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# Gallic acid as a model of tannins in condensation with formaldehyde

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## Abstract

In this work, gallic acid (Ga), as a model of hydrolyzable tannins, has been reacted with formaldehyde (F) at different pH values, molar ratios F/Ga, temperatures and for different reaction times. The products obtained from these reactions were analyzed, after acetylation, by size exclusion chromatography (SEC).

The kinetic parameters of the gallic acid–formaldehyde condensation have been determined by enthalpic analysis using differential scanning calorimetry (DSC). It appears from these results that gallic acid–formaldehyde condensation depends on the aforementioned preparation conditions. The optimal values of these reactions have been obtained at pH 8, with the molar ratio F/Ga equal to two, for 4 h at 60°C. The results obtained by SEC and enthalpic analysis confirm these conclusions.

*Keywords:* Condensation; DSC; Enthalpic analysis; Formaldehyde; Gallic acid; Size exclusion chromatography

## 1. Introduction

Eucalyptus bark and other vegetable material, such as the fruit pods of *Caesalpinia spinosa* (tara) contain an important proportion of hydrolyzable tannins [1–5]. Hydrolyzable tannins are a mixture of simple sugars (such as glucose) and polyhydric phenolic acids (such as gallic acid, hexahydroxydiphenic acid or ellagic acid), and

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substances built up from them through hydrolyzable ester linkages. Gallic acid is, for instance, easily decarboxylated by the action of heat to pyrogallol, whose ring has reactive sites to add formaldehyde in alkaline conditions. Sugars are also reactive with formaldehyde and methylolphenols, thus participating in resin–formaldehyde reactions [6, 7]. It has been shown that hydrolyzable tannins are suitable as cure accelerators for phenolic adhesives. Indeed, hydrolyzable tannins from chestnut wood extract [8,9], can replace up to 50% of the synthetic phenol in ordinary alkaline phenol–formaldehyde adhesives for the manufacture of exterior-grade wood composite boards.

Hydrolysis of hydrolyzable tannins produces gallic acid to a large extent [4, 5]. Other phenolic acids, such as ellagic acid and hexahydroxydiphenic acid, also are present, but in low proportions. These acids come from the condensation of two gallic acid molecules. Gallic acid has been suggested as a precursor of hydrolyzable tannins [10, 11].

Gallic acid (Ga) was, therefore, chosen as a model compound to study the reaction of hydrolyzable tannins with formaldehyde (F) (Scheme 1). Up to now, little is known about this reaction. A study of the different conditions of time, temperature, pH values and molar ratio (F/Ga) was thus undertaken to assist the study of complex tannins–formaldehyde reactions, and as an aid to the use of this raw material in adhesive formulations. The kinetic parameters for the cure of such adhesives at different pH values were determined as well as the evolution of molecular weight with increasing reaction time. Also, the molecular size and degree of polymerization of compounds during early stages of cure has been detected by size exclusion chromatography (SEC) analysis.

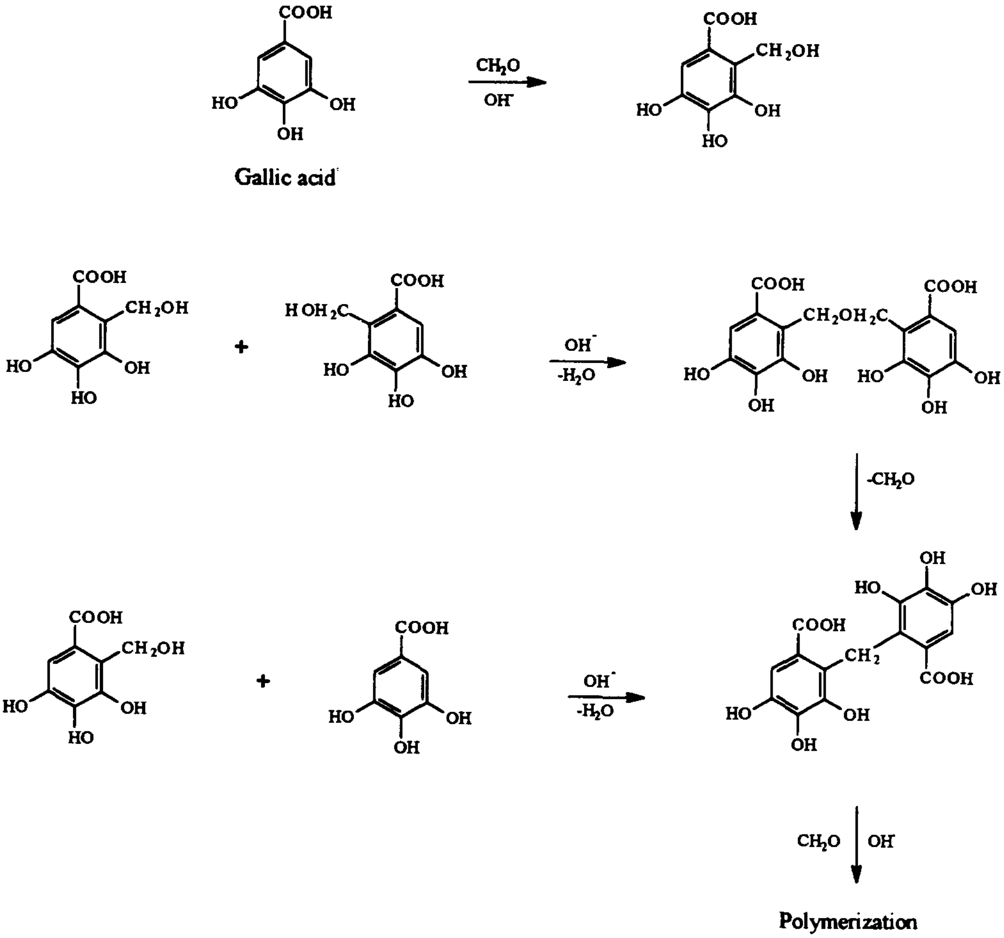
## 2. Experimental

### 2.1. Materials

Gallic acid was from Aldrich and paraformaldehyde from Sigma Co. These were used without further purification.

### 2.2. Methylolation

340 mg (2 mmol) of gallic acid in 200 mL of distilled water was heated in a 500 mL three-necked boiling flask to the reaction temperature in a constant temperature bath. Paraformaldehyde was added to the reaction mixture, with the amount depending on the desired molar ratio of formaldehyde to gallic acid (F/Ga). The appropriate amount of 0.1 N NaOH was added immediately to adjust the pH. Solutions with different pH were reacted for 3 h at 85°C or for 4 h at 60°C. Thereafter, the reaction mixture was cooled and freeze-dried. Samples (30 mL) were removed from the reaction media at regular times intervals. These samples were freeze-dried and acetylated in order to determine the molecular weight.



Scheme 1. Reaction of gallic acid with formaldehyde.

### 2.3. Acetylation

Freeze-dried samples (100 mg) were dissolved in a mixture of acetic anhydride–pyridine (1:1, v/v) [12] and immersed in a boiling water bath for 1 h. The reaction continued at ambient temperature overnight. When samples contained traces of water, it was necessary to add an excess of acetic anhydride to the reaction mixture [13].

The reaction mixture was quenched with water and extracted with dichloromethane. The dichloromethane solution was dried ($MgSO_4$) and concentrated in vacuo at 40°C. Toluene was added and evaporated repeatedly (four or five times) until no odour of pyridine was detectable. Then, the samples were dried under high vacuum at ambient temperature for 1 h.

### 2.4. Apparatus and operating conditions

Size exclusion chromatography (SEC) measurements were performed with a Waters Associates instrument: WISP 710 B injection system, Waters M45 B pump, Waters R401 differential refractometer and Waters programmable system controller with data module, with μStyragel (Waters) 100 Å and 500 Å columns in series with THF/0.4% trichloroacetic acid (*v*/*w*) as eluent at 25°C with a flow rate of 0.5 mL $\text{min}^{-1}$. The advantage of using this type of eluent is that it minimizes aggregation [14]. The concentration of the samples was 0.2% (*w*/*v*) for standards, 0.1% (*w*/*v*) for the samples, and the injection volume was 30 μL. Calibration was performed with low molecular weight monodisperse samples of poly(ethylene glycol) (PEG) of molecular weights 106, 194, 440, 600, 960, 1470, 4250, 7100 and 12600. Fig. 1 gives the calibration curve of retention time as a function of log molecular weight of PEG samples.

Thermoanalytical measurements were carried out in a Mettler TA 4000 thermal analysis system with DSC 20 and TG 50. The treatment of data was performed with software furnished by Mettler which contained the Borchardt and Daniels (B/D) kinetic model as well as the Avrami and most of the kinetic models usually encountered in thermal analysis. A 7 to 15 mg sample was sealed in a high-pressure capsule pan

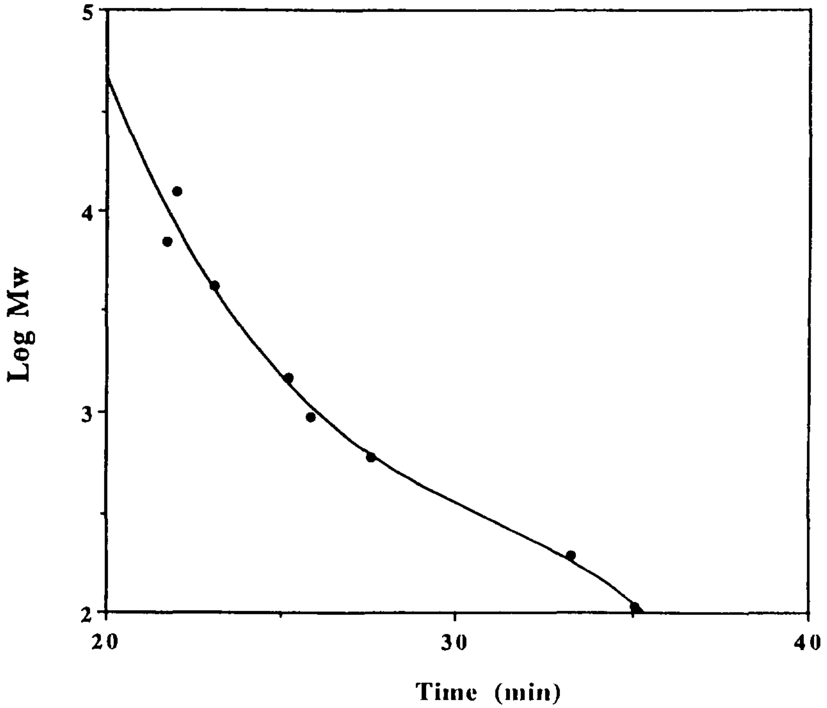


Fig. 1. Calibration of SEC columns (Ultrastyragel 100 and 500 Å in series) with poly(ethylene glycol) using THF–0.4% trichloroacetic acid as eluent at 25°C.

which can withstand up to 20 bar. The capsule containing the sample and the reference capsule were transferred to the DSC sample holder assembly which had been set at 25°C. Different heating rates (2.5, 5.0, 10.0 and 20.0°C $\min^{-1}$) were used at temperatures up to 250°C. Temperature and enthalpy calibrations were performed with indium. Cure kinetics data were analyzed by the Borchardt–Daniels technique (single isotherm) and by the ASTM E-698 technique (multiple isotherms and peak temperatures) [15].

## 3. Results and discussion

### 3.1. Size exclusion chromatography

The gallic acid–formaldehyde condensation products were acetylated with acetic anhydride–pyridine [13], and the peracetates subsequently characterized as to molecular weight by size exclusion chromatography (SEC). The SEC columns were calibrated with poly(ethylene glycol) standards as described before (cf. Experimental). The molecular weight of tetracetylgallic acid is ca. 338. The SEC technique is used to estimate the number-average and weight-average molecular weights ($M_n$, $M_w$) of wood adhesives [12–14, 16]. The results obtained from this study are given in Figs. 2–4. The

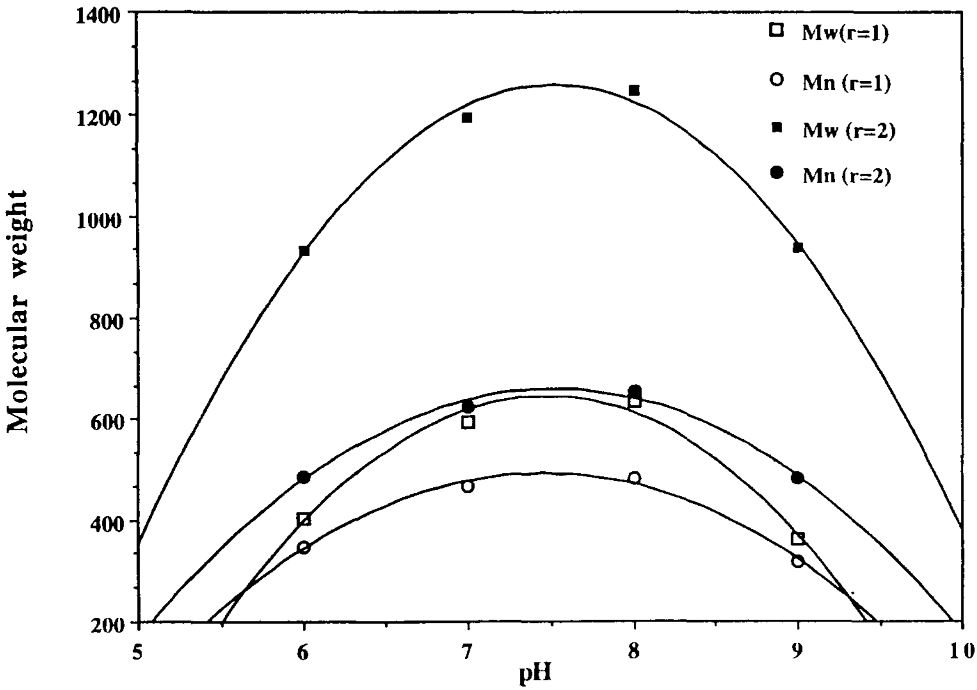
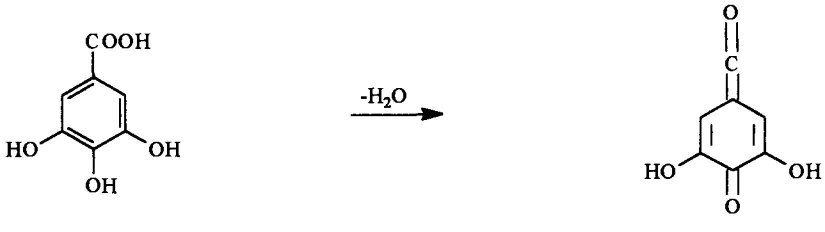


Fig. 2. Distribution of $M_n$ and $M_w$ of acetate derivatives of gallic acid–formaldehyde reactions as a function of pH value and molar ratio ($r$ = F/Ga).

$M_n$ and $M_w$ distributions of peracetates obtained from gallic acid–formaldehyde reactions as a function of pH are given in Fig. 2. These results indicate that the highest and optimum values have been obtained at molar ratio F/Ga equal to 2 and at pH 7 to 8. The $M_n$ and $M_w$ are, respectively, 660 and 1250 (the molecular weights of gallic acid condensation products with formaldehyde are a little more than 50% of those of the tetracetates). At a molar ratio F/Ga equal to 1 the weight-average molecular weight varied from 362 at pH 9, to 634 at pH 8. The $M_w/M_n$ ratio varied from 1.14 to 1.32. This indicates that distribution is almost monodisperse. The values obtained at pH 6 or 9 are closer to the molecular weight of the monomer which is about 340 (338). This indicates that gallic acid is less reactive with formaldehyde at these pH values. At pH 7 or 8, the weight-average molecular weight obtained from the tetracetates corresponds almost to that of dimers (bis-(tetracetyl-galloyl acid)-methane). When the F/Ga is 0.5, the values of $M_n$ and $M_w$ are closer to those of the monomers ($M_n$ and $M_w$ are, respectively, 312 and 330). In contrast, the molecular size distribution is polydisperse at F/Ga equal to 2; the $M_w/M_n$ ratio is higher than 1.

This shows that at a molar ratio lower or equal to 1 and at higher acid or basic pH the gallic acid reactivity becomes low. This is probably caused by the instability of gallic acid in relatively highly acidic or basic conditions. Gallic acid can undergo, under acid or alkaline conditions, a rearrangement to its enonic form (Scheme 2). This instability was shown by Self et al. [17] in a study of polyphenols by fast atomic bombardment mass spectrometry (FABMS). The low reactivity of gallic acid may be attributed to the steric hindrance caused by hydroxyl aromatic groups as described previously [18].

Fig. 3 gives the proportion of tetracetates obtained as gallic acid–formaldehyde condensation products at pH 7.42 and F/Ga equal to 1 as a function of reaction time. These proportions have been estimated by determination of molecular weights corresponding to oligomers of different degrees of polymerization (e.g. the molecular weight of disubstituted monomer is about 454, that of dimers is 454 to 776, that of trimers is 776 to 1157 and so on). This reaction thus gives a mixture of monomers, dimers and a lesser proportion of trimers, tetramers and polymers. The proportion of these compounds becomes almost constant after 2 h reaction. The SEC curves after 2 and 4 h are similar (Fig. 4). This distribution shows, as has already been noted, that the gallic acid–formaldehyde condensation is not very fast at F/Ga equal to 1.



Scheme 2. Rearrangement of gallic acid to its enonic form.

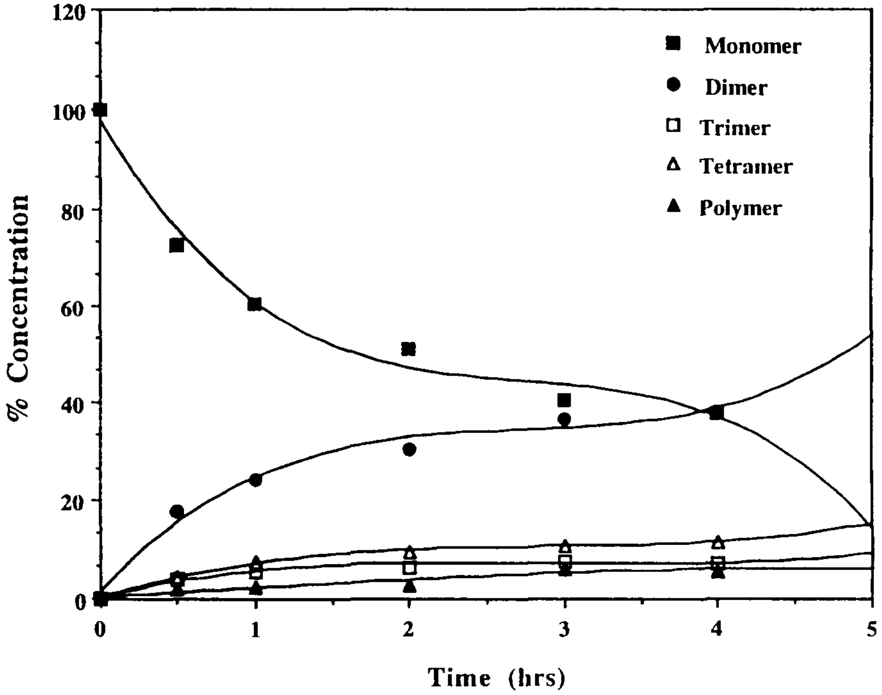


Fig. 3. Concentration of monomers, dimers, trimers, tetramers and polymers of the equimolecular condensation of gallic acid with formaldehyde as a function of the reaction time at pH 7.42 at 85°C.

### 3.2. *Thermogravimetry*

Gallic acid is easily decarboxylated to pyrogallol by the action of heat [19]. In relation to the formulation and cure of tannin-modified phenolic resins, this might be a good thing since pyrogallol has three potential sites for formaldehyde addition. Therefore, a three-dimensional network would be formed upon reaction with formaldehyde. On the other hand, this might be bad, especially if the carbon dioxide is released during pressing of a wood composite panel. During pressing and heating to cure the adhesively bonded panel, carbon dioxide could build up within the composite panel. On releasing the pressure, the panel could possibly "blow" apart, i.e. delaminate.

In order to investigate this potential further we have used TGA with gallic acid to determine the release of $CO_2$. Three main peaks were detected in the DTG curve (Fig. 5). The first, at 260°C (26–27%), corresponds to carbon dioxide being liberated upon heating, the second, at 308°C (29%), probably corresponds to the further loss of the hydroxyls either as water or perhaps even as $CO_2$ or CO. Finally the third peak, at 503°C (45%), corresponds to the residual decomposition of gallic acid. This indicates that decarboxylation of gallic acid occurs at temperatures far removed from those usually encountered in board pressing.

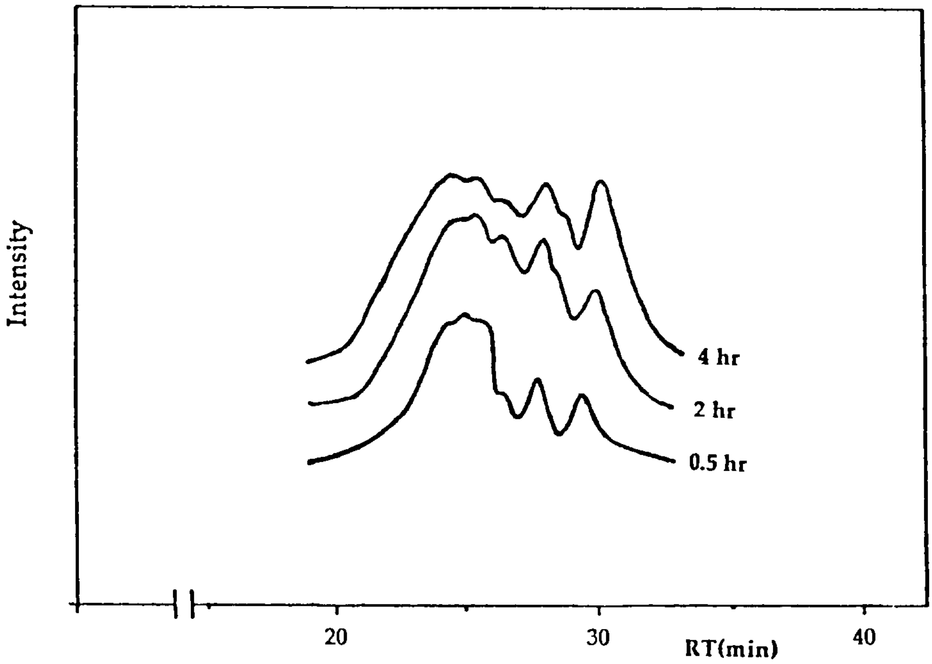


Fig. 4. SEC curves of acetate derivatives of gallic acid-formaldehyde reaction products at 0.5, 2 and 4 h (pH = 7.42, temp. = 85°C).

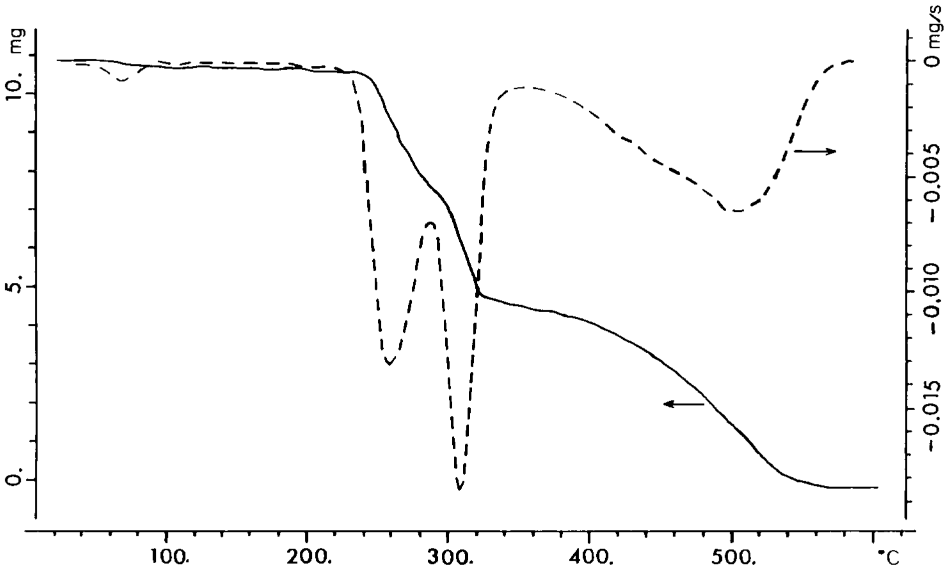


Fig. 5. TG and DTG curves of gallic acid (10°C min$^{-1}$). A weight loss of 1% (80°C) is attributed to the humidity; 26-27% (260°C) to $CO_2$ liberated; 29% (308°C) to further loss of hydroxyls and 45% (503°C) to the residual decomposition of gallic acid.

### 3.3. Differential scanning calorimetry

Dynamic DSC measurements have been extensively used for the investigation of the kinetic and thermodynamic parameters of polymerization reactions of phenolic resins [20,21]. A kinetic model describes the time- and temperature-dependence of material reactivity. We have used two software packages for DSC kinetic studies:

(1) Analysis of one exotherm: method of Borchardt and Daniels [22,23].
(2) Variation of peak exotherm temperature with heating rate: method ASTM E-698 [24].

The first method is very attractive because of the abundance of information contained in a single temperature programmed experiment. The Borchardt and Daniels (B–D) kinetics program enables the calculation of activation energy, pre-exponential factor, heat of rate, reaction order and rate constant. 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 area under the exotherm is assumed to be proportional to the heat of the curing reaction. The reaction rate ($\mathrm{d}x/\mathrm{d}t$) is directly proportional to the rate of heat generation ($\mathrm{d}H/\mathrm{d}t$) following the equation $\mathrm{d}x/\mathrm{d}t = (\mathrm{d}H/\mathrm{d}t)/\Delta H$, where $\Delta H$ 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 curing reaction [15]. On the basis of the information furnished by DSC, the parameters of the curing reaction are calculated from the following equation:

$$\mathrm{d}x/\mathrm{d}t = k_0 \exp(-E_a/RT)(1-x)^n$$

where $k_0$ is the preexponential factor ($S^{-1}$), $E_a$ the activation energy (kJ mol$^{-1}$), $R$ the gas constant (8.31 J mol$^{-1}$ K$^{-1}$), $T$ the absolute temperature (K), $x$ the extent of the curing reaction, and $n$ the order of the reaction.

The second method (ASTM E-698) is based on the linear relationship between the peak temperature of the exotherm and the logarithm of the heating rate (Fig. 6). The kinetic parameter $E_a$ can be obtained from the following relation:

$$\log \beta = -0.4567 E_a/RT_p + \mathrm{CTE}$$

where $\beta$ is the heating rate (°C min$^{-1}$), $E_a$ the activation energy (kJ mol$^{-1}$), $R$ the gas constant (8.31 J mol$^{-1}$ K$^{-1}$) and $T_p$ the peak temperature (K)

According to Prime [24], $E_a$ can be obtained from the slope of the $\log \beta$ vs $1/T_p$ graph.

The method requires a minimum of three DSC scans at different heating rates and assumes that:

(1) the peak maximum represents a point of constant conversion for each heating rate;
(2) the temperature-dependence of the reaction rate constant obeys the Arrhenius equation; and
(3) the reaction is first order.

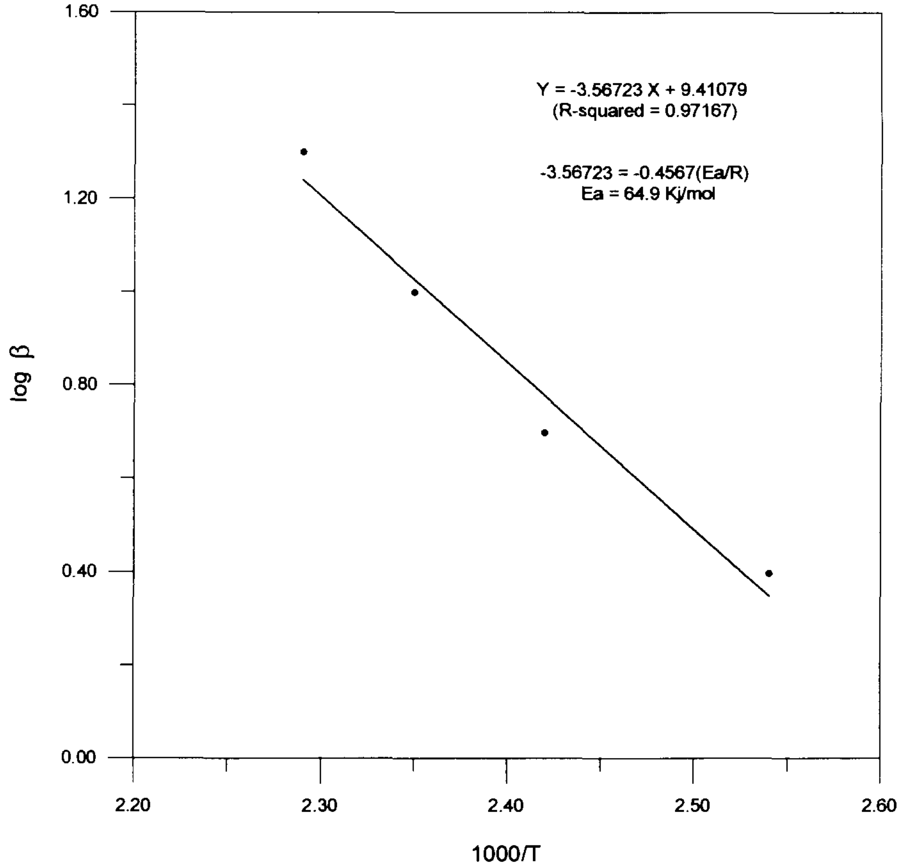


Fig. 6. Gallic acid–formaldehyde reaction product analysis using ASTM E-698 method at pH 8.10.

The peak temperatures at different heating rates are used to calculate the kinetic parameters. Note that this peak parameter is fairly obvious and independent of baseline shift. In comparison, B–D uses reaction rate and fractional conversion for the calculations, both parameters are dependent on the peak area which is greatly affected by the selection of the baseline.

Thermograms of the gallic acid–formaldehyde reaction (Fig. 7) were recorded as a function of pH values (6.1, 7.2, 8.1, 9.6, 11.0 and 12.4) under optimal conditions determined through SEC analysis: F/Ga = 2 reacted for 4 h at 60°C.

Thermograms at pH 6.1 and 7.2 (Fig. 7; a and b) show two overlapping reaction peaks. Accordingly, no information can be obtained from the B–D method. The ASTM method was carried out at 2.5, 5.0, 10.0 and 20.0°C min$^{-1}$ on each reaction exotherm separately and $E_a$ was calculated for each of the two peaks. Following a similar experiment of Sebenik et al. [20] with phenol and formaldehyde (PF), the first exotherm can be assigned to the addition of formaldehyde to gallic acid and the second to the condensation reaction. Table 1 shows the kinetic analysis of the DSC data. Very

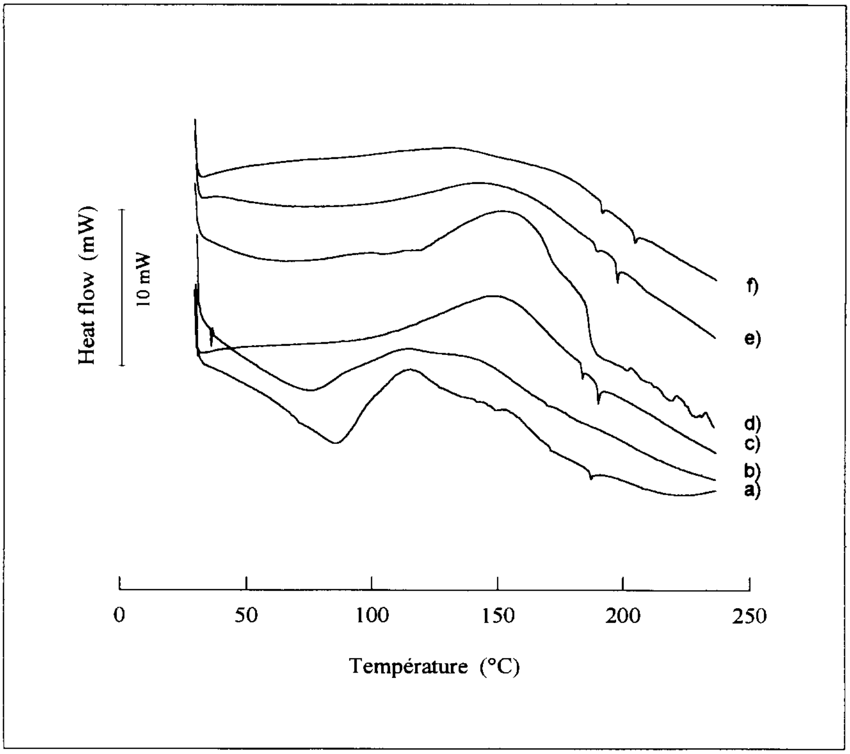


Fig. 7. Thermograms of gallic acid–formaldehyde reaction products at different heating rates as a function of pH (F/Ga = 2, temp. = 60°C for 4 h): a) pH = 6.1, b) pH = 7.2, c) pH = 8.1, d) pH = 9.6, e) pH = 11.0 and f) pH = 12.4.

Table 1
Kinetic analysis of the DSC data for gallic acid–formaldehyde reaction products at pH 6.1 and 7.2 carried out by the ASTM E-698 method

| Heating rate | | $T_{max}$ (pH = 6.1) | | | | $T_{max}$ (pH = 7.2) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1st peak | | 2nd peak | | 1st peak | | 2nd peak | |
| °C min$^{-1}$ | log $\beta$ | $T$/°C | 1000/($T$/K) | $T$/°C | 1000/($T$/K) | $T$/°C | 1000/($T$/K) | $T$/°C | 1000/($T$/K) |
| 2.5 | 0.3979 | 94.6 | 2.72 | 126 | 2.50 | 91.9 | 2.74 | 126.0 | 2.50 |
| 5.0 | 0.6989 | 102.0 | 2.66 | 142.1 | 2.40 | 103.0 | 2.66 | 137.7 | 2.43 |
| 10.0 | 1.0000 | 109.9 | 2.61 | 154.5 | 2.34 | 112.0 | 2.59 | 142.9 | 2.40 |
| 20.0 | 1.3010 | 122.5 | 2.53 | 169.3 | 2.26 | 126.3 | 2.50 | 168.3 | 2.26 |
| | | $E_a$/(kJ mol$^{-1}$) = 87.6 | | $E_a$/(kJ mol$^{-1}$) = 69.6 | | $E_a$/(kJ mol$^{-1}$) = 69.2 | | $E_a$/(kJmol$^{-1}$) = 67.8 | |

similar values of $E_a$ for each peak were obtained by Sebenik et al. [20] but, as said before, on PF.

Thermograms at pH 8.1, 9.6, 11.0 and 12.4 (Fig. 7; c,d,e and f) show only one reaction peak. The kinetic parameters obtained from B–D method at different heating rates are summarized in Table 2. The kinetic parameters obtained from the ASTM method are summarized in Table 3.

Values of the activation energy from B–D do not vary very consistently with increasing pH (Table 2). For instance at 2.5°C min$^{-1}$, $E_a$ decreases from 88.8 to 46.1 KJ mole$^{-1}$ as the pH goes from 8.1 to 12.4. However, at the other heating rates, no overall trend is detectable. Thus B–D kinetics do not offer the resolution needed to resolve a trend. Compared to the ASTM method results (Table 3), B–D kinetics overestimates $E_a$ at pH 8.1 and 9.6, gives about the same results at pH 11 and underestimates $E_a$ at pH 12.4.

Values of the enthalpies of reaction, $\Delta H$, in Table 2, provide additional insight. These are the integrated area of the DSC curves, divided by the amount of material. This value should remain about constant if the number of chemical bonds formed remains the same as pH or temperature scan rate vary. The value of $\Delta H$ is halved at pH 8.1 as temperature scan rate increases from 2.5 to 20°C min$^{-1}$, from 217 to 128 J g$^{-1}$. This may be due to non-equilibrium conditions being reached at high scan rates: this is

Table 2
Kinetic analysis of the DSC data for gallic acid–formaldehyde reaction products at pH 8.1, 9.6, 11.0 and 12.4 carried out by the Borchardt–Daniels method

| Heating rate/(°C min$^{-1}$) | Kinetic parameters | pH = 8.10 | pH = 9.6 | pH = 11 | pH = 12.4 |
|---|---|---|---|---|---|
| | $E_a$/(kJ mol$^{-1}$) | 88.8 | 80.8 | 77.1 | 46.1 |
| 2.5 | $\Delta H$/(J g$^{-1}$) | 216.7 | 229.7 | 91.8 | 117.6 |
| | $n$ | 1.7 | 1.6 | 0.9 | 0.6 |
| | Peak temp./°C | 120.9 | 130.5 | 131.5 | 122.7 |
| | $E_a$/(kJ mol$^{-1}$) | 75.1 | 77.4 | 85.2 | 43.8 |
| 5.0 | $\Delta H$/(J g$^{-1}$) | 243.0 | 191.0 | 219.2 | 118.9 |
| | $n$ | 1.1 | 1.2 | 2.1 | 1.0 |
| | Peak temp./°C | 140.9 | 143.6 | 146.1 | 130.5 |
| | $E_a$/(kJ mol$^{-1}$) | 79.8 | 83.2 | 73.6 | 75.9 |
| 10.0 | $\Delta H$/(J g$^{-1}$) | 192.2 | 214.2 | 97.6 | 16.3 |
| | $n$ | 1.2 | 1.1 | 1.3 | 0.7 |
| | Peak temp./°C | 151.5 | 158.4 | 154.0 | 132.4 |
| | $E_a$/(kJ mol$^{-1}$) | 88.3 | 54.2 | 62.6 | 137.9 |
| 20.0 | $\Delta H$/(J g$^{-1}$) | 128.8 | 103.6 | 73.0 | 8.2 |
| | $n$ | 1.5 | 0.8 | 0.9 | 1.3 |
| | Peak temp./°C | 162.4 | 169.0 | 166.0 | >200 |

Table 3
Kinetic analysis of the DSC data for gallic acid–formaldehyde reaction products at pH 8.1, 9.6, 11.0 and 12.4 carried out by the ASTM E-698 method

| Heating rate | | $T_{max}$(pH = 8.1) | | $T_{max}$(pH = 9.6) | | $T_{max}$(pH = 11.0) | | $T_{max}$(pH = 12.4) | |
|---|---|---|---|---|---|---|---|---|---|
| (°C min$^{-1}$) | log($\beta$/°C min$^{-1}$) | $T$/°C | 1000/($T$/K) | $T$/°C | 1000/($T$/K) | $T$/°C | 1000/($T$/K) | $T$/°C | 1000/($T$/K) |
| 2.5 | 0.3979 | 120.9 | 2.54 | 130.5 | 2.48 | 131.5 | 2.47 | 122.7 | 2.53 |
| 5.0 | 0.6989 | 140.9 | 2.42 | 143.6 | 2.40 | 146.1 | 2.39 | 130.5 | 2.48 |
| 10.0 | 1.0000 | 151.5 | 2.35 | 158.4 | 2.32 | 154.0 | 2.34 | 132.4 | 2.46 |
| 20.0 | 1.3010 | 162.4 | 2.29 | 169.0 | 2.26 | 166.9 | 2.27 | 140.5 | 2.42 |
| | | $E_a$/(kJ mol$^{-1}$) = 64.9 | | $E_a$/(kJ mol$^{-1}$) = 74.1 | | $E_a$/(kJ mol$^{-1}$) = 83.7 | | $E_a$/(kJ mol$^{-1}$) = 152.8 | |

especially possible when one recalls that the high pressure capsules may have significant thermal lag due to their large mass. The variation of $\Delta H$ with respect to pH is much larger, especially at high scan rates. The value of $\Delta H$ is halved at 25°C $\min^{-1}$ from 217 to 118 J $g^{-1}$ as pH increases from 8.1 to 12.4, while at 20°C $\min^{-1}$, it decreases from 129 to 8 J $g^{-1}$, clearly showing reaction is minimal in these conditions.

The trend for $E_a$ from the ASTM method is a regular increase (Table 3). At low pH, for the second peak (Table 1), $E_a$ is slightly higher than at pH 8.1. Fig. 8 gives activation energy ($E_a$) in terms of pH values for the ASTM method.

These results show that the optimal value is obtained at pH 8.1 with a minimal $E_a$ of 64.93 kJ $mol^{-1}$. Generally, a lowered activation energy means the reaction will proceed faster at a given temperature. These results also show that the peak temperature for the optimal condition (pH 8.1) changes from 120.9°C (2.5°C $\min^{-1}$) to 162.4°C (20°C $\min^{-1}$). These limits are far away from the descarboxylation temperature of gallic acid (260°C). This indicates that carbon dioxide will not be released during pressing of a wood composite panel and no problem associated with the pressure release will appear.

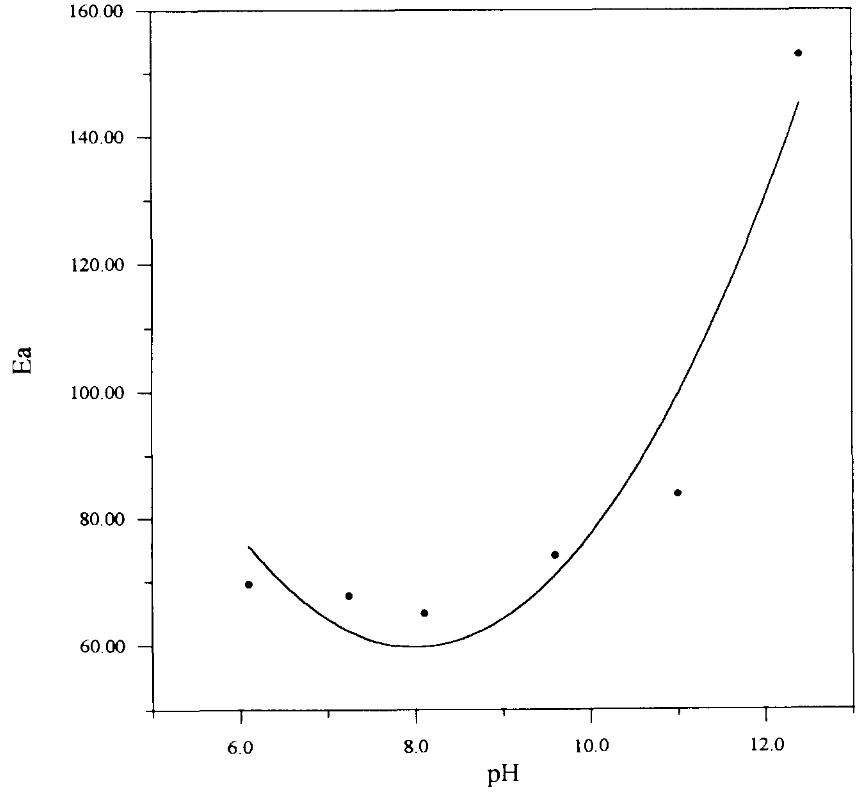


Fig. 8. Activation energy ($E_a$) of gallic acid–formaldehyde condensation reactions as a function of pH using ASTM E-698 method.

## 4. Conclusion

In this work, the gallic acid–formaldehyde condensation has been studied as a function of pH value, molar ratio, temperature, and reaction time. The optimal conditions of this condensation were estimated by SEC and enthalpic analysis on DSC. It appears from these analyses that optimal pH is 8, the stoichiometry of these reactions is bimolecular, and the reaction time should be about 4 h at 60°C.

Hydrolyzable tannins are esters of glucose and phenolic acids as gallic acid and/or their derivatives. These tannins can react with formaldehyde in the optimal conditions determined to be used in wood adhesive formulations.

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