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Lignin-derived non-toxic aldehydes for ecofriendly tannin adhesives for wood panels

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ABSTRACT

An adhesive based on the reaction of a very fast reacting procyanidin-type condensed tannin, namely purified pine bark tannin, and food-grade non-toxic slow-reacting aldehydes derived from lignin was shown to satisfy well the relevant standards for bonding wood particleboard. Vanillin and a dialdehyde derivative of vanillin were the aldehydes used. The oligomers obtained and their distribution have been determined by matrix assisted laser ionization desorption time-of-flight (MALDI-TOF) mass spectrometry for the reactions with catechin used as a model compound and with the pine tannin itself, and by cross polarization magic angle spinning ^{13}C nuclear magnetic resonance (CP MAS ^{13}C NMR) for the reaction with pine tannin.

1. Introduction

Tannin adhesives have now been around for a long time, a considerable amount of research on them has been published [1,2] and they have also been used industrially in a number of different countries [3–5]. However, the older industrially-used technology already in operation from the early 1970s still relies on the use of paraformaldehyde [1,3]. The proportion of formaldehyde used for these adhesives is anyhow only about 1/10th of the one used in equivalent synthetic adhesives. Nonetheless, there is now intense pressure to diminish or even eliminate formaldehyde from wood adhesives as it has been classified Carcinogenic Mutagenic Reprotoxic (CMR) [6]. In the case of tannin adhesives some substitutes have been tested [1,7,8] but three have dominated research on formaldehyde alternatives, namely hexamethylenetetramine (hexamine) [4,9–11], glyoxal [12], glyoxalated lignin [13] and furanic materials such as furfural and furfuryl alcohol [1,13,14]. Two of these approaches have been tried industrially [3–5]. Hexamine on the basis that, in presence of a fast reacting condensed flavonoid tannin, it does not decompose to formaldehyde but to extremely reactive intermediate compounds cross-linking without elimination of formaldehyde [9–11]. Glyoxal has been promoted and used for the more reactive procyanidin-type tannins such as pine bark tannin and other similar tannins [12]. Notwithstanding this, and the demonstrated advantages (and disadvantages) of hexamine and the limitation of glyoxal to the more reactive condensed tannin types, the search is still on for a compound capable to cross-link some tannins and being totally environment friendly.

Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages at reactive positions on the flavonoid molecules, mainly the A rings. Other aldehydes react also in the same manner as formaldehyde, but are less reactive [1]. The phloroglucinol-like A rings of procyanidin-type tannins, such as pine bark tannin, show reactivity toward formaldehyde comparable to that of phloroglucinol [15–17]. Assuming the reactivity with formaldehyde of phenol to be 1 and that of phloroglucinol to be 100, the A rings of pine tannins, as all procyanidin-type tannins, have a reactivity of around 40 [1,18]. They are thus far more reactive than phenol itself. Tannins present minimal reactivity at pHs around 3.5–4.5 and their reactivity progressively increases as the pH increases to eventually almost stabilize at around pH 10 and higher. Thus, if an aldehyde of lower reactivity needs to be used, such as glyoxal, or even less reactive, to ensure that a thermoset cross-linked resin is obtained, a very reactive tannin, such as a procyanidin type tannin needs to be chosen, as well as a range of pH in which the cross-linking reaction is relatively fast. In commercial mimosa tannin adhesives for wood particleboard

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Table 1
Gel times of purified pinus pinaster condensed flavonoid tannin with vanillin and with Hyd-BzAld.

Resin type	pH	Gel time
Commercial Mimosa tannin adhesive + formaldehyde control	6.8	2 min 10 s
Pinus pinaster + formaldehyde control	3.2	1 min 30 s
Pinus pinaster + vanillin	3.2	15 min 12 s
Pinus pinaster + vanillin	10	2 min 47 s
Pinus pinaster + Hyd-BzAld	10	3 min 24 s

panels when using formaldehyde, the gel time at 100 °C at which the resin is set to obtain optimal results is around 110–130 s [1,3]. Conversely the much slower gelling synthetic phenol formaldehyde resins gel in anything between 9 and 40 min at 100 °C according to the presence or not of accelerators in the glue-mix.

First of all it is necessary to remind that flavonoid and hydrolysable tannins have been certified as non-toxic in their REACH evaluation [19,20]. Thus, to maintain a totally environment friendly, non-toxic classification of wood adhesives based on these materials nothing short than a cross-linker both non-toxic and

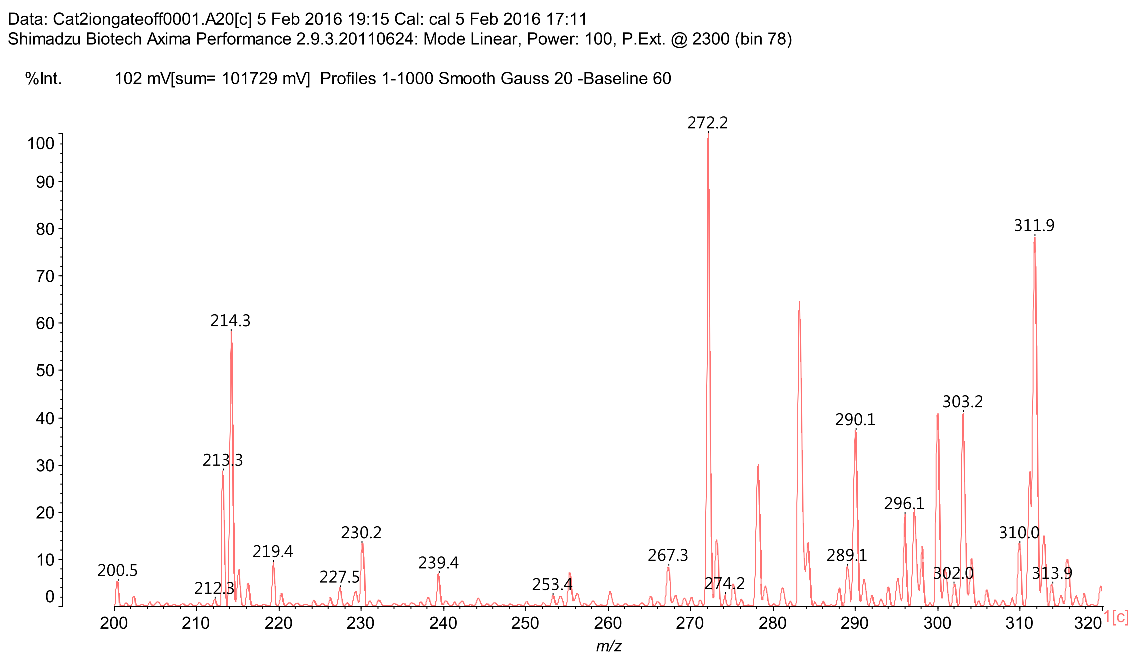

Fig. 1. MALDI-TOF mass spectrum of catechin-vanillin resin. Range 200 Da – 320 Da.

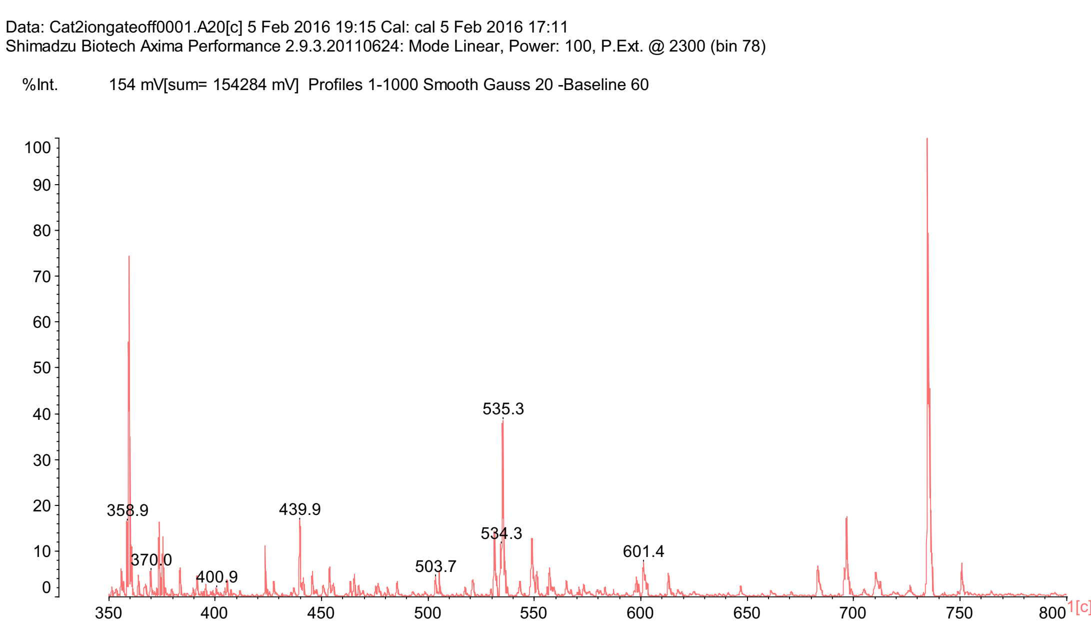

Fig. 2. MALDI-TOF mass spectrum of catechin-vanillin resin. Range 340–800 Da.