



Tannin plywood bioadhesives with non-volatile aldehydes generation by specific oxidation of mono- and disaccharides

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ABSTRACT

Sodium periodate has been shown to cleave glucose by specific oxidation to yield a number of non-volatile aldehydes which can react with the phenolic compounds in tannin extract and lead to tannin cross-linking and hardening. This approach to prepare a tannin resin useable for wood adhesives can be used by either treating with periodate a mixture of tannin and glucose, or to treat glucose beforehand with periodate to cleave it and generate the aldehydes, and only afterwards to mix it with the tannin. The results obtained with these two methods are identical, but the latter method avoids oxidation of tannin. The aldehydes were generated either by direct cleavage of glucose C–C bonds carrying vicinal oriented hydroxyls, or by recombination of the aldehydes so formed by aldol condensation or by water elimination between two aldehyde groups. MALDI ToF analysis indicated that all the three types of aldehydes appeared to react with the polyphenols in the tannin. Thermo-mechanical analysis (TMA) and plywood bonded with the tannin + glucose + periodate mixes gave good bonding results, with dry, 24 h cold water soaking and 3 h at 63 °C shear strength values improving concomitantly to the proportion of periodate used for the oxidation step.

1. Introduction

Recently, to meet new environmental standards a number of different approaches to the use of natural materials have been taken to prepare wood adhesives without the use of formaldehyde. Among the more recent ones the use of specific oxidants of oligomeric carbohydrates in soy flour have shown particularly interesting results allowing not only the protein fraction but also the carbohydrate fraction to participate positively in the preparation of the adhesive. In this approach soy flour adhesives have been successfully prepared by treating soy flour with either potassium permanganate or sodium periodate [1]. Sodium periodate is a specific oxidant for carbohydrates reacting with adjacent vicinal hydroxyl groups to form dialdehydes [1–12] according to the reaction shown in Scheme 1.

The aldehydes so generated react with the active sites of the soy protein leading to cross-linking and yielding plywood panels presenting very encouraging shear bond strengths, especially under wet testing conditions [1,2].

The oxidation with the periodate ion, resulting in 1,2-glycol scission, is one of the most widely used reactions in carbohydrate chemistry. The

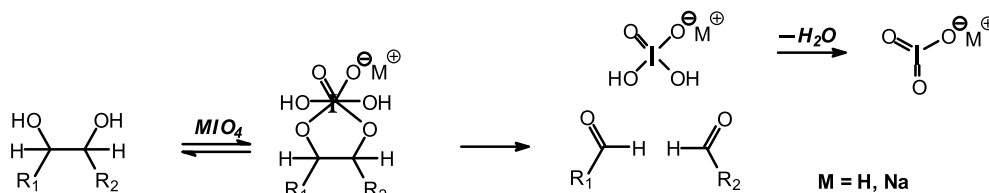
mild reaction and the aqueous solvent conditions for periodate oxidation are particularly apt to use with the water-soluble carbohydrates. The development and wide application of the reaction are due to its high degree of selectivity [1].

Such an approach can be used to prepare adhesives also with other natural materials, such as condensed polyflavonoid tannins, which are even more reactive than proteins towards aldehydes, possibly even such carbohydrate-generated aldehydes. The chemical and physical characteristics of commercial condensed tannin extracts, such as those from mimosa, quebracho and pine bark, are influenced by the notable presence of simple carbohydrates (hexoses, pentoses and disaccharides) and complex glucuronates (hydrocolloid gums) as well as oligomers derived from hydrolysed hemicelluloses when these are present in sufficient quantity, that is often the case [13,14]. The percentage of these carbohydrates in commercial tannin extracts is, in general, between 5% and 10% of the total tannin extract weight [13].

The research presented here investigates the use of the specific oxidation approach outlined above to prepare plywood adhesives without formaldehyde from condensed tannin extracts added with glucose to further increase the proportion of aldehydes-yielding

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Scheme 1. Cleavage by periodate of C-C bonds carrying vicinal hydroxyl groups [1–9].

carbohydrates. It also investigates what types of aldehydes are formed by treating glucose with sodium periodate.

2. Experimental

2.1. Preparation of the resins

10 g mimosa tannin was dissolved in water to prepare a 30% solution, the pH adjusted to 10, then 5 g glucose was added and stirred well, after this, 5%, 8% and 10% of sodium periodate based on tannin and glucose total solids were added and mixed to obtain TG-5, TG-8 and TG-10 adhesives. A T and TG controls without periodate were tested as well. For the MALDI analysis the 10 g tannin+5 g glucose+ 1.5 g NaIO₄ mixture was placed in an oven at 120 °C for 1 h. For the plywood instead the reagents were mixed at ambient temperature for 20 min, then spread on the veneers and then hot pressed.

2.2. Plywood bonding

Wood veneers of 2 mm thickness of *Populus tremuloides* were cut into boards of dimensions 100 mm × 180 mm × 6 mm. The glue spread used was of 260 g/m² double glue line, and the joints were hot-pressed at a pressure of 1.75 N/mm² and a temperature of 160 °C for 3 min. Three-ply laboratory panels were prepared. Three bonded panels were prepared with each adhesive combination. Each bonded joint was cut into six samples with a bonded area of 2.5 cm × 2.5 cm and tested according to GB/T17657-2013 [15]. For each adhesive combination 6 samples were tested dry, 6 samples were immersed in cold water for 24 h then tested wet, and 6 specimen were immersed in 60 ± 3 °C water for 3 h then cooled and tested wet. The tests were done in tension in an Instron 3300 dual column universal testing machine (Instron France, Elancourt, France) at a head rate of 2 mm/min.

2.3. Thermomechanical analysis (TMA)

The resins were tested by thermomechanical analysis according to a system already used and tested [16–21]. The samples were prepared by applying each adhesive between two beech wood plies, with dimensions of 21 mm × 6 mm × 1.1 mm. These beech resin-beech sandwich specimens were tested in non-isothermal mode between 25 °C and 250 °C at a heating rate of 10 °C/min with a Mettler Toledo 40 TMA equipment in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 s (6 s/6 s). The classical mechanics relationship between force and deflection allows the calculation of Young's modulus E for each case tested. Such a measuring system has been introduced and is used to follow the progressive hardening of the adhesive with the increase of temperature and to indicate comparatively if an adhesive system is faster or slower hardening and if it gives stronger joints than another one.

$$E = [L^3/(4bh^3)]/[F/(\Delta f_{\text{wood}} - \Delta f_{\text{adhesive}})]$$

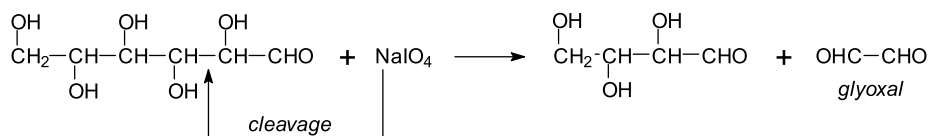
2.4. Matrix assisted laser desorption ionization (MALDI ToF) mass spectrometry

Tannin structure and reactions have been extensively researched and determined by MALDI-ToF mass spectrometry [22–24]. Samples for matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were prepared first dissolving 5 mg of sample of NaIO₄-treated glucose in 1 mL of a 50:50 v/v acetone/water solution. Then 10 mg of this solution is added to 10 μL of a 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 μL of a NaCl solution 0.1 M in 2:1 v/v methanol/water, and predried. Then 1 μL of the sample solution was placed on its dedicated location and the plaque is dried again.

Table 1

Assignments of oligomer structures formed in the tannin + glucose + sodium periodate reaction and determined by MALDI-ToF spectrometry.

Peak	Chemical species
81 Da	glyoxal, with Na ⁺
137–138 Da	Dihydroxysuccinaldehyde
176–177 Da	linear or branched aldehyde no Na ⁺ .
199 Da	linear or branched aldehyde with Na ⁺ OHC-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CHO and or/OHC-CH(OH)-CH(OH)-CH(OH)(CHO) ₂
231 Da	OHC-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CHO with Na ⁺
365 Da	OHC-[CH(OH)] ₄ -CH ₂ -O-CH ₂ -[CH(OH)] ₄ -CHO with Na ⁺
394 Da	Fis-CH(OH)-CH(OH)-CH(OH)-CHO and/or Gall-CH(OH)-CH(OH)-CHO and/or OHC-[CH(OH)] ₄ -CH ₂ -O-CH ₂ -[CH(OH)] ₅ -CHO with Na ⁺
274 Da	Fis monomer, no Na ⁺
290 Da	Rob and/or Cat monomer, no Na ⁺
466 Da	Cat-[CH(OH)-CH(OH)-CHO] ₂ no Na ⁺
489 Da	Cat-[CH(OH)-CH(OH)-CHO] ₂ with Na ⁺
523 Da	OHC-[CH(OH)] ₄ -CH ₂ -O-CH ₂ -[CH(OH)] ₄ -CH(-CHO)-OCH ₂ -(CHOH) ₄ -CHO
587–588 Da	no Na ⁺
610–611 Da	with Na+HOCH ₂ - Cat-[CH(OH)-CH(OH)-CHO] ₃ and/or Fis-[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₃ -CHO,
616 Da	Fis-[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₄ -CHO, no Na ⁺
638–640 Da	OHC-[CH(OH)] ₅ -Rob-[CH(OH)] ₄ -CHO with Na ⁺
669–670 Da	OHC-[CH(OH)] ₅ -Rob-[CH(OH)] ₅ -CHO with Na ⁺ and/or Gall-Glyox-Gall, no Na ⁺
699–700 Da	Gall-CH(-OH)-CH(-OH)-CH(-OH)-Gall
712–713 Da	Fis-[CH(OH)] ₅ -Fis no Na ⁺
726 Da	Fis-[CH(OH)] ₅ -Fis no Na ⁺
742 Da	Cat-[CH(OH)] ₆ -Fis or Rob-[CH(OH)] ₆ -Fis no Na ⁺
748–749 Da	Fis-[CH(OH)] ₅ -Fis with Na ⁺
765 Da	Cat-[CH(OH)] ₆ -Fis or Rob-[CH(OH)] ₆ -Fis with Na ⁺
801 Da	CHO-CH(OH)-Cat-[CH(OH)] ₆ -Fis no Na ⁺
889–890 Da	CHO-[CH(OH)] ₄ -Cat-[CH(OH)] ₆ -Fis no Na ⁺ and/or Fis-[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₅ -Fis
906 Da	CHO-[CH(OH)] ₄ -Cat-[CH(OH)] ₆ -Cat or Rob-CHO-[CH(OH)] ₄ -Rob-[CH(OH)] ₆ -Rob no Na ⁺
923 Da	Rob-[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₅ -Rob no Na ⁺
964 Da	CHO-[CH(OH)] ₄ -Rob-[CH(OH)] ₅ -Rob-CH(-OH)-CHO no Na ⁺
1063 Da	Rob-[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₅ -Rob-[CH(OH)] ₃ -CHO with Na ⁺
1101 Da	Rob-[CH(OH)] ₅ -CH ₂ -O-CH ₂ -[CH(OH)] ₅ -Rob-[CH(OH)] ₅ -CHO no Na ⁺
1149 Da	Fis-[CH(OH)] ₅ -Fis-[CH(OH)] ₆ -Fis no Na ⁺
1178 Da	Fis-[CH(OH)] ₆ -Fis-[CH(OH)] ₆ -Fis no Na ⁺



Scheme 2. Cleavage by periodate of open form of glucose showing formation of glyoxal.

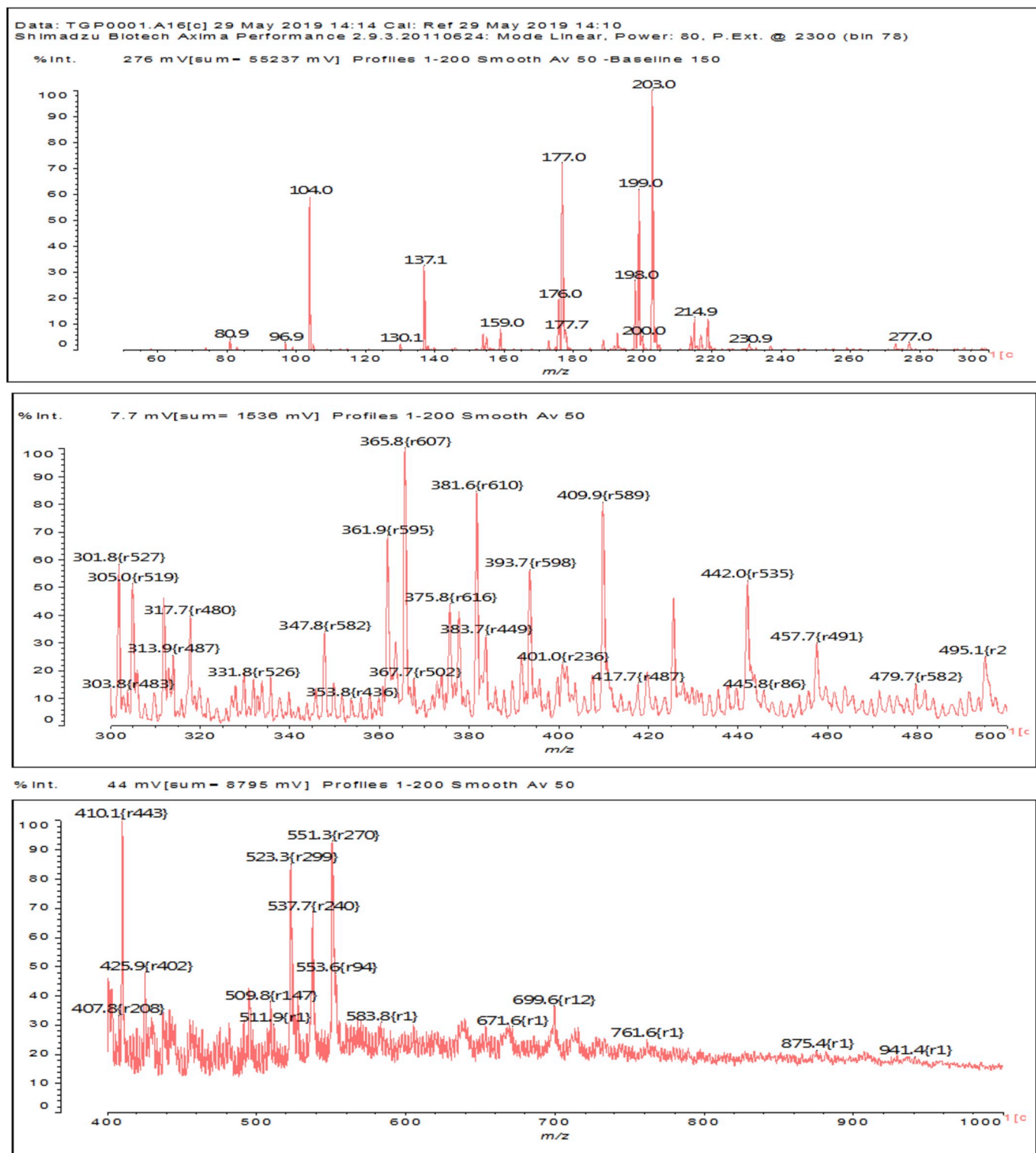
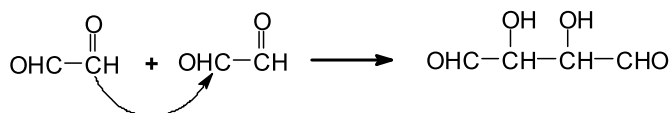
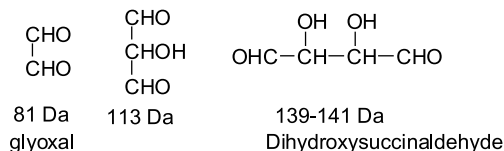


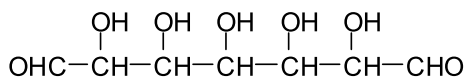
Fig. 1. MALDI-ToF spectra of glucose treated with 10% sodium periodate at 120 °C for 1 h. (a) 50 Da–300 Da range. (b) 300 Da–500 Da range. (c) 400 Da–1000 Da range.



Scheme 3. Schematic example of the aldol reaction of glyoxal to form another aldehyde.



Scheme 4. Example of simple aldehydes formed by periodate cleavage of glucose.



Scheme 5. Species at 231 Da by MALDI ToF.

MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode. The measurements were carried out making 1000 profiles per sample with 2 shots accumulated per profile. The spectrum precision is of ± 1 Da.

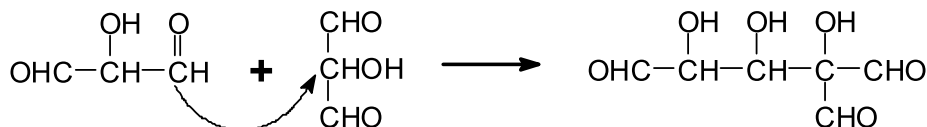
2.5. FTIR

To confirm the presence of relevant structures observed by MALDI ToF, a Fourier Transform Infra-Red (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer. FTIR spectra of glucose and glucose treated with 10% sodium periodate were compared. Equally, FTIR spectra of tannin extract, tannin extract treated with 10% sodium periodate and tannin + glucose treated with either 5% or 10% sodium periodate were compared. A blank sample tablet of potassium bromide, ACS reagent from ACROS Organics, was prepared for the reference spectrum. A similar tablet was prepared by mixing potassium bromide with 5% w/w of the sample powders to analyze. The spectrum was obtained in transmission measurement by combining 32 scans with a resolution of 2.0.

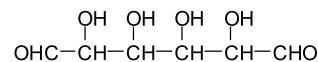
3. Results and discussion

3.1. Glucose oxidation reactions

MALDI ToF has been shown to be an ideal technique to follow reactions of natural polymers for different reactions and under a set of different conditions, and particularly useful in identifying the oligomers formed [13,22–24]. The first three oligomers shown in the MALDI ToF spectra in Table 1 detailing the reaction products obtained by action of the periodate on glucose are given by the aldehyde formation by periodate (or permanganate) cleavage of C–C bonds with vicinal –OH groups of the glucose.



Scheme 6. Aldol condensation to form a higher aldehyde during reactions after periodate treatment of glucose.



Scheme 7. Isomer of aldehyde obtained by the reaction in Scheme 6.

In the case of glyoxal the literature states that peroxide cleaves C–C bonds presenting vicinal –OH groups [1–11]. Thus, in the case of glyoxal and other simple aldehydes obtained by periodate cleavage of glucose the reaction can be represented as in Scheme 2.

The extent of the reaction in Scheme 2 depends strongly on the reaction conditions used and the relative proportions of peroxide. Thus, cases in which cleavage of the HO–CH₂–CH(OH)- of a different terminal site of glucose occurs forming formaldehyde can be envisaged too [15] as well as cases in which separation of small molecular weight aldehydes does not occur at all [10,11]. Under the conditions used here formaldehyde clearly did not appear to form while glyoxal definitely appeared to form.

The others are given by recombination of these species by dialdehydes aldol condensation. Aldol condensation can occur under acid or alkaline conditions [25]. Thus, while glyoxal is formed by direct periodate cleavage of glucose (small peak at 81 Da in Fig. 1), due possibly to the acid environment induced by periodate, the aldol condensation reaction starting from the glyoxal formed is for example as in Scheme 3.

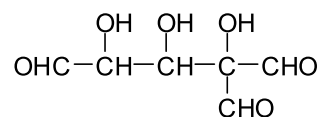
Thus, from the 113 Da peak onward (to the 231 Da peak and further) the series that follows derives by the progressive addition of glyoxals by aldol condensation. The species that can be seen in the MALDI ToF spectra in Fig. 1 a-e are discussed as follows. The 81 Da (with Na⁺) peak representing glyoxal is very small indicating that this species is likely to react further. Due to direct cleavage of glucose other dialdehydes are formed, thus the peaks with Na⁺ (Scheme 4).

All of these peaks take in consideration the Na⁺ (23 Da) used as enhancer in the MALDI ToF analysis. The species at 139 Da can be formed by direct cleavage of glucose but equally by subsequent aldol condensation of the glyoxal formed by glucose cleavage. Also by aldol condensation is the species at 231 Da (with Na⁺) (Scheme 5).

The species at 177 Da and 154 Da are due to the 2,3-dihydroxybenzoic acid (DHB) with and without Na⁺ used as the MALDI matrix, and should not be considered for evaluation. However there are indications late on the reaction with the tannins that these peaks could be a superimposition of compounds having a different origin. Thus, there are two other reactions occurring and giving a different combination of compounds by reaction with periodate (or with permanganate).

The first of these, causing also among others the peaks at 177 Da and 199 Da superimposed to the DHB signals, is again an aldol condensation of different aldehyde fragments obtained by periodate cleavage. This reaction is for instance shown in Scheme 6.

Where 176–177 Da without Na⁺ and 199 Da with Na⁺,



these two peaks can also be attributed to the contribution of species obtained by direct cleavage to form a species such as the isomer in Scheme 7.

Such a reaction may increase the number of reactive groups on the molecule rendering it particularly apt to cross-linking and network

formation. However such type of reaction can be confused with the signals of the DHB matrix (2,3-Dihydroxybenzoic acid) used to carry the sample for MALDI ToF analysis which has molecular weight of 154 Da + 23 Da (Na+) = 177 Da. For this reason such a reaction can be looked at from the second term of the series (Scheme 8).

Where the aldehyde produced has molecular weight of 206 Da + 23 Da (Na+) = 229 Da. Both peaks at 206 Da and at 231 Da are present (Fig. 1a) indicating that the possibility of the existence of branched aldehyde is probable if not certain.

A third type of reaction appears also to occur due to water elimination between two aldehyde groups. Aldehydes in water are in general present as hemiacetals, these being due to the reaction of an aldehyde with an alcohol or water [25]. This is the case, for example, of formaldehyde forming hemiformals in water in the preparation of formaldehyde based resins [26] (Scheme 9).

To this reaction of elimination are due the following peaks assigned to the corresponding compounds.

Where in the 523 Da (calc. 527 Da) species branching can occur and again 3 aldehyde groups are present on the same oligomer, facilitating cross-linking. In the same category is the species represented by the peak at 402 Da (exp. 401 Da) without Na⁺ (Scheme 10).

Compounds obtained by the combination of the three reactions outlined do occur, at higher molecular weights, but aldehyde groups are always present thus maintaining the reaction capacity of these compounds with the available reactive sites on the tannin. It must also be pointed out that the reactivity of the higher molecular weight aldehydes is likely to be relatively lower than that of more active, lower molecular weight aldehydes such as glyoxal and the one at 113 Da, namely OHC-CHOH-CHO. It must also be noted that all the aldehydes involved in the subsequent reactions with the tannin are also non-volatile, eliminating VOC emission.

The formation of aldehydes by reaction of glucose with periodate is confirmed by the comparing the FTIR spectra of periodate-treated and untreated glucose in Fig. 2. In Fig. 2 are clearly visible the carbonyl peaks of aldehydes on the form of a peak doublet the higher peak of which is at 1755 cm⁻¹. The existence of doublet shows that at least two different types of aldehydes have formed. Furthermore the disappearance of the peak at 840 cm⁻¹ characteristic of ethers, attests the opening of the glucose pyran ring as the dialdehydes are formed by periodate cleavage.

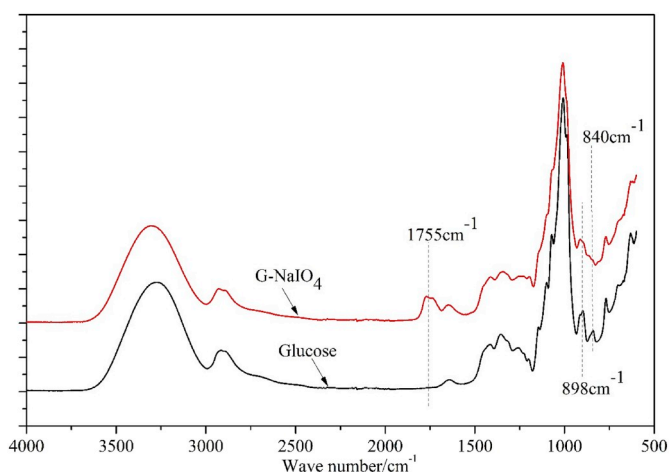
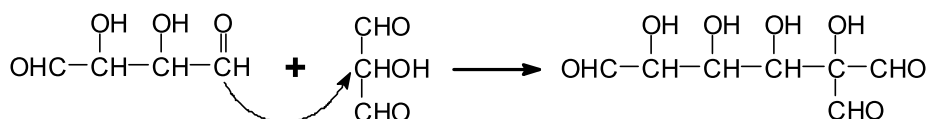


Fig. 2. Comparison of the FTIR spectra of periodate-treated glucose and untreated glucose.

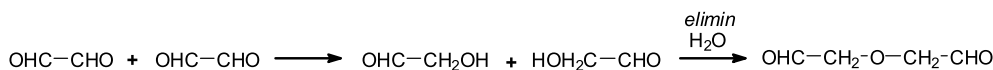
3.2. Tannin reaction with glucose oxidation products

It is also of interest to observe the products obtained by reaction of the tannin present when the glucose/tannin mixture is treated with sodium periodate. In Fig. 3 a,b,c are shown the MALDI spectra of the reaction product obtained and the peak assignments and compounds identified are listed in Table 1. The polyphenolic part of commercial mimosa tannin extract is 70% composed of robinetinidin with lesser but still noticeable amounts of fisetinidin (20%–25%) and of catechin (5%–10%) (Scheme 11). The polyphenolic part, including phenolic monomers and dimers, constitute approximately ≥85% of the commercial tannin extract, with the rest being approximately 6% hydrocolloid gums, 3% various minor constituents and 5%–6% residual water [3].

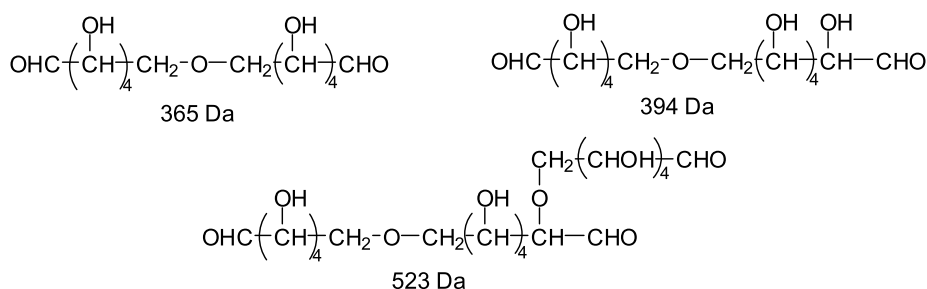
Minor amounts of gallicocatechin (MW = 306) are also present (Scheme 11). The molecular weight of robinetinidin and catechin are the same, rendering impossible which of the two flavonoids enter into reaction just on the basis of the MALDI spectra. One can consider that the predominance of robinetinidin indicates that this unit is the main one reacting and forming the compounds shown in Table 1. In Table 1 the three main units are indicated as Fis, Rob and Cat, with the



Scheme 8. Schematic example of reaction increasing the reactive aldehyde groups by aldol condensation.



Scheme 9. Example of reaction occurring due to water elimination between two aldehyde groups.



Scheme 10. Examples of complex aldehydes formed by the type of reaction outlined in Scheme 9.

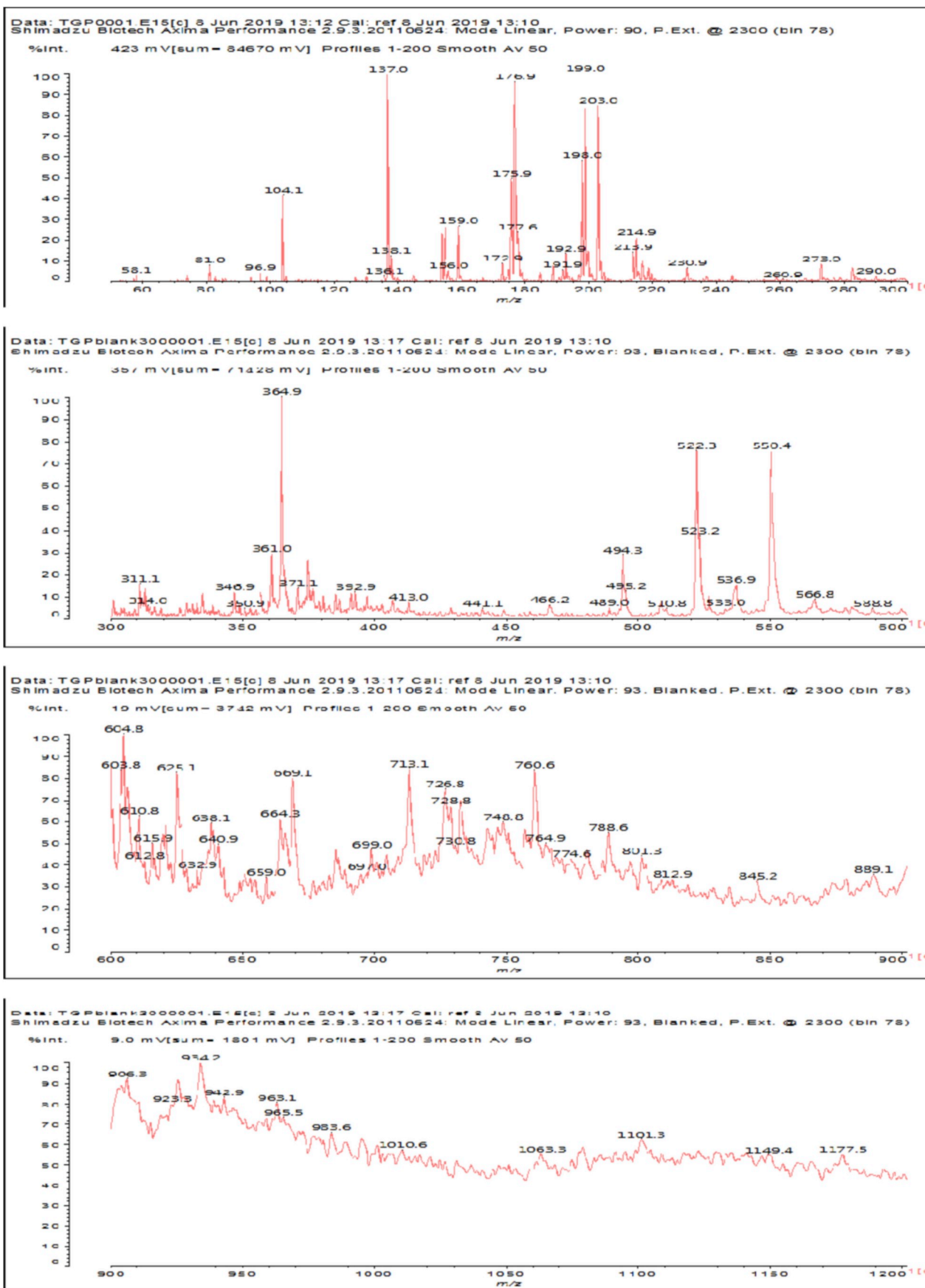
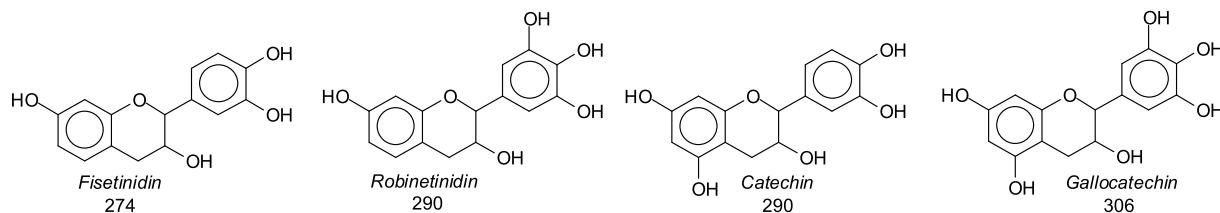
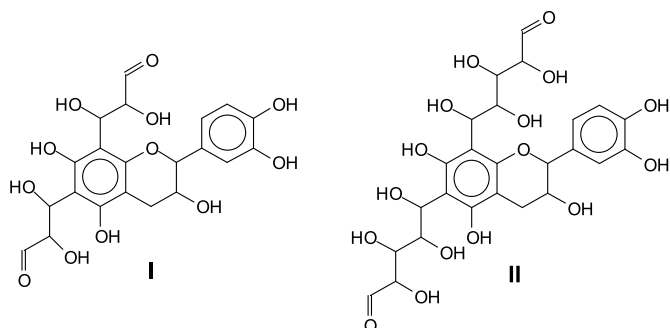


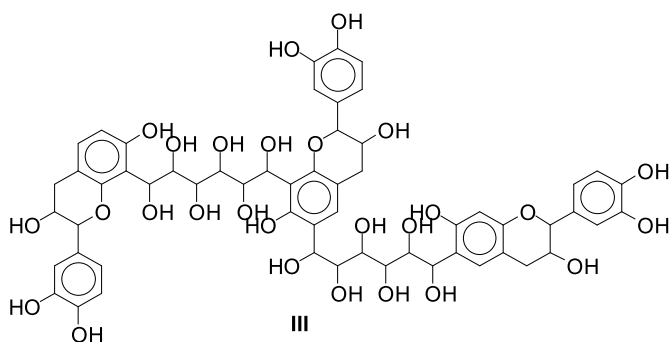
Fig. 3. MALDI-ToF spectra of the tannin/glucose 10/5 mixture treated with 10% sodium periodate at 120 °C for 1 h. (a) 50 Da–300 Da range. (b) 300 Da–600 Da range. (c) 600 Da–900 Da range. (d) 900 Da–1200 Da range.



Scheme 11. The four types of flavonoid units entering in the composition of the tannin.



Scheme 12. Example of species formed by the reaction of flavonoid units with dialdehydes.



Scheme 13. Example of a species formed by the reaction of several flavonoid units with dialdehydes of different type.

Gallicatechin indicated as Gall.

It is interesting to note that the main aldehydes reacting with the flavonoids are glyoxal (OHC-CHO) and OHC-CHOH-CHO, with just some peaks in which the dialdehyde OHC-CHOH-CHOH-CHO may also have reacted, 699 Da and 394 Da, although for this latter an alternative interpretation also exists. Some aldehydes of higher molecular weight

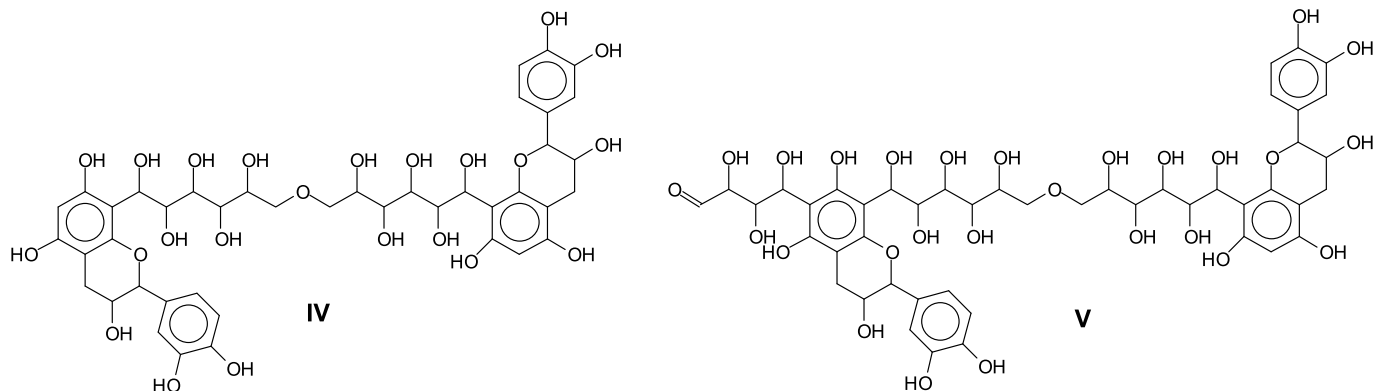
seem also to have reacted and formed bridges between two flavonoids such as for the peak at 761 Da, while others such as that at 177Da, appear to have reacted less, and are still present in the MALDI spectra, while the corresponding 199 Da is much smaller indicating that the sodium salt of the same species has instead reacted. This does not mean that they do not react, but simply that the molecular weight of the compounds formed may be outside the range of the MALDI analysis, or that they are much slower reacting, or both. As a matter of fact the higher molecular weight chemical species formed indicate that also the aldehydes of higher molecular weights do react and do form bridges between flavonoid units, indicating that cross-linked networks are formed on hardening.

A greatest number of species are formed by reaction of a flavonoid unit with one or two dialdehydes but with just one of the aldehyde groups of each dialdehyde, as for the 466/489 Da (I) and the 587/588 Da (II) ones (Scheme 12).

The aldehydes reacting with a flavonoid unit may be all of the same type as for (I) and (II), monomer species, or oligomer species such as (III) at 1178 Da (Scheme 13).

or of different type as for all the species of series 801 Da, 889 Da, 906 Da, 964 Da, 1063 Da, 1101 Da, 1149 Da and 1241 Da. All these species are moreover bridged species with the some of the dialdehydes involved having reacted and connecting with two flavonoid units. These species are most abundant in the higher molecular weights range, and give an idea of how the polymers are formed and how this process leads to cross-linking.

In Table 1, several higher molecular weight oligomers are present in which low and high molecular weight dialdehydes have formed bridges between flavonoid units. In this respect is interesting to note that all the dialdehydes identified in the oxidation of glucose can and do react with the flavonoid units and participate to the bridging of the tannins flavonoid units. This is the case for example of structures (I), (II) and (III) where the aldehyde comes from direct periodate cleavage of glucose. But these same species can also be formed by reaction with aldehydes formed by aldol condensation such as branched structures. A third category of oligomers are those formed by cross-linking with aldehydes having reacted with each other by water elimination (Scheme 9), such as structures IV (923 Da) and V (1063 Da) (Scheme 14).



Scheme 14. Example of species formed by the reaction of several flavonoid units with dialdehydes having reacted with each other by water elimination according to the reaction in Scheme.

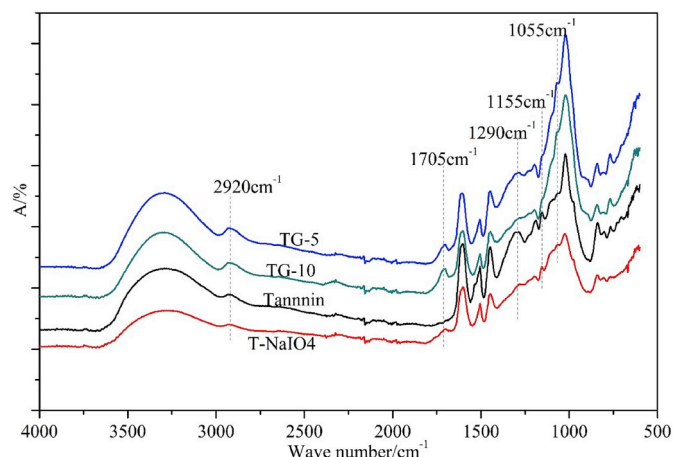


Fig. 4. Comparison of the FTIR spectra of untreated tannin, periodate-treated tannin and of the TG5 and TG10 adhesives.

Where structure V is bridged by aldehydes of one origin but has also reacted with an aldehyde of different origin (Scheme 14).

At the higher molecular weight the structures formed starting from 712 Da and continuing with 726 Da, 742 Da, 748 Da, 765 Da, 801 Da, 889 Da, 906 Da, 923 Da, 964 Da, 1063 Da and 1101 Da are all dimers formed by two flavonoid units linked by a dialdehyde, while the peaks at 1149 Da, 1178 Da (structure III) and 1241 Da are trimers where three flavonoid units are linked by two dialdehydes. In Table 1 are given the simplified formulas of the species formed, while the corresponding structural formulas are given in the Supplementary Material. In Table 1 each type of flavonoid unit within a reaction product is indicated as Fis (=Fisetinidin), Rob (= Robinetinidin), Cat (= Catechin) and Gall (= Gallocatechin). It must be noted that due to the identical molecular weights of robinetinidin and catechin, whenever one of Rob or Cat is mentioned in Table 1 the equal compound could be formed with the other molecule.

Fig. 4 presents the comparison of the FTIR spectra of untreated tannin, periodate-treated tannin and TG5 and TG10 adhesives. Noticeable is the disappearance of the 1290 cm^{-1} peak of the tannin once this is treated with periodate. This means that an alcoholic C-OH has been affected by the treatment, namely has reacted and disappeared. The only such group is that of the OH group linked to the C3 of the pyran ring of the flavonoid. This peak equally disappears in the TG5 and TG10 spectra. Simultaneously as one passes to from tannin to TG5 and TG10 there is the progressive appearance of the carbonyl 1705 cm^{-1} peak

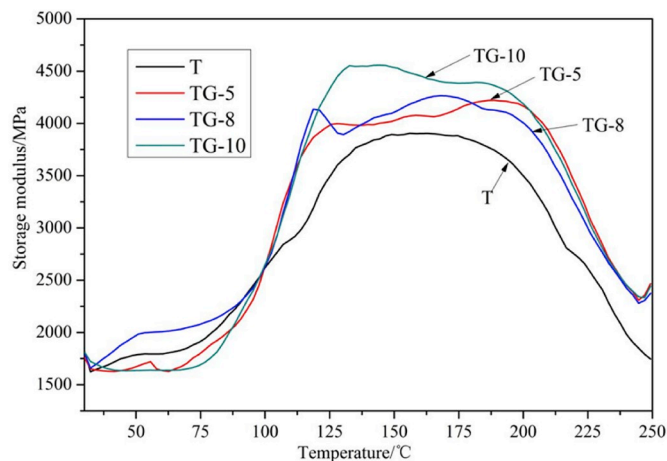
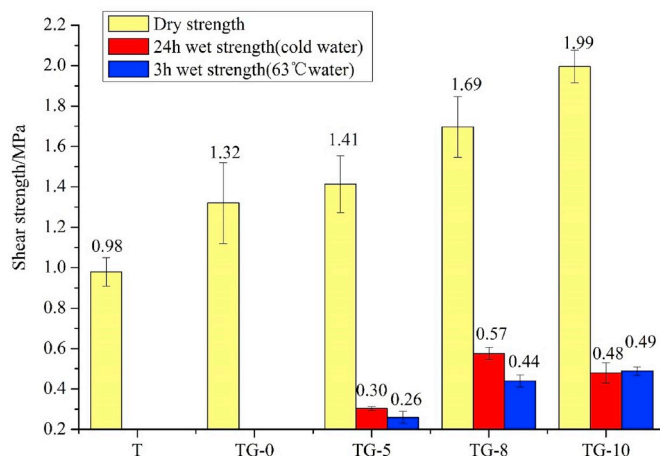


Fig. 5. Thermomechanical analysis graphs of Young's modulus variation of joint bonded with T, TG5, TG8, TG10, as a function of time.



T: Only tannin. Control 1

TG-0: Tannin+glucose (NO periodate). Control 2

TG-5: 5%NaIO₄+(10gtannin+5g glucose)

TG-8: 8%NaIO₄+(10gtannin+5g glucose)

TG-10: 10%NaIO₄+(10gtannin+5g glucose)

Fig. 6. Shear strength results of plywood panels bonded with the T, TG5, TG8 and TG10 adhesive resins, dry, after 24 cold water soaking and after 3 h on hot water at 63 °C.

attributed to aldehyde groups, more evident as the more periodate has been used. Equally noticeable is the increase passing from the tannin to TG5 and TG10 of the 2920 cm^{-1} peak assigned to a methylene bridges ($-\text{CH}_2-$) linking two other groups, these occurring in some of the more complex oligomers such as structures IV and V.

The tannin alone and the TG5, TG8 and TG10 resins were first tested by thermomechanical analysis (Fig. 5). The results show that TG5, TG8 and TG10 all give a higher Young's modulus than the control T, and this maximum value is reached faster in the tannin + glucose + periodate mix than in the control T. The laboratory plywood results shown in Fig. 6 confirm the TMA analysis, with the average dry shear strength of the plywood panels progressively increasing as the proportion of NaIO₄ increases from 5% to 8% and 10% of total resin solids. As regards the cold water resistance of the plywood panels after 24 h immersion in cold water, the shear strength reaches a maximum for TG8. As regards instead the resistance to hot water, after 3 h at 63 °C [5], the wet shear strength increases progressively from TG5 up to TG10.

4. Conclusions

Treatment of glucose with sodium periodate yields a number of non-volatile aldehydes of low and high molecular weight obtained from the cleavage of glucose by periodate. These aldehydes are obtained either by direct glucose cleavage or by cleavage + recombination according to a few different mechanisms. Reaction of these various aldehydes so generated with tannin extract leads to tannin cross-linking and hardening. The combination of tannin extract + glucose + periodate has been shown to be useful in the bonding of plywood panels, satisfying the requirements of the GB/T17657-2013 standard [5]. The same effects have been shown to occur by just adding to the tannin in the same proportions as used in this paper the glucose pretreated beforehand by the periodate.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijadhadh.2019.102499>.

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