Autocondensation-based, zero-emission, tannin adhesives for particleboard

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Interior grade particleboard prepared with tannin adhesives to which no aldehyde hardener was added were prepared. The hardening of the tannin adhesive was induced by the reaction of autocondensation tannins undergo when catalyzed by a lignocellulosic substrate or by a weak Lewis acid as alkali dissolved silica. The more alkaline the tannin extract solution the higher the ceiling internal bond strength that the particleboard bonded with it can reach. Differences between four commercial tannins are discussed. Pecan nut tannin and pine tannin need only lignocellulosic induced autocondensation to give excellent interior grade particleboard. Slower reacting tannins such as mimosa need instead both the catalytic effect of the substrate as well as that of a weak Lewis acid such as silica. Only pecan nut tannin appears at this stage to be able to give boards of acceptable dry internal bond strength at industrially significant pressing times.

Tanninkleber für Spanplatten, hergestellt durch Autokondensation und ohne Emission von Schadstoffen
Spanplatten für die Innenverwendung wurden mit Tanninklebern hergestellt ohne Zugabe von Aldehyden als Härter. Die Härtung der Tannine erfolgt durch Autokondensation. Diese wird katalysiert durch ein lignocellulosisches Material oder eine schwache Lewis-Säure wie in Alkali gelöster Kieselsäure. Je alkalischer die Tanninlösung ist, desto höher ist die Querzugfestigkeit, die erreicht werden kann. Unterschiede zwischen vier kommerziellen Tanninen werden diskutiert. Tannine aus Hickorynuß und Kiefern können schon mit Lignocellulosen zur Autokondensation gebracht werden und eignen sich für hochgradige Spannplatten zur Innenverwendung. Langsamer ragierende Tannine aus Mimosa-Arten benötigen außer diesem Substrat noch eine schwache Lewis-Säure wie z.B. Kieselsäure. Zur Zeit scheint aber nur Hickory-Tannin geeignet zu sein, Spanplatten mit ausreichender Querzugfestigkeit innerhalb industriell vertretbarer Preßzeiten herzustellen.

1
Introduction

Thermosetting polyflavonoid tannin-formaldehyde resins have performed well in industrial applications as wood adhesives for exterior particleboard for more than 20 years (Pizzi 1983). While the reactions of these natural polymeric materials with formaldehyde to give polycondensates have been used extensively, autocondensation reactions characteristic of, and

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inherent to tannins have never been used to prepare adhesives in absence of aldehydes. Tannins autocondensations are known but their effect on polymeric systems has neither been studied nor even been considered for resin preparation and hardening.

Recently a predominantly prodelphinidin tannin, pecan (*Carya illinoensis*) nut pith tannin extract has been found to undergo with ease fairly rapid autocondensation reactions (Pizzi and Stephanou 1993a, b, c; Pizzi 1994). Although this reaction leads to noticeable increases in viscosity (Pizzi and Stephanou 1993a) of concentrated (40%) tannin solutions, gelling does not occur: the reaction by itself then does not lead to cross-linked, hardened resins. Even more recently however, a series of catalysts to induce accelerated autocondensation of this and other tannins has been described and its mechanism studied in depth on the natural polymers (Meikleham et al. 1994). The autocondensation to gelation of tannin extracts has been found to be induced by weak Lewis acids (Meikleham et al. 1994; Pizzi 1994), and in particular by dissolved silica (Meikleham et al. 1994; Pizzi 1994), boric acid (Meikleham et al. 1994; Pizzi 1994) and others, when used in very small proportions (3%) of tannin extracts solids. For example, addition of an alkaline solution of silica to a 40% tannin extract solution at a pH of 10 to 12 gels and hardens the tannin solution in just a few minutes even at ambient temperature (Meikleham et al. 1994; Pizzi 1994). Even the addition of finely powdered silica ("silica smoke", Aerosil) to a tannin solution at pH 12 causes a similar effect (Meikleham et al. 1994; Pizzi 1994). A dissolved silica catalyzed system is of particular interest because both the tannin resin and the catalyst are of natural origin and not toxic. Even of greater interest has been the finding that the presence of a lignocellulosic substrate catalyses and accelerates not only the curing of synthetic formaldehyde-based resins (Pizzi et al. 1995; Pizzi 1994) but also the autocondensation and hardening of tannin extracts alone. This is particularly noticeable at high pH (Pizzi et al. 1995; Pizzi 1994). The preparation of particleboard eclusively by application of a tannin extract at high pH, with no formaldehyde, or rather no aldehydes being used, or at most by the addition of a few percentages of dissolved silica, is then a real and exciting possibility. It would give a panel completely composed of natural, non-toxic materials and consequently very environmentally acceptable.

This paper then describes the results obtained by applying the induced, catalysed autocondensation of tannins for interior and exterior grade particleboard.

2
Particleboard preparation and testing

2.1
Substrate catalysis – Tannins alone

Duplicate single layer laboratory particleboard of 400 × 400 × 12 mm dimension were prepared using industrial core particles

of *pinus radiata* wood of 3% moisture content. The core chips used were obtained from a particleboard mill and had average dimensions of 15 × 1.2 × 0.5 mm and contained 10% powdered wood fines. The wood particles were sprayed with 40% aqueous solutions of four commercial tannin extracts: Pecan (*Carya illinoensis*) nut pith extract, Pine (*Pinus radiata*) bark tannin extract, Mimosa (*Acacia mollissima*) bark tannin extract, and Quebracho (*Schinopsis balansae*) wood tannin extract. The aqueous solution of the four tannin extracts were applied at pHs of approximately 5, 6, 8, 9, 10, 11, 12 and 13 (the exact pH values for each tannin are indicated in Fig. 1). The tannin solutions were applied at a resin solids content of 11% by weight on dry wood particles. The pressing conditions used were: 25 kg/cm² maximum pressure with a pressing cycle of 2 minutes up to, and maintaining maximum pressure followed by 2.5 minutes at a pressure of 10 kg/cm² and by 3 minutes at a pressure of 3 kg/cm², for a total of 7.5 minutes pressing time. Pressing temperature was of 190 °C. The densities obtained were of 0.680–0.700 g/cm³. The boards were tested for dry internal bond (IB) strength according to standard specifications (DIN 68763; SABS 1300). Each test comprised 10 specimens. The results are shown in Fig. 1.

2.2
Substrate catalysis – Mix of tannins

Mixes of pecan nut tannin extract and of the other three tannins in different proportions as indicated in Fig. 2 were prepared. All the tannin solutions were at pH 10.2 and resin solids content on dry wood particles was of 11% by weight. Duplicate one layer particleboard were prepared under identi-

Fig. 2. Dry internal bond (IB) strengths of laboratory particleboard bonded with mixtures of different tannin extracts, without any aldehyde hardener, as a function of percentage of pecan nut tannin extract, using the lignocellulosic substrate-induced tannin autocondensation. All mixes were at pH 10.2

Bild 2. Querzugfestigkeit (trocken) von Laborplatten, die mit einer Mischung verschiedener Tannine verleimt wurden ohne Aldehyd–Härter. Die Autokondensation wurde induziert durch Ligncelluslosen bei pH 10,2

cal conditions as indicated for the previous case. The results are shown in Fig. 2.

2.3
Silica + substrate catalysis

Finely powdered silica (Aerosil "silica smoke") was added in proportions by weight of 0%, 3%, 6%, 9% and 18% , by separate application, during the spraying of the 40% tannin solutions to the wood particles. The pH of the tannin solutions were of 8.3, 10.2, and 12 as indicated for the different tannins in Fig. 3. Boric acid was also used in the case of pecan nut tannin at a level of 3% and 6% according to the same separate application technique. Duplicate particleboard were pressed under the identical pressing conditions outlined in the previous cases. The results are shown in Fig. 3.
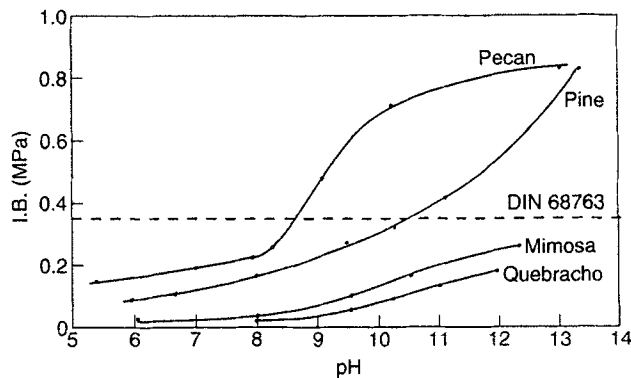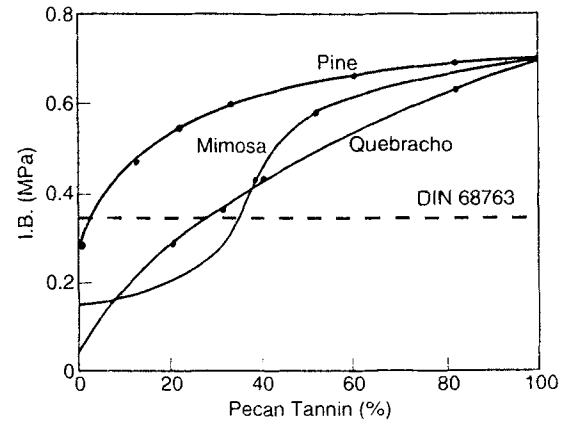

Fig. 1. Dry internal bond (IB) strengths as a function of tannin solution pH of laboratory particleboard prepared with four different tannin extracts without any aldehyde hardener, using the lignocellulosic substrate – induced tannin autocondensation

Bild 1. Querzugfestigkeit (trocken) als Funktion des pH-Wertes der Tanninlösung bei der Herstellung von Laborplatten mit vier verschiedenen Tanninen ohne Aldehyd–Härter. Die Autokondensation wurde induziert mit Lignocellulosen

Table 1. Formaldehyde emission results of particleboard prepared with substrate-induced pecan nut tannin autocondensation at different pressing times by perforator method (DIN EN 120) (Fig. 5)

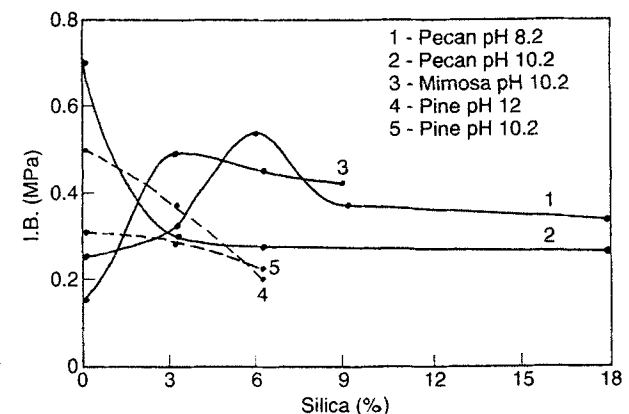| Press time (s/mm)	Formaldehyde emission (mg/100 g board)
10.0	– 0.01
15.0	– 0.01
25.0	0.01
37.5	0.03
37.5 Wood only control	0.03

Fig. 3. Dry internal bond (IB) strengths of laboratory particleboard bonded with different tannins, without any aldehyde hardener, using both Lewis acid-induced (silica; boric acid) and substrate-induced tannin autocondensation, as a function of weight percentage of silica catalyst.

Bild 3. Querzugfestigkeit (trocken) von Laborplatten, die mit verschiedenen Tanninen verleimt wurden ohne Aldehyd–Härter, in Abhängkeit vom Gehalt am Kieselsäure als Katalysator. Die Autokondensation wurde induziert durch schwache Lewis-Säuren (Kieselsäure; Borsäure) und Lignocellulosen
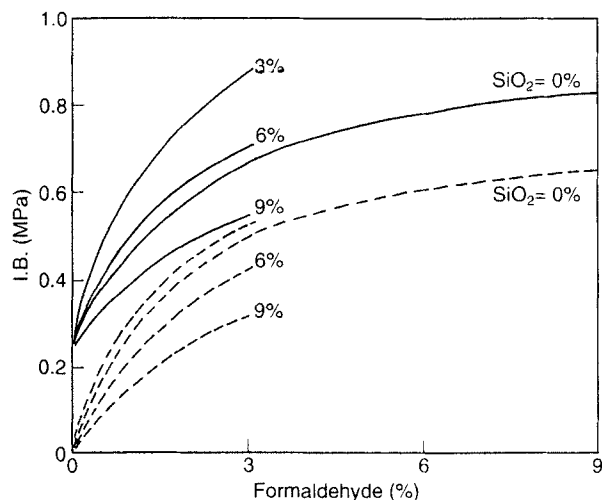
Fig. 4. Dry internal bond (IB) strengths and IB strengths after 2 hours boiling, tested dry, as a function of varying proportions of silica and paraformaldehyde of laboratory particleboard bonded with pecan tannin extract

Bild 4. Querzugfestigkeit (Trockenfestigkeit: --- und nach 2stündigem Kochen ---) von Laborplatten, die mit einem Tanninextrakt aus Hickorynüssen verleimt wurden. Variert wurde der Gehalt an Kieselsäure und Paraformaldehyd

2.4
Mixed silica + formaldehyde particleboard

Duplicate particleboard were prepared according to the identical conditions outlined in the preceding paragraphs but mixing 0%, 3%, 6%, and 9% paraformaldehyde fine powder 96% grade to a pecan nut tannin extract solution of pH 8.2 and by separate application of 0%, 3%, 6% and 9% finely powdered silica smoke. The boards were tested for both dry IB strength and IB strength after 2 hours boiling, tested dry (SABS 1300). The results obtained are shown in Fig. 4.

2.5
Substrate catalysis – pressing time effect

Duplicate particleboard were prepared using a 40% solution of pecan nut tannin extract of pHs 10.2 and 13.0 under the same pressing conditions outlined for the preceding cases. The pressing time of the panels was varied between 7.5 minutes (37.5 s/mm), 5 minutes (25 s/mm), 3 minutes (15 s/mm), 2 minutes (10 s/mm). The IB strength results obtained are shown
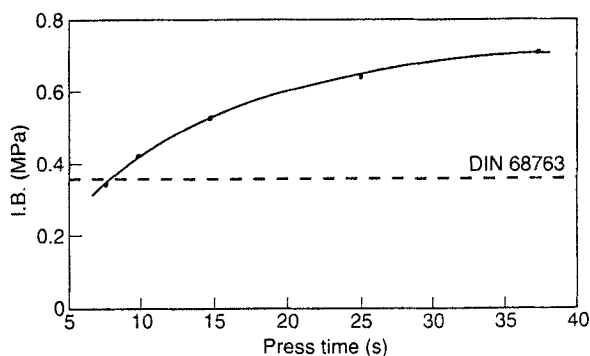

Fig. 5. Effect of pressing time on the dry internal bond (IB) strength of laboratory particleboard bonded with a pecan tannin extract of pH 10.2, without any aldehyde hardener, using the lignocellulosic substrate-induced tannin autocondensation

Bild 5. Einfluß der Preßzeit auf die Querzugfestigkeit von Laborplatten, die mit Tanninextrakten aus Hickorynüssen bei pH 10,2 ohne Aldehydhärter verleimt wurden. Die Autokondensation wurde mit Lignocellulosen induziert

in Fig. 5. The boards were also tested for formaldehyde emission according to the perforator method (DIN EN 120, 1984); the results are shown in Table 1.

3
Discussion

In Fig. 1 are reported the values of Internal Bond (IB) strength of laboratory particleboards made with four different commercial flavonoid tannins, to which no aldehyde has been added, in function of the pH of the tannin solution applied. The results in Fig. 1 only describe what ultimate maximum strengths are possible with such systems; it is for this reason that long pressing times (37.5 seconds/mm) are used. The results must then be interpreted as the strength ceilings which are possible with a system in which autocondensation is exclusively induced by the wood substrate, and must not be taken at this stage as industrially feasible results. It is however interesting to note that predominantly procyanidin and prodelphinidin tannins such as pine and pecan can give dry IB strength ceilings as high as 0.8 MPa for 12 mm thick particleboard. Profisetinidin and prorobinetinidin tannins such as mimosa and quebracho are only capable of much lower IB strengths of the particleboard, tending to a maximum of 0.3 MPa. The difference between the two sets of tannins is understandable: as the autocondensation is partly driven by the reactivity as a nucleophile of the A-rings of the tannin, then tannins presenting phloroglucinolic A-rings (pecan and pine) cross-link more extensively and with relatively greater ease than tannins with a much less reactive resorcinolic A-ring (mimosa and quebracho). The IB strength values of the boards in Fig. 1 appear to improve with increasing pH of the tannin solution. This is expected as the reaction of autocondensation is firstly driven by the opening of the heterocycle ring of the flavonoids and secondly by the subsequent autocondensation of the reactive site formed with the A-ring of another flavonoid unit in another tannin chain (Pizzi and Stephanou 1993a, 1993 c; Pizzi et al. 1995; Pizzi 1994).

In Fig. 1 it is also noticeable that the dry IB strength of particleboard bonded with mimosa and quebracho tannin extracts is not able, even at the higher pHs, to reach the relevant dry IB strength requirements of internationally accepted standards (DIN 68765; SABS 1300). The faster pine and pecan nut tannin extracts instead need respectively only a pH of 10.7 and 8.5 or higher, for the catalysis induced by the lignocellulosic substrate to bring the dry IB strength of the particleboard to a level equal to, or higher than the requirements of the relevant standard (DIN 68765; SABS 1300).

The drawbacks indicated in Fig. 1 for mimosa and quebracho tannins can however be remedied in two ways. Fig. 2 indicates the first one of these. At pH 10.2, mixing the tannin most prone to autocondensation, namely pecan nut tannin, with the other tannins induces a considerable improvement of all the other three tannins. Thus, just 10% pecan nut tannin extract upgrades the IB strength of particleboard (now bonded with a 10:90 pecan: pine mix) from 0.3 MPa to 0.45 MPa; a 30% and 40% pecan nut tannin extract addition is capable of improving the IB strength of particleboard bonded with mimosa and quebracho tannin extracts from 0.12 and 0.07 MPa to 0.44 and 0.37 MPa respectively (Fig. 2). This is so under identical amounts of adhesive solids content and under identical application and pressing conditions. The effect appears to be more marked with increasing proportions of pecan nut tannin extract (Fig. 2). This is consistant with the mechanism of autocondensation advanced for pecan nut tannin extract (Pizzi et al. 1995). Thus, the induced opening of the pecan heterocycle occurs as described (Meikleham et al. 1994; Pizzi et al. 1995), but the presence of a preponderance of another tannin ensures that the

second step of the reaction, the intermolecular autocondensation, occurs also with flavonoid units belonging to another tannin. This also ensures some copolymerization between the two types of tannin.

The second way to upgrade the IB strength results of particleboard bonded with the slower tannins is to combine the two catalysis systems, silica-based and substrate-based, favouring opening of the heterocycle ring of the flavonoid. Figure 3 shows what happens when this is done with the two fast tannins and with one of the slower tannins (mimosa). In the case of the fast tannins combination of the two catalysis systems is damaging to the IB strength results of the particleboard: this is so because the reaction of autocondensation becomes so fast that very noticeable precuring of the adhesive occurs. The double catalysis system of autocondensation can however be used for obtaining good IB strength results at lower pHs. Thus, pecan nut tannin at pH 8.2 bonds particleboard to an increased value of IB strength when increasing the % silica from 0% to 6%, the IB strength passing from 0.25 to 0.53 MPa. At silica percentages higher than 6% however, fast precuring is again evident and the IB strength value decreases markedly (Fig. 3). In the case of the much slower mimosa tannin the combination of the two catalyst systems appears instead to be beneficial: even a low amount of silica improves the IB strength of the particleboard to a maximum value of 0.47 MPa from the low value of 0.16 MPa obtained without dissolved silica. Here too, at silica percentages higher than 3%, precuring sets in and the IB strength of the particleboard starts to decrease, although not as markedly as for the fast tannins.

It is also of interest to see if exterior grade properties can be obtained when using a much reduced amount of formaldehyde hardener if the silica catalysis system is used. Without formaldehyde, the silica-based tannin autocondensation system is not capable of imparting exterior properties to particleboard (Pizzi et al. 1995). Figure 4 indicates that addition of a small percentage of silica (up to 3%) improves dry IB strength of the particleboard when a very low amount of formaldehyde is used. However, it does not change the value of the IB strength after 2 hours boil, tested dry (SABS 1300). Thus, it appears that there is no advantage in mixing a reduced amount of formaldehyde with the silica catalysis of the tannin autocondensation, except perhaps to obtain an increase in dry IB strength or a reduced amount of formaldehyde in boards prepared with slower tannins (such as mimosa and quebracho). This however, means to introduce an aldehyde in the system: it renders it much less interesting as it is not anymore an aldehyde-free system. Such a system however presents still some interest because allows the preparation of exterior grade particleboard needing a lower level of formaldehyde addition.

All the discussion above refers to ultimate strength of the board, thus to results obtained at pressing times too long (37.5 s/mm) to be of any industrial significance. In Fig. 5 instead, the effect of shortening the pressing time of particle board bonded with the tannin presenting easier autocondensation (pecan) is shown. At 10 s/mm pressing time, dry IB strengths of 0.4 MPa are obtained, thus satisfying the requirement of relevant standard specifications (DIN 68765; SABS 1300). A pressing time of 12.5 s/mm, resulting in an IB strength of 0.5 MPa, might however be safer for industrial application.

Of interest is to observe the results of formaldehyde emission obtained with the lignocellulosic-induced tannin-autocondensation system. The result in Table 1, obtained by perforator method (DIN EN 120), indicate clearly that the very low amount of formaldehyde detected is only due to the high temperature heating of the timber, as indeed it would be expected from an adhesive system not containing any aldehyde.

4
Conclusions

In conclusion, the results show that a tannin adhesive system for interior grade particleboard based on tannin autocondensation reactions and without the use of any aldehyde hardeners can work and work quite well. Limitations of pressing time exist however, and only the faster tannin more prone to autocondensation, namely pecan nut tannin, appears to allow the use of pressing times even vaguely approaching industrial significance. The silica-based autocondensation system however can be used to upgrade IB strengths and pressing times of the slower reacting profisetinidin/prorobinetinidin tannins.

5
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