Polyflavonoid Tannins Self-Condensation Adhesives for Wood Particleboard

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Work done in the author's laboratory has indicated that polyflavonoid tannins can self-condense to a hardened network without the addition of any hardeners. This allows their use as interior grade adhesives for wood panels. For fast-reacting tannins, such as procyanidins, the catalytic effect exercised solely by the lignocellulosic substrate is enough to give strength performance satisfying relevant standards. For slower-reacting tannins such as prorobinetinidins and profisdetinidins, small amounts of finely divided SiO_2 dissolved in a tannin solution in water at pH of 11–12 is sufficient to catalyse such a self-condensation effect. As there are no added aldehydes, there is little or no detectable formaldehyde.

INTRODUCTION

Tannins are polyhydroxyphenols, which are soluble in water, alcohols, and acetone and can coagulate proteins. They are yielded by extraction from wood substance, bark, leaves, and fruits. Other components of the extraction solutions are sugars, pectines, and other polymeric carbohydrates, aminoacids, and other substances. The content of non-tannins can reduce wood failure and water resistance of glued bonds. The polymeric carbohydrates especially increase the viscosity of the extracts.

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Usually spray dried powders are sold. Purification steps are not usually undertaken at the industrial scale. The modification of the extracts is especially aimed at decreasing the sometimes excessive viscosity to allow better handling and application, but also a longer pot life and a better crosslinking [1].

As tannins contain many "phenolic"-type subunits, one may be tempted to think that they will exhibit a similar reactive potential to that of phenol and, therefore, procedures used in standard phenol-formaldehyde (PF) production can be transferred to those containing tannin. This, however, is not the case. The real situation is that tannin is far more reactive than unsubstituted phenol due to the resorcinol and/or phloroglucinol rings present in the tannin. For example, this increase in hydroxyl substitution on the two aromatic rings affords an increase in reactivity to formaldehyde by 10 to 50 times when compared with simple phenol, the reactive sites being those indicated by an asterisk in Scheme 1.

Cross linking *via* methylene or methylene ether bridges in a poly-condensation reaction has been traditionally used for the tannins to fulfill their traditional role as exterior weather resistant adhesives (Scheme 2). Possible crosslinkers are paraformaldehyde [1], methylolurea mixtures such as urea-formaldehyde precondensate or
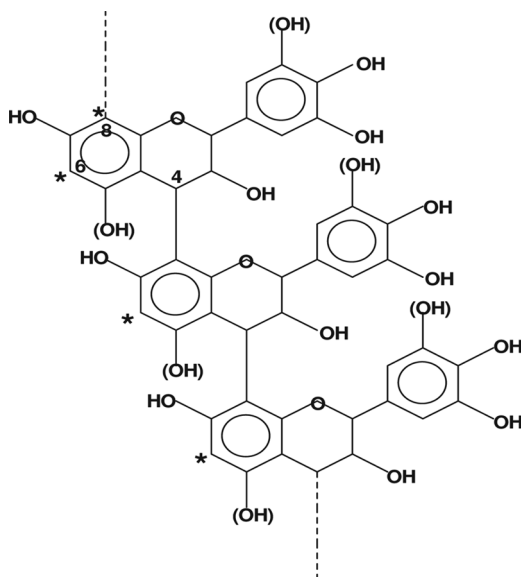
SCHEME 1 Typical structure of condensed flavonoid tannins.
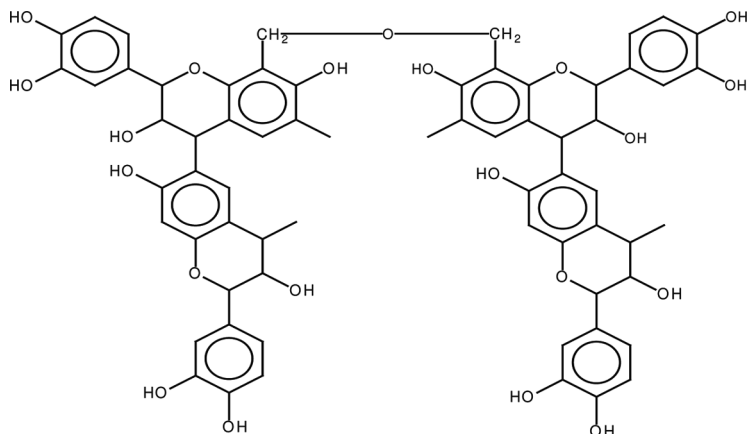
SCHEME 2 An example of a type of cross-linking of flavonoid tannins with formaldehyde. The link shown is a dimethylene ether type.

formurea [2], or urea and phenol methylols with longer chains to overcome steric hindrance.

Tannins can also be hardened by addition of hexamethylentetramine (hexamine) [3–5], whereby these boards show no formaldehyde emission [5,6], this technology being used industrially and being in straight competition with tannnin autocondensation as we describe it in this article.

The autocatalytic hardening of tannins without addition of formaldehyde or another aldehyde as crosslinker is possible, if small traces of alkaline SiO_2 are present as catalyst under high pH conditions, or with certain more reactive tannins, such as pine tannin, just by the catalytic action induced by the wood surface [7–9].

Tannin-based wood adhesives for panel products are slowly gaining industrial acceptance in markets such as in Europe and Japan, other than those where they have been traditionally used for many years [5]. On top of traditional, well studied, and reported formulations [1,3], formulations based on new principles [6,7,10–12] targeting new or revised market needs have been developed. New concepts and principles have been used to produce a new generation of tannin-based adhesives. There are mainly two examples of topical importance: (1) the experiences with the autocondensation and hardening of tannins without any aldehyde to give interior grade particleboard not just of zero formaldehyde emission but of zero aldehyde content [6] and of the associated fundamental research on tannin autocondensation [7–9,13–20], and (2) the demonstration that hexamine does not

behave as a formaldehyde yielding compound when in presence of a polyflavonoid tannin [21,22]. This latter technology, now in use in two countries in Europe and in Japan [5,23], will not be described here. This article instead will concentrate on tannin autocondensation.

DISCUSSION

Fundamentals of Tannins Ionic Self-Condensation

Polyflavonoid tannins self-condense and harden when in the presence of small amounts of silica (SiO_2) at high pH. The mechanism of self-condensation and hardening was found to depend on the Lewis acid behaviour of the additives used. Such a mechanism involves Lewis acid acceptance of electrons from the ether oxygen of the flavonoid unit pyran ring with subsequent facilitation of base-induced heterocycle opening. The reactive C2 site created by the heterocycle ring opening proceeds to autocondense with the reactive A-ring of a flavonoid unit of another chain, denying to the flavonoid the possibility of intramolecular rearrangements to catechinic acid and phlobatannin which occur in model compounds. Si has been shown by CP-MAS ^{29}Si NMR to pass through an intermediate coordination state of five. The portion of Si which has not been able to complete the reaction due to premature hardening remains attached to the flavonoids, in this coordination state, in the hardened network. The Si portion which has completed the reaction and caused the hardening reverts instead to SiO_2 and is detached from the flavonoid. The SiO_2 mechanism shows that the presence of this type of catalyst also reverses the relative ease of cleavage between interflavonoid bond and heterocycle opening in mainly procyanidin and profisetinidin tannins. Several variations of the self-condensation mechanism have been presented [7], the most usual being as follows (Scheme 3).

Equally, tannin self-condensation was found to be facilitated by the reaction occurring on cellulose and lignocellulosic substrates. Although the mechanism of polyflavonoid self-condensation induced by cellulose differs from that induced by the action of Lewis acid [9], the subsequent self-condensation reaction appears to be similar. Catalysis of polycondensation reactions for both synthetic and for natural resins has been clearly demonstrated by kinetic experiments in previous work [24]. The determining step of the tannin rearrangement pathway under alkaline conditions, when cellulose-induced, is the preferential heterocycle pyran ring opening over the usual interflavonoid bond cleavage and catechinic acid rearrangement. This is caused by the weakening of relevant flavonoid bonds and their easier cleavage induced by the strong attractive forces between flavonoid and cellulose substrate.
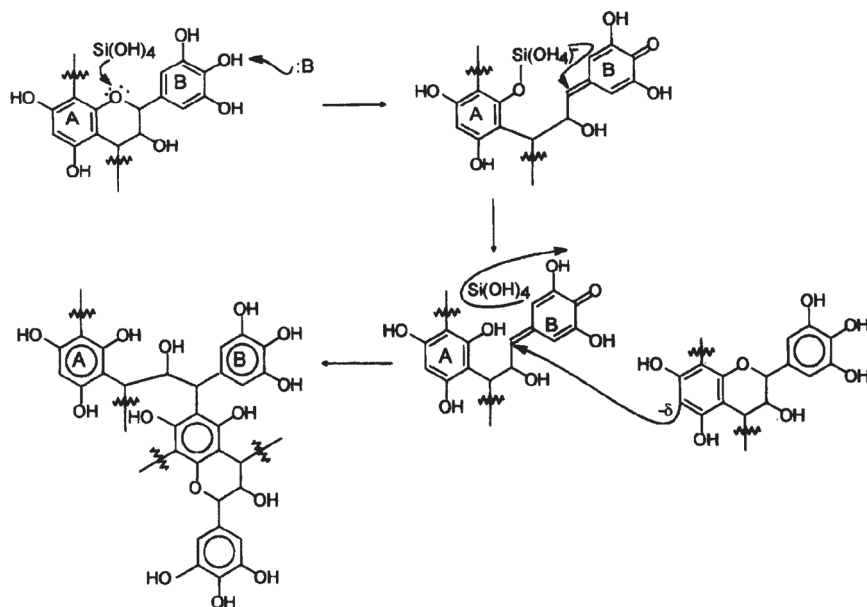
SCHEME 3 Mechanism of ionic self-condensation of tannin adhesives.

Fundamentals of Tannins Radical Self-Condensation

Comparative kinetcs of the radical autocondensation induced by SiO_2 on a series of polyflavonoid tannins, such as pine, pecan, mimosa, quebracho, and gambier tannins, and on catechin as their model compound, have been carried out by electron spin resonance (ESR). The induced radical self-condensation appeared to be independently catalyzed by a base mechanism, as well as by SiO_2 and Lewis acid attack directly at the herocyclic oxygen of the flavonoid. The reaction occurs in two definite steps: (1) radical anion formation and (2) condensation with other flavonoid of the reactive sites formed. The rate determining step depends on both the main flavonoid unit structure of each tannin and, particularly, on the level of colloidal state of the tannin solution and the number average degree of polymerisation (DP_n), with the latter two parameters being the main determining ones for the second reaction step and the first two for the first reaction step. It is, however, the combination of the three parameters that determines the total observable effect for each of the flavonoid tannins. The SiO_2 attack at the heterocyclic ether oxygen is of such an intensity that the A-rings phenoxide radicals, which drive the reaction, surge very rapidly to such a higher proportion than the B-rings

phenoxide radicals that the B-rings also start to surge later by shifting to the left the $B° \leftrightarrows A°$ radicals equilibrium. There have also been clear indications that ionic mechanisms are more important for the second step of the reaction and that they occur at the same time. Different radical-anion species and the relative movements of the relevant equilibria involved can be identified by ESR spectra. The initial, maximum intensity of the peaks has been shown to refer to the first step of the reaction, while the radical decay rate has been shown to undergo neither any silica-induced radical surge nor auto-condensation as predictable from their structures.

The radical decay reaction of the phenoxyl radicals was followed [14–17] by the variation as a function of time of the peak intensities of the resolved fine structure of the phenoxyl signal in the presence of different co-reactants such as SiO_2 and urea [25]. In general, between eight and ten peaks appeared, in reality representing only four to five radical-anion species as each peak is the mirror image around the symmetry centre of the spectrum of another peak repre-senting the same species [14–20]. Of these, the four peaks closer to the symmetry centre of the spectrum represent radical anions on the tannin B-rings. The four to six peaks further away from centre of sym-metry of the spectrum represent the radical anions on the tannin A-rings. The curve of the rate of decrease of each peak intensity, for each peak, for each of four polyflavonoid tannins (mimosa, quebracho, pine, and pecan) when alone or in the presence of either SiO_2 or urea, for each tannin, was modelled by double exponential equations of the type:

$$Y = Y_0 i + A_1 e^{-x/T_1} + A_2 e^{-x/T_2}, \tag{1}$$

where x is the reaction time, Y and Y_0 are, respectively, the total ESR peak intensity of the peaks at a time, t, and the residual intensity (time$(\rightarrow\infty)$, A_1 and A_2, are the preexponential factors, and $1/T_1$ and $1/T_2$ are the two rate constants (s^{-1}) [16–18].

Considering the number of peaks which could be followed for all the different cases, this gave rise to a number of equations [15–18] of this type for which Y_0, A_1, A_2, T_1, T_2, the coefficient of correlation between model and experimental data, and the value of Y at time $= 0$ were determined and recorded [16–18].

While these equations describe, to an acceptable level (typically coefficients of correlation 0.92–0.999), the decrease of the phenoxyl radicals concentration, the results [18] indicated that reactions other than simple radical decay appear to be present. Thus, equilibria between the different radical-anions were observed. Thus, the B-ring
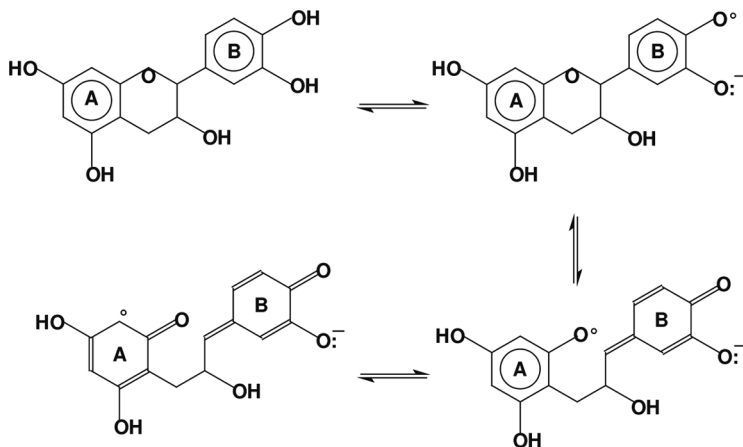
SCHEME 4 Equilibrium of the different radical-anions in flavonoid tannins leading to a radical self-condensation of tannin adhesives.

radical concentration for quebracho tannin just in the presence of a base decreases so rapidly that its concentration is supplemented by the A-ring's radical anions converting to B-ring radicals by a shift in the equilibrium (Scheme 4) [16–19].

Increases in the concentration of the B-ring radical as a result of a shift in the above equilibrium (Scheme 4) becomes very noticeable from the kinetics curves. Different radical-anion combinations are in equilibrium at different rates, resulting in various levels of each radical anion during specific radical decay reactions.

Electron spin resonance studies show that, in certain cases, hardening by ionic co-reactants can occur with simultaneous hardening of the tannin by radical autocondensation. In these cases, the ionic mechanism greatly predominates. Synergy between ionic and radical mechanisms are instead induced by other ionic co-reactants, while still others do not show any interference between the two types of reactions. The mechanisms of synergy and interference of ionic and radical condensation were found to be very complex [18].

Applied Results

Figure 1 shows the values of Internal Bond (IB) strength of laboratory particleboards made with four different commercial flavonoid tannins, to which no aldehyde has been added, as a function of the pH of the tannin solution applied. These results (based on pressing times of 37.5 s/mm board thickness) describe possible maximum strength with

such adhesive systems. The results shown must then be interpreted as the strength ceilings which are possible with a system in which self-condensation is exclusively induced by the wood substrate, and must not be taken as an industrially applicable result, the pressing time being too long. Catalysis of polycondensation reactions for both synthetic and for natural resins has been clearly demonstreated by kinetic experiments in previous work [24]. It is, however, interesting to note that predominantly procyanidin and prodelphinidin tannins such as pine and pecan tannins can give dry IB strengths as high as 0.8 MPa for 12 mm thick particleboard (Standards require IB strengths $\geq$ 0.35 MPa). Profisetinidin and prorobinetinidin tannins such as mimosa and quebracho are only capable when alone of much lower IB strengths of the wood particleboard, reaching a maximum of 0.3 MPa (Fig. 1).

The difference between these two sets of tannins can be readily defined. Self-condensation is partly driven by the nucleophilic reactivity of the A-rings of the tannin. Thus, tannins containing phloroglucinol-type A-rings (such as pine and pecan tannin) cross-link more extensively and with relatively greater ease than tannins with much less reactive resorcinol-like A-rings. The IB strength values of the boards in Fig. 1 appear to improve with increasing pH of the tannin solution. This is so because the reaction of self-condensation is, firstly, driven
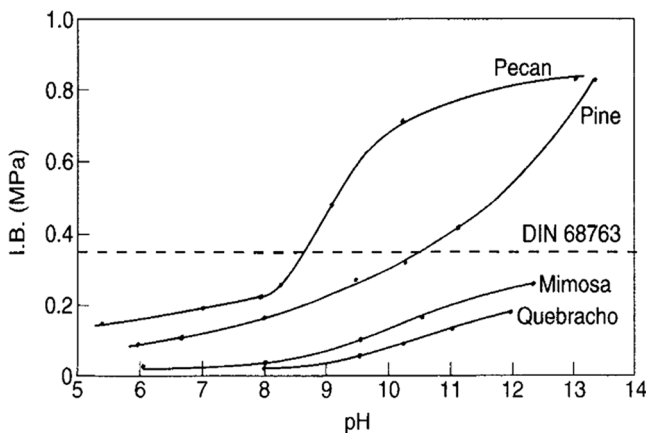

FIGURE 1 Dry internal bond (I.B.) strengths as a function of pH of tannin solution, for laboratory particleboard prepared with four different tannin extracts without any aldehyde hardener, using the lignocellulosic substrate-induced tannin self-condensation.

by the opening of the flavonoids heterocyclic rings and, secondly, by the subsequent self-condensation of the reactive sites formed with the A-rings of other flavonoid units on other tannin chains.

It is also noticeable from Fig.1 that the dry IB strength of particleboard bonded by mimosa and quebracho tannin self-condensation is not able, even at higher pHs, to reach the relevant dry IB strength requirements of internationally accepted standards [6,26]. The faster reacting pine and pecan nut tannin extracts require only a pH of 10.7 and 8.5, respectively, or higher, for catalysis induced by the lignocelulosic substrate to bring the dry IB strength to a level equal to, or higher than, the requirements of the relevant standards [6,26].

The drawbacks indicated in Fig. 1 for mimosa and quebracho tannins can, however, be remedied. To upgrade the Internal Bond (IB) strength results of particlaboard bonded with the slower tannins it is possible to combine the two systems of catalysis, namely by silica addition and by lignocellulosic substrate effect, thus favouring opening of the heterocyclic ring of the flavonoid [6–8]. Figure 2 shows that this is beneficial and what happens when this is done with mimosa, one of the two slower reacting tannins: even a low amount of silica (3%) improves the IB strength of the particleboard to a value of 0.47 MPa from the low value of 0.16 MPa obtained without dissolved silica. At silica percentages higher than 3%, precuring sets in and the
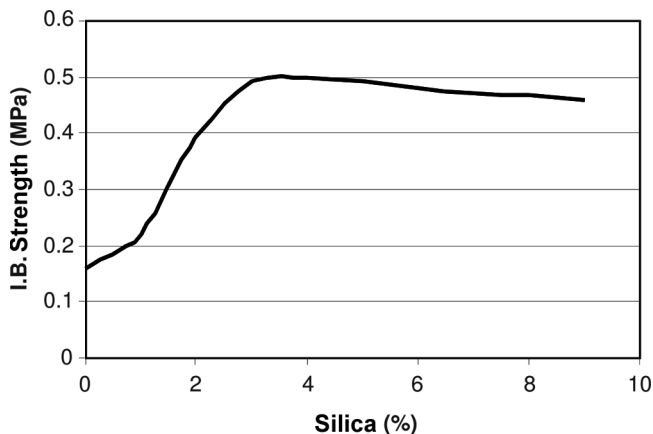

FIGURE 2 Dry internal bond (IB) strength of laboratory particleboard bonded with mimosa tannin extract without any aldehyde hardener using Lewis-acid induced (silica) and substrate-induced tannin self-condensation as a function of weight percentage of silica catalyst.
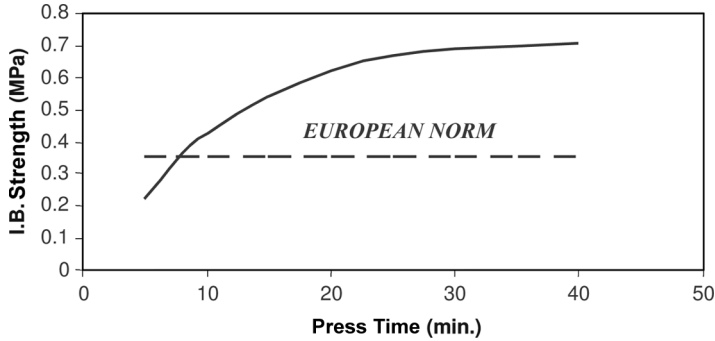
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FIGURE 3 Effect of pressing time on the dry internal bond (IB) strength of laboratory particleboard bonded with a pecan nut tannin extract of pH 10.2, without any aldehyde hardener, using the lignocellulosic substrate-induced tannin self-condensation.

IB strength of the particleboard starts to decrease, although not as markedly as for the faster tannins.

All the discussion above refers to the ultimate strength of the board, thus, to results obtained at pressing times too long (37.5 s/mm board thickness) to be of industrial significance. The effect of shortening the pressing time of particleboard bonded with the tannin capable of easier self-condensation (namely, pecan nut) may be demonstrated (Fig. 3). At 10 s/mm pressing time at a temperature of 190°C, dry IB strengths of 0.4 MPa are obtained, thus, satisfying the requirements of relevant standard specifications (EN 312) [6,26].

The results of formaldehyde emission obtained with the lignocellulosic-induced tannin self-condensation system are of some interest. The very low formaldehyde emission values, measured by the perforator method [6,27] according to European Norm EN 120 [27], indicate clearly that emission is limited to that due to just heating the wood (Table 1). Thus, the emission varies according to the hot pressing time (Table 1) but it is only due to the heat degradation reaction in the wood. This is expected from an adhesive system not containing any formaldehyde.

Laboratory trials using the tannin self-condensation system, without the addition of any additives, were tried by the use of steam injection. In this case, panels 40 mm thick were obtained in Japan by pressing with a particular technique for only 2 minutes with results satisfying the relevant standard requirements for both IB strength and formaldehyde emission [28]. It must be clearly pointed out that, contrary to the

TABLE 1 Typical Formaldehyde Emission Values from Particleboards Bonded by Tannin Autocondensation

Press time (s/mm)	Formaldehyde emission (mg/100 g board)*
37.5	0.8
10	0.6
EN 120 requirements	≤6.5

*By perforator method.

traditional exterior adhesives niche market, these self-condensation tannin adhesives are exclusively able to satisfy the interior panels market, constituting 90% of European board production.

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