700 ± 26	13.0 ± 0.5	1.6 ± 0.1	988 ± 33
Resin b	8	120	4.5	10.9 ± 0.1	684 ± 12	3.7 ± 0.4	0.7 ± 0.0	<5
Resin a	8	200	4.5	11.2 ± 0.1	644 ± 24	1.9 ± 0.2	0.4 ± 0.1	<1
Ref.	—	—	—	Grade R		14	2.0	500

Ref: Canadian Standards Association (CSA 1978).

So, even though pyrogallol-formaldehyde is a fast curing adhesive, which could even cure at temperatures below 100°C, in order to reach a low moisture content in the final particleboard, prevent blows, and promote a good heat transfer in the mat, platen temperature was set to 120°C,

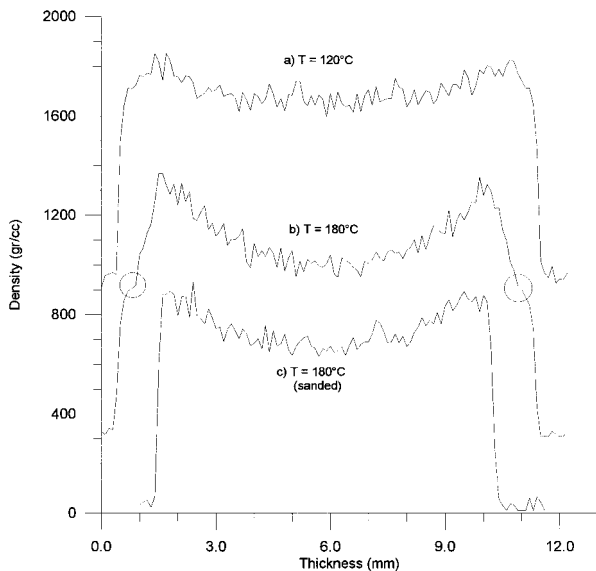


Figure 7 Density profiles for (a) sample pressed at 120°C, (b) sample pressed at 180°C, and (c) sample pressed at 180°C and sanded.

and pressing cycle time was reduced to 3.5 min [Fig. 6(b)] instead of 4.5 min.

The particleboard test results showed that pyrogallol-formaldehyde (resin c) produced particleboards of acceptable mechanical properties using 4.5-min press cycles, at temperatures between 110 and 130°C. Thus, an important quantity of energy could be saved by reducing temperature of the platens during the press.

Results obtained at 3.5-min press cycle also gave very similar values (MOR, MOE, and IB) to those obtained with phenol-formaldehyde (Table IV).

The values from the IB test are in accord with Canadian standards¹⁹ for which the minimum stipulated for exterior particleboard is 500 KPa. However, the results obtained from MOR and MOE are partly below those stipulated by the CSA. Probably, addition of a slightly higher amount of adhesive could improve the results above those of the standards. This modification and the possibility of using pyrogallol as a cure accelerator of phenol-formaldehyde adhesives are the object of a separate study.

Particleboards made from tara tannin and gallic acid had mechanical properties much below those of standards. As previously discussed, from thermal analysis, hydrolyzable tannins, and gallic acid are principally limited by their two-dimensional network polymerization and by the pres-

ence of a deactivating carboxylic group. Its possibility as a renewable resource for wood adhesives is exclusively limited to furnish economical pyrogallol. The obtention of pyrogallol from tara tannins is currently being studied.

CONCLUSION

In this work, thermoanalytical studies (DSC) carried on the polymerization of formaldehyde with tara tannin, gallic acid, pyrogallol, and phenol were used to determine kinetic parameters.

It was demonstrated that hydrolyzable tannins (i.e., tara tannin) and gallic acid are less reactive than pyrogallol and phenol towards formaldehyde. They are limited to a bidimensional network, and this is in accordance with mechanical property results.

However these products (tara tannin and gallic acid), unusable by themselves, could lead to economical pyrogallol, an interesting new starting material that can be used in the manufacture of wood adhesives. Preparation of pyrogallol-formaldehyde resin takes only 10 min in very mild conditions. Particleboard panels elaborated with this adhesive presents comparable mechanical properties to those manufactured with phenol-formaldehyde and Canadian standard requirements. Moreover, in comparison with current industrial pressing conditions, temperature is reduced by 40% and time by 22%.

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