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1 Condensed tannins from grape pomace : characterization by FTIR and MALDI
2 TOF and production of environment friendly wood adhesive

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15

16 **Abstract**

17 Condensed tannins were extracted from grape pomace using a water medium in presence of
18 three different bases as catalyst (NaOH, Na₂CO₃ or NaHCO₃) and were characterized by FT-
19 IR and MALDI-TOF spectrometry. It was demonstrated that the tannin extracts contained
20 oligomers up to 6 repeating flavonoid units, with dominant procyanidin with a minor amount
21 of prodelphinidin units. The structure of grape pomace tannin extracted did not present
22 noticeable discrepancy exception of the ratio of the opening pyran ring which was different as
23 a function of the catalyst used. Two different formulations (nonfortified tannin adhesive and

1 fortified with addition of 20% of polymeric 4,4'-diphenyl methane diisocyanate (*p*-MDI)
2 were used to press one layer particle board. It has been proved that the extraction processes
3 largely affect the adhesive properties of the extracts obtained from the same raw material.
4 Especially the particleboards prepared from tannins extracted using Na₂CO₃ as catalyst and
5 without *p*-MDI, give a high internal bonding value (IB = 0.45 MPa), which was good enough
6 to pass relevant international standard specifications for interior grade panels. Formaldehyde
7 emission of these panels is very low, well under the European Norm requirements (≤ 6.5 mg/
8 100g panel).

9

10 **Key words:** grape pomace; tannin-based adhesives; MALDI-TOF spectrometry;
11 formaldehyde emission; wood particleboard.

1 **1. Introduction**

2 Phenolic-type compounds obtained from natural resources have been used for the
3 production of wood adhesives since 1970s (Tondi and Pizzi, 2009). Among the possible
4 alternatives of the petroleum-derived phenolic compounds, condensed tannin is an excellent
5 renewable resource (Kim et al., 2003, Sowunmi et al., 1996). It was demonstrated in previous
6 works that condensed tannins can be not only successfully used as substitutes for phenol in
7 the production of phenol-formaldehyde resins (PF), resorcinol-formaldehyde (RF), phenol-
8 resorcinol-formaldehyde (PRF) but also for the preparation of condensed tannins-
9 formaldehyde wood adhesives for interior and exterior wood bonding of products such as
10 particleboard and plywood (Tondi and Pizzi, 2009, Lei et al., 2008, Pichelin et al., 2006,
11 Pizzi, 2003 and 2006). Condensed tannins consist of chains of flavan-3-ol units as oligomeric
12 constituents linked mainly through C4-C8 (or C6) bonds, widely distributed in the plant
13 kingdom including tree bark and grape (Souquet et al., 1996, Kenndy et al., 2001). The
14 industrial extraction of tannins from barks is generally a fairly simple procedure, using water
15 as solvent, in the presence of a base (carbonate, soda) and of sodium sulfite or metabisulfite,
16 at temperature around 80°C (Pizzi, 2003). At present, the commercial and industrial tannin
17 extracts usable for wood adhesives are mainly obtained from mimosa, quebracho and pine
18 barks (Fradinho et al., 2002, Panamgama, 2007, Vazquez et al., 2000).

19 Grape is one of the world's largest fruit crops and grape pomace is one of wastes generated
20 by grape juice and wine-making processes. This pomace consists of skins, seeds, and in certain
21 case of some stems, with the skins and seeds making up the major part (Zocca et al., 2007).
22 Because of a low extraction during winemaking, the solid residues still retain high levels of
23 condensed tannins. However, the majority of the grape pomace is currently not upgraded, but
24 used for composting or discarded in open areas potentially causing environmental problem
25 (Northup et al., 1998). Only small amounts of these by-products are up-graded by different

1 solvent extraction methods for recovery of the phenolics to use as natural health remedies,
2 food supplements, or as novel nutrifunctional food ingredients (Guerrero et al., 2008, Ruberto
3 et al., 2007, Spigno and De Faveri, 2007, Monrad et al., 2010, Pinelo et al., 2005 and 2007,
4 Vatai et al., 2009). Therefore, grape pomace potentially constitutes a very abundant and
5 relatively inexpensive source for tannin adhesive production.

6 In previous papers, extraction of condensed tannins from grape pomace was described in
7 water medium using NaOH, Na₂CO₃, NaHCO₃ in the presence of Na₂SO₃ (Ping et al 2011a
8 and 2011b). These extracts were characterized by ¹³C NMR and we selected the milder
9 conditions of extraction to prepare the very first grape pomace extract-based particleboards. In
10 the present paper, the grape pomace tannin extracts were characterized by FT-IR, MALDI-
11 TOF spectrometry and thermomechanical analysis (TMA). The effect of the tannins
12 extraction conditions on the chemical structure and the reactivity of the tannins was studied.
13 The addition of a synthetic cross linking agent (polymeric 4,4'-diphenyl methane
14 diisocyanate, pMDI) in the adhesive formulations and the formaldehyde emission of the
15 panels was also examined.

16

17 **2. Materials and Methods**

18 The samples correspond to mixtures of by-products of the winemaking process of red grape
19 variety (*Vitis vinifera*), growing in south-east of France and were provided by a French
20 distillery. The air-dried grape pomace was composed by grape skin, seeds and stalks manually
21 separated. It was stored at room temperature during the course of this study. Moisture content
22 was determined using KERN MRS 120-3 infrared moisture analyser.

23

24 **2.1. Tannins extraction**

1 Grape pomace was treated with an aqueous solution of base (NaOH, Na₂CO₃ or NaHCO₃)
2 and Na₂SO₃ (2.5% or 5% w/w, see Table 4) with a solid-to-liquid ratio of 1:8. The tannins
3 extraction was carried out by heating at 100°C during 120 min in a round bottle flask
4 connected by water condenser. After heating, the pomace was cooled, washed and filtered
5 through filter paper. The washed liquid was evaporated to a moderate concentration (rotary
6 evaporator, temperature: 60°C), then lyophilised to yield tannins. A sample of tannins was
7 stored in a freezer at -5 °C before analysis.

8

9 **2.2. Characterization of tannin extracts**

10 FT-IR was used to study the functional groups and molecular structure of the tannin extracts.
11 The experiment was determined using Nexus 870 FT-IR instrument. Tannins (0.2 mg) were
12 added into KBr powder (30 mg), mixed and grinded to powder which diameter reached 2 µm,
13 then pressed to a small piece sample in a press machine. Elemental analyses were obtained on
14 a Perkin Elmer 240C micoranalyser. The protein was calculated from the formula: protein (%)
15 = Nitrogen (%) × 6.25. MALDI-TOF spectrometry is a suitable method for examining
16 polyflavonoid tannin oligomers. The spectra were recorded on a KRATOS Kompact MALDI
17 4 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm.
18 The length of one laser pulse was 3 ns. The experimental conditions used were: mass- high
19 (20 kV acceleration voltage), polarity-positive, flight path -linear 100-150 pulse per spectrum
20 and 200-800 ns time of delayed extraction technique. The best results for tannin analysis were
21 obtained by using the combination of matrix DHB/NaCl ([Pash et al., 1996](#), [Hoong et al.,](#)
22 [2010](#)). Grape pomace tannin powder (4 mg) was dissolved in 1ml H₂O. 2, 5-Dihydroxy
23 benzoic acid (DHB) was used as the matrix and 10 mg NaCl were added to the matrix
24 solution to enhance the ion formation. The solutions of the sample and the matrix were mixed

1 in equal amounts and 0.5-1 μl of the resulting solution were placed on the MALDI target.
2 After evaporation of the solvent the MALDI target was introduced into the spectrometer.

3

4 **2.3. Analysis of modulus of elasticity (MOE)**

5 Modulus of elasticity (MOE) of the tannins formulations were studied using thermal
6 mechanical analyzer with TA controller (Mettler TMA 40), STARe data processing software.
7 TMA is to study the rigidity of the wood-adhesive joint as a function of temperature. The
8 experiments were conducted under the conditions at a heat rate of $10^{\circ}\text{C}/\text{min}$ from 25°C to
9 250°C , 30 mg of resin, three points bending TMA mode. The maximum of MOE and its
10 increase corresponding to temperature or time for wood-adhesive systems indicated the
11 performance of the adhesive and the strength of the final application.

12

13 **2.4. Preparation of resin formulation**

14 Two different adhesive formulations were investigated in this paper, the first formulation is
15 nonfortified tannin-formaldehyde adhesive, a certain concentration of tannin solution was
16 prepared, 5 % of powdered *para*formaldehyde, by weight of dry tannin extract, was added.
17 The second Formulation is fortified with a synthetic cross linker: 5 % of powdered
18 *para*formaldehyde, 20% of polymeric 4,4'-diphenyl methane diisocyanate(p-MDI), by weight
19 of dry tannin extract, were added to a certain concentration of tannin solution respectively.

20

21 **2.5. Particleboard manufacture and testing**

22 Single layer laboratory particleboards of $340\text{ mm} \times 300\text{ mm} \times 14\text{ mm}$ dimension were
23 prepared using particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) at 35.7
24 kg/cm^2 maximum pressure, 195°C press temperature and 7.5 min press time. 10 % (w/w
25 based on dry particles) of adhesive resin solid was loaded. The dry internal bond (IB) strength

1 of the particleboards was tested according to a relevant international standard European Norm
2 EN 312, wood particleboard-specifications.

3

4 **2.6. Measurement of formaldehyde emission**

5 The formaldehyde emissions from the particleboards were determined according to the
6 European Norm (EN-717-3) using a 500 ml glass jar. Three test pieces, with dimensions of 25
7 mm×25 mm×14 mm, which were cut from Single layer laboratory particleboards, are
8 positioned in the jar. The formaldehyde released from the test pieces at $40\pm 1^{\circ}\text{C}$, during 180
9 min is absorbed in 50 ml distilled water and determined from absorbance at 412 nm with
10 spectrophotometer.

11

12 **3. Results**

13 The tannin extraction experiments from grape pomace were carried out considering
14 previously described studies (Ping et al., 2011b) using 2.5% or 5% (w/w) of NaOH, Na_2CO_3
15 and NaHCO_3 in the presence of Na_2SO_3 at 100°C during 120 min in an aqueous medium.

16

17 **3.1. FT-IR study of tannin extracts**

18 The functional groups of the grape pomace extracts using three different basic reagents
19 (NaOH, Na_2CO_3 and NaHCO_3 , extraction conditions A, B and C respectively, see Fig. 1) were
20 analysed by FT-IR. The spectra are presented in Fig.1 and the assignments are given in Table
21 1. The band at 3318 cm^{-1} was assigned to hydroxyl both contribute to phenolic and sugar
22 content. The bands at 2973 cm^{-1} and 1743 cm^{-1} were due to C-H stretching vibration assigned
23 to methyl and methylene groups. A weak signal at 1750 cm^{-1} is assigned to carbonyl groups.
24 The presence of carbonyl groups could be rationalized by the well known catechinic acid
25 rearrangement occurring during the extraction process. As previously described, the formation

1 of catechinic acid is to be minimized because it should decrease the reactivity of the extract
2 toward cross linking agent. The bands at 1308 cm^{-1} , 1264 cm^{-1} and 1212 cm^{-1} were assigned to
3 saturated C-C stretching attribute to $\text{CR}_2\text{-CHR-CR}(\text{SO}_3^{2-})$ structure caused by the opening of
4 the pyran ring during sulfitation of flavonoid tannins (Hoong et al., 2009). This reaction has a
5 positive effect because it increases the solubility of tannins and reduces the viscosity of the
6 extracts allowing the use of adhesive solutions of higher resin content. The mechanism of the
7 opening of pyran ring is given in previous papers (Ping et al., 2011b). A comparison of the IR
8 signals for A, B and C and of their relative intensities indicates that the ratio of the
9 heterocyclic C-ring opening of flavonoid unit is function of the nature of the base used for the
10 tannins extraction. It appears from Fig. 1 that the opening of pyran ring during the tannins
11 extraction seems to be more important by using Na_2CO_3 and NaHCO_3 (respectively conditions
12 B and C) than when using NaOH (condition A). This observation is in accordance with the
13 sulfite group contents of the three tannin fractions established based on elemental
14 compositions given in Table 2 (A : 1 sulfitated moiety every 25 residues; B and C : ~ 1
15 sulfitated flavonoid moiety for approximately every 15 residues). From nitrogen compositions
16 (Table 2), it can also be deduced that the extracts contained about 10 % w/w of proteins.

17

18 **3.2. MALDI-TOF study of tannin extracts**

19 Fig.2 shows a typical MALDI-TOF analysis of grape pomace tannins extract with the
20 molecular weight ranging from 500 to 3000 Da. It could be concluded that grape pomace
21 extracts contain flavonoid oligomers up to 6 repeating units, based on the largest tannin
22 oligomer detected in the sample which showed a peak at 1924.2 Da. The MALDI-TOF mass
23 spectra showed clear repetitive patterns of peaks that allow the identification of specific
24 oligomer series present in the tannin sample. The major peak-to-peak mass increments
25 observed were 288 Da, 304 Da, 450 Da and 440 Da. These masses corresponded to (I)

1 procyanidin, (II) prodelphinidin, (III) glucosylated procyanidin, (IV) gallated procyanidin
2 repeating units, respectively (Fig.3). The number of repeating units in each oligomer was
3 calculated using the expression $M + Na^+ = 23.0 (Na) + 2.0 (endgroups, 2 \times H) + 288.3 A +$
4 $304.3 B + 450.3 C + 440.4 D$ (table 3) with I, II, III and IV representing the four relevant
5 monomers in the tannin oligomer according the method previously described (Hoong et al.,
6 2010). Table 3 showed the possible combinations of different repeating units and the degree
7 of polymerization corresponding to each of them. These values were obtained based on the
8 m/z value of types I, II, III and IV of tannin structures. The dominant series of peaks at 604.1,
9 905.1, 1193.4, 1484.6, 1771.5 Da for tannin extracts were dimers, trimers, tetramer, pentamer,
10 hexamer respectively. It could be seem that the main repeating units in each oligomer group
11 were identified as those of procyanidin composing of catechol unit (I).

12

13 3.3. TMA study of tannins adhesive

14 The influence of 3 parameters (i.e., nature of the base for the extraction of tannins,
15 concentration of the chemical reagents and effect of the addition of a cross linking agent
16 (polymeric 4,4'-diphenyl methane diisocyanate, *p*-MDI)) on the properties of the adhesive
17 formulations was examined. The formulations of tannins solution-paraformaldehyde 5% (w/w)
18 (based on oven dry tannin weight) were scanned by thermo mechanical analysis in three
19 points in bending according to a technique already reported (Laigle et al., 1998). The curves
20 of the modulus of elasticity (MOE) as a function of increasing temperature are given in Fig. 4;
21 MOE values at 195 °C are also given in Table 4.

22 F1, F7 and F11 correspond to the same formulations but using three different bases for the
23 extraction of tannins (respectively NaOH, Na₂CO₃ and NaHCO₃, 2.5% w/w). It clearly
24 appears that grape pomace tannins extracted using NaOH (F1) and NaHCO₃ (F11) gave lower
25 performance (MOE < 2000 MPa) than those extracted with Na₂CO₃ (F7) with a MOE nearly

1 3500 MPa. The TMA results of the curing of F1 and F2, F11 and F12, F14 and F15 indicated
2 that, in most of the essays, an increase in tannin concentrations used for the preparation of the
3 formulation yielded noticeable improvements in the value of MOE. A comparison of the
4 TMA profiles (given in the Fig.4) of F2 and F3, F4 and F5, F6 and F7, F9 and F10 shows that
5 the addition of *p*MDI did not yield an important increase in the maximum MOE value. On the
6 other hand, concerning F12, it appears that addition of *p*MDI has a positive effect: MOE
7 values of F13 are still higher in the range of temperatures corresponding to industrial wood
8 panel press conditions ($190^{\circ}\text{C} < T < 250^{\circ}\text{C}$).

9

10 **3.4. Mechanical testing for particle boards**

11 Grape pomace tannins based adhesive were used to press one layer particleboard. The
12 internal bond (IB) strength of a panel is a direct measure of the performance of the adhesive.
13 In this study, two different formulations (the nonfortified tannin adhesive and fortified with
14 diisocyanate adhesive) were analysed. The results are shown in Table 4. The IB strengths
15 demonstrate that the nature of the extraction reagent (NaOH, Na_2CO_3 or NaHCO_3) greatly
16 impacts the value of panel IB strength. It can be seen that formulations F1 to F6 using NaOH
17 for the tannins extraction yielded low panel performances and did not satisfy the IB strength
18 results required (≥ 0.35 MPa) even with addition of *p*MDI in the formulation (F3 and F6). In
19 the same way, the utilization of NaHCO_3 for the tannins extraction (F12) led to an adhesive
20 bearing poor properties; however, with addition of 20% of *p*MDI in the formulation, the
21 adhesive F13 yielded a good internal bond strength t (IB = 0.36). These results are in
22 accordance with the TMA experiments previously exposed. The best results were obtained
23 from Na_2CO_3 extracts and it is noteworthy that F7 and F8 yielded very good internal bond
24 strength results (IB = 0.45 and 0.68 respectively). Concerning F7, it is important to note that
25 for the first time a resin formulation composed of 95% of pomace extracts solution, 5%

1 formaldehyde and without *p*MDI, yielded good internal bond strength which passed relevant
2 international standard specifications for interior-grade panels (IB > 0.35 MPa).

3

4 **3.5. Formaldehyde emission of particle boards**

5 Formaldehyde emission has become one of the major concerns in wood-based panels
6 industry, especially the interior wood bonding products, such as particle boards used as a
7 major component in the production of decoration and furniture materials. In this study, the
8 best IB value performance particleboards (F7 to F10) were chosen to determine the emission
9 levels of formaldehyde. The results in Table 4 show that the formaldehyde emission of the
10 particleboards was very low, largely below the European Norm requirements (≤ 6.5 mg/ 100g
11 panel).

12

13 **3.6 Discussion**

14 In this study, it was shown by MADI TOF experiments that grape pomace extracts are mainly
15 composed of flavonoid oligomers up to 6 repeating units, with dominant procyanidin units.
16 This result is in accordance with ^{13}C -NMR and gel times analyses described in a previously
17 study (Ping et al., 2011b). In fact, we described that the grape pomace extracts exhibited gel
18 times below 100 sec at pH 7 and then can be classified under the same group as the faster
19 reacting procyanidin-prodelphinidin tannins such as pine bark and pecan nut pith extracts
20 (Pizzi, 1994). Thus, a ring of grape pomace tannins possess only the phloroglucinol moiety,
21 much more reactive toward formaldehyde than a resorcinol-type structure (10 to 50 times
22 higher than phenol (Kim et al., 2003), with important consequences in the use of these tannins
23 for adhesives. Thus, this high nucleophilicity and reactivity of the tannins can explain the
24 good to very good properties of the extracts isolated in the present study for adhesive
25 applications and also the very low formaldehyde emission of particleboards observed, lower

1 than others wood adhesives, such as phenol-formaldehyde, urea formaldehyde, etc... Based
2 on previous papers (Pizzi, 1994), mechanisms are proposed for formation the grape pomace
3 tannins adhesives (Fig.5). The catechin-formaldehyde condensates are formed through
4 methylene bridges (path a). Concerning adhesives fortified with diisocyanate, the
5 methylolated catechins undergo two reactions of almost equal rate. The first is the standard
6 condensation reaction according the path a (Fig.5); the second is the attack of the *p*MDI on
7 the hydroxyl of the methylol group (-CH₂OH) formed onto the catechin moities (see Fig.5,
8 path b).

9 Sulfitation of tannins is one of the oldest reactions in flavonoid chemistry and can be useful in
10 the preparation of tannin-based adhesives (Pizzi, 1994). In this study, the sulphite group
11 contents were established by elemental analysis and FT-IR spectroscopy. It was observed that
12 using NaOH as extraction reagent, the resulting extracts had a lower sulphite group content
13 and in addition yielded low panel performance than when using carbonate salts as base. This
14 suggests that the introduction of a sulfonic group through sulfitation could increase not only
15 extraction yields and tannin solubility but also the reactivity of the extracts towards a cross
16 linking agent.

17 The grape pomace tannins used in this study are crude extracts, with a considerable proportion
18 of nonphenolic materials, mainly simple sugars and polymeric carbohydrates. Relatively high
19 carbohydrate contents were previously deduced by from ¹³C NMR spectrum and low Stiasny
20 numbers were obtained from the extracts (~0.5-0.6) (Ping et al., 2011b). The presence of non
21 phenolic compounds in the formulations can explained (1) the poor results obtained in terms
22 of mechanical properties of the panels for some of the extracts, (2) the improved performance
23 for some of the adhesive formulations prepared with *p*MDI. In fact, the reactive isocyanate
24 group of *p*MDI can rapidly react with the hydroxyl groups of the monomeric and polymeric

1 carbohydrates (see Fig.6). The formation of sugar- *p*MDI polyurethane could then enhance
2 the joint performance of grape tannin fortified adhesive.

3

4 **4. Conclusion**

5 Tannins were extracted from grape pomace using water media in presence of NaOH,
6 Na₂CO₃ or NaHCO₃. The MALDI TOF analysis showed that the crude extracts are composed
7 of oligomers up to 6 repeating units, with dominant procyanidin units with a minor amount of
8 prodelphinidin. The tannin fractions reactivity towards formaldehyde was studied by
9 thermomechanical analysis in bending and through the production of particleboards. Two
10 different formulations (nonfortified tannin adhesive and fortified with addition of 20% of
11 polymeric 4,4'-diphenyl methane diisocyanate (*p*-MDI)) were used to press one layer particle
12 board. It was shown that the nature of the extraction reagent (NaOH, Na₂CO₃ or NaHCO₃)
13 greatly impacts the properties of the resins and the mechanical properties of the panel internal
14 bonding strengths. The particleboards bonded by the tannins extracted using Na₂CO₃ as
15 catalyst give the best performance and were good enough to pass relevant international
16 standard specifications for interior grade panels. Formaldehyde emission of these panels was
17 below the European Norm requirements (≤ 6.5 mg/ 100g panel). Thus, this work proposes an
18 economically valuable utilization of grape pomace, a by-product currently largely
19 underexploited, for the production of an environment friendly adhesive for particleboards
20 production.

21

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4

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1 Table 1. Assignment of FT-IR spectra of grape pomace tannin extracted by different
 2 extraction conditions
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Peak cm^{-1}	assignment
3318	-OH stretching vibration
2973,2931	-CH ₃ , -CH ₂ - stretching vibration
1878	C=O stretching vibration
1619,1534,1501	Aromatic squel vibration
1439	CH deformation and aromatic ring vibration
1412	Aromatic vibration
1341	saturated CH in plane bending vibration
1308,1264 , 1212	C-C frame stretching(C-CHR-C)
1111	aromatic CH in plane bending vibration
1066	C-O stretching vibration
921	aromatic CH out of plane bending vibration

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9 Table 2. Elemental analysis of grape pomace tannin extracted using different extraction
 10 conditions
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extraction conditions	C%	H%	N%	S%
A (NaOH, 5%)	35.92	3.84	1.43	0.01
B (Na ₂ CO ₃ (2.5%)	36.64	3.81	1.48	0.03
C (NaHCO ₃ (2.5%)	36.43	3.80	1.27	0.04

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1 Table 3. Distribution of polyflavonoid oligomer by MALDI-TOF for grape pomace tannin
 2 extracts.

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	M+Na ⁺ experiment	M+Na ⁺ calculated	Unit type			
			I	II	III	IV
Dimer(2)	604.1	601.6	2	0	0	0
	767.6	763.6	1	0	1	0
Trimer(3)	905.1	905.9	2	1	0	0
	920.8	921.9	1	2	0	0
	1068.0	1067.9	1	1	1	0
Tetramer (4)	1193.4	1194.2	3	1	0	0
	1354.4	1356.2	2	1	1	0
Pentamer (5)	1484.6	1482.5	4	1	0	0
	1635.1	1634.5	3	1	0	1
Hexamer(6)	1771.5	1770.8	5	1	0	0
	1924.2	1922.8	4	1	0	1

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18 Table 4. Adhesive formulation compositions, thermomechanical analysis and particle board
 19 testing.

Extraction reagents ^a	Formulation number	Composition Tannin / H ₂ CO/pMDI	Tannin concentration% ^b	TMA		
				MOE ^c at 195°C(MPa)	Density (kg/m ³)	IB ^d
NaOH(2.5%) Na ₂ SO ₃ (2.5%)	F1	20/1/0	30	1937.1	N/A	
	F2	20/1/0	40	2812.5	696.3	0.23
	F3	20/1/5	40	2662.5	693.7	0.28
NaOH(5%) Na ₂ SO ₃ (5%)	F4	20/1/0	30	2846.9	N/A	
	F5	20/1/0	40	2455.1	702	0.28
	F6	20/1/5	40	3062.8	698.4	0.32
Na ₂ CO ₃ (2.5%) Na ₂ SO ₃ (2.5%)	F7	20/1/0	30	3322.9	706.1	0.4
	F8	20/1/5	30	2833.5	710.4	0.6

Na ₂ CO ₃ (5%)	F9	20/1/0	30	2179.4	711.5	0.30
Na ₂ SO ₃ (5%)	F10	20/1/5	30	2605.9	706.9	0.60
NaHCO ₃ (2.5%)	F11	20/1/0	30	1369.7	N/A	
Na ₂ SO ₃ (2.5%)	F12	20/1/0	45	2776.8	692.6	0.20
	F13	20/1/5	45	3520.7	708.5	0.30
	F14	20/1/0	30	2932.9	N/A	
NaHCO ₃ (5%)	F15	20/1/0	45	3878.8	705	0.30
Na ₂ SO ₃ (5%)	F16	20/1/5	45	3589.0	703.4	0.30

- ^a % based on weight of dry pomace
^b in water, % based on weight of dry pomace
^c Modulus of elasticity
^d Internal bond strength

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1 Fig.1. FT-IR spectra of grape pomace tannin extracted by different extraction conditions

2 A: NaOH(2.5%), B: Na₂CO₃(2.5%), C: NaHCO₃(2.5%)

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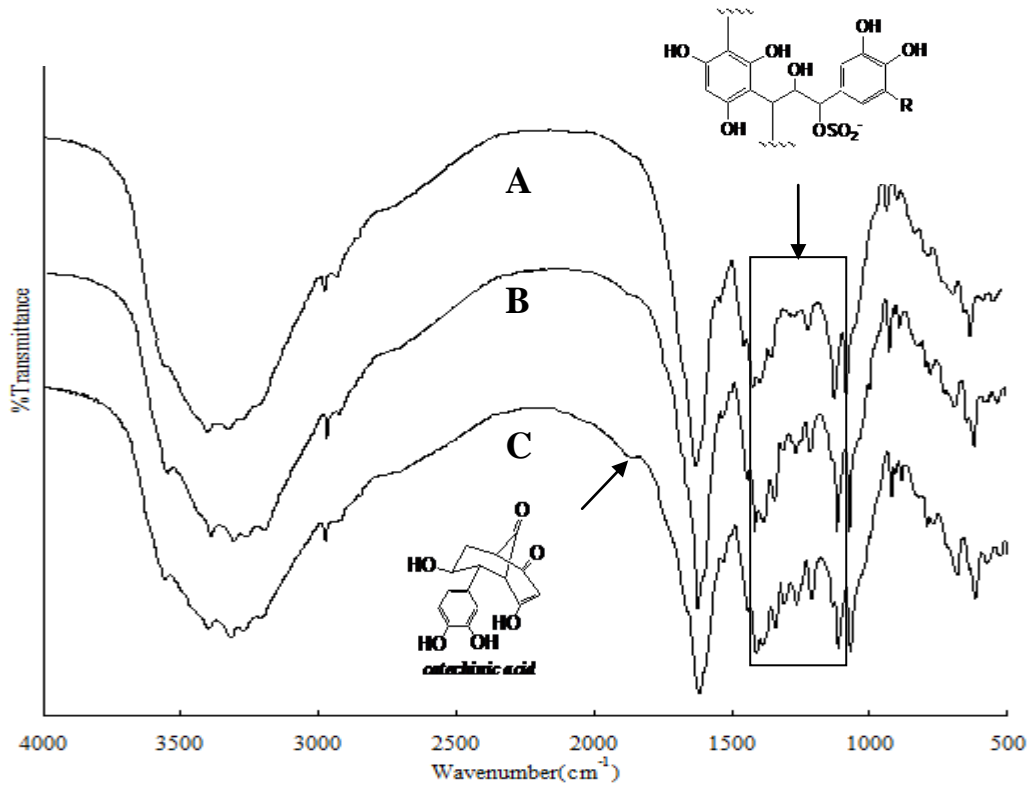
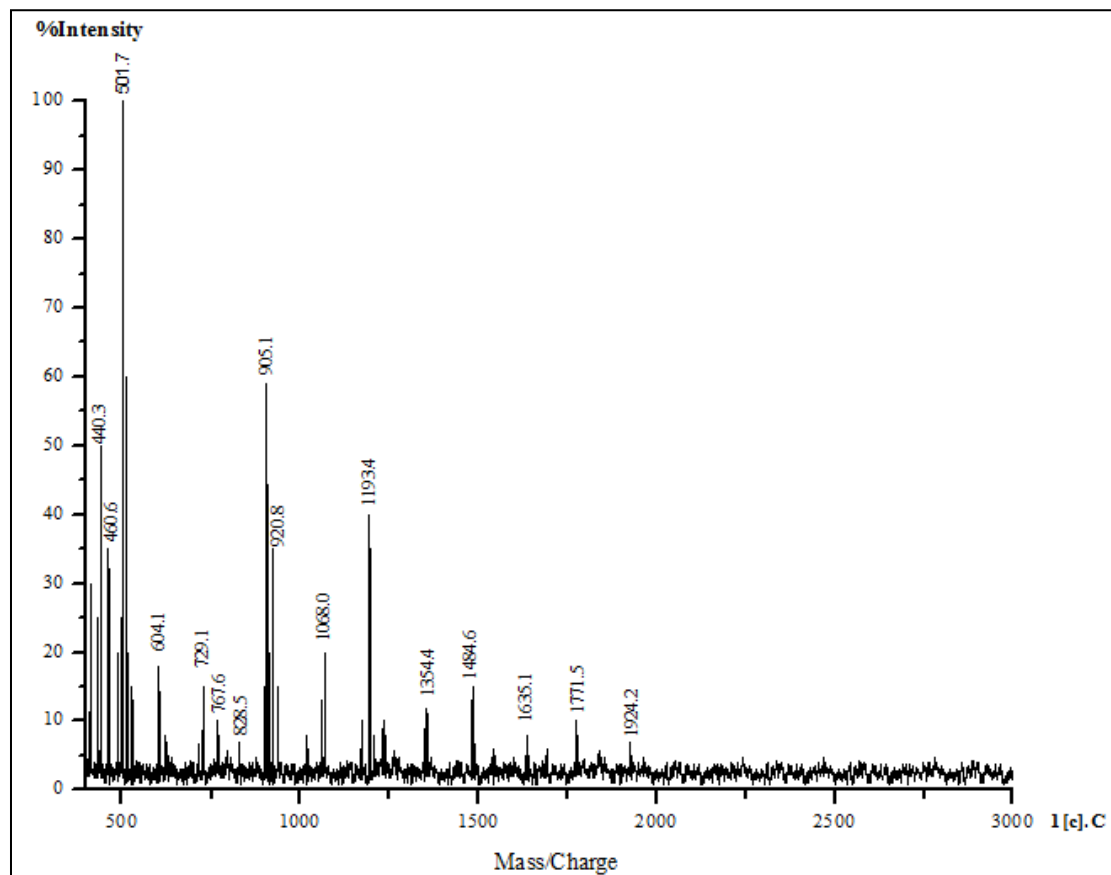
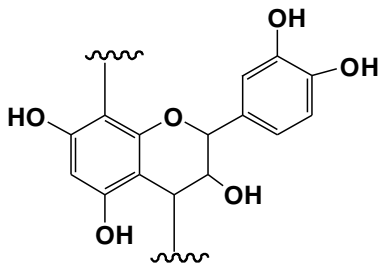


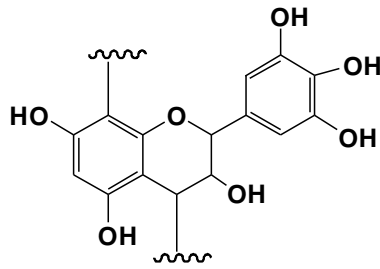
Fig.2. MALDI mass spectrum of grape pomace tannin (conditions A)



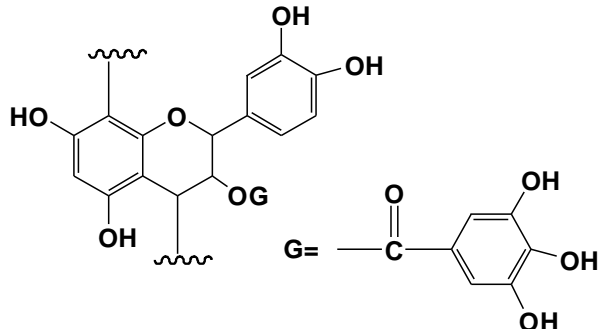
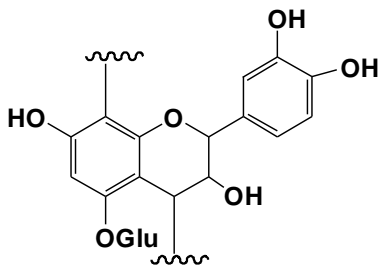
1 Fig.3. Polymer structure of grape pomace tannin repeating unit: (I) procyanidin, (II)
2 prodelphinidin, (III) glucosylated procyanidin, (IV) gallated procyanidin.
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1 Fig. 4. TMA measuring MOE as a function of temperature to describe the curing of resins of
 2 grape pomace tannins.
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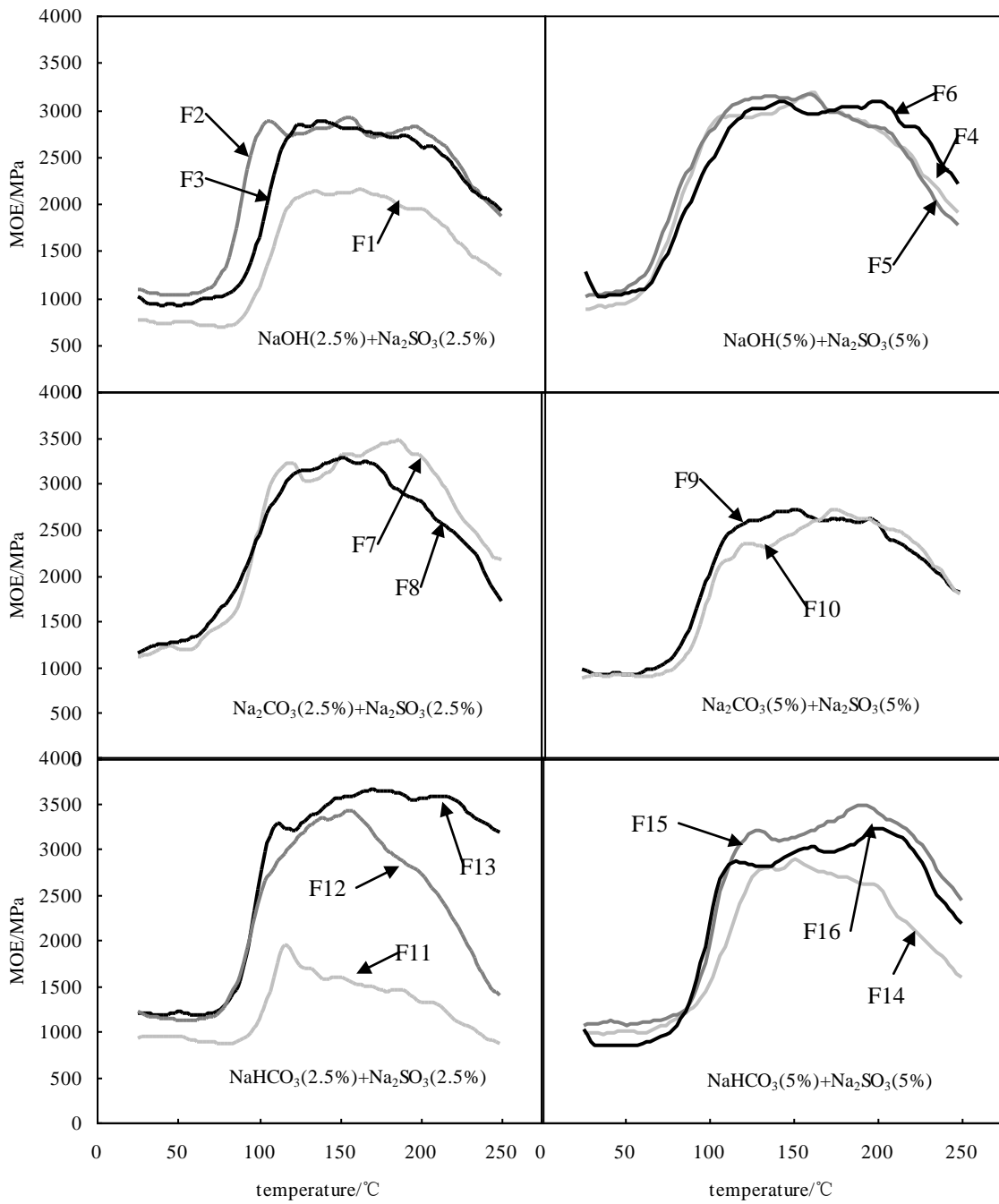
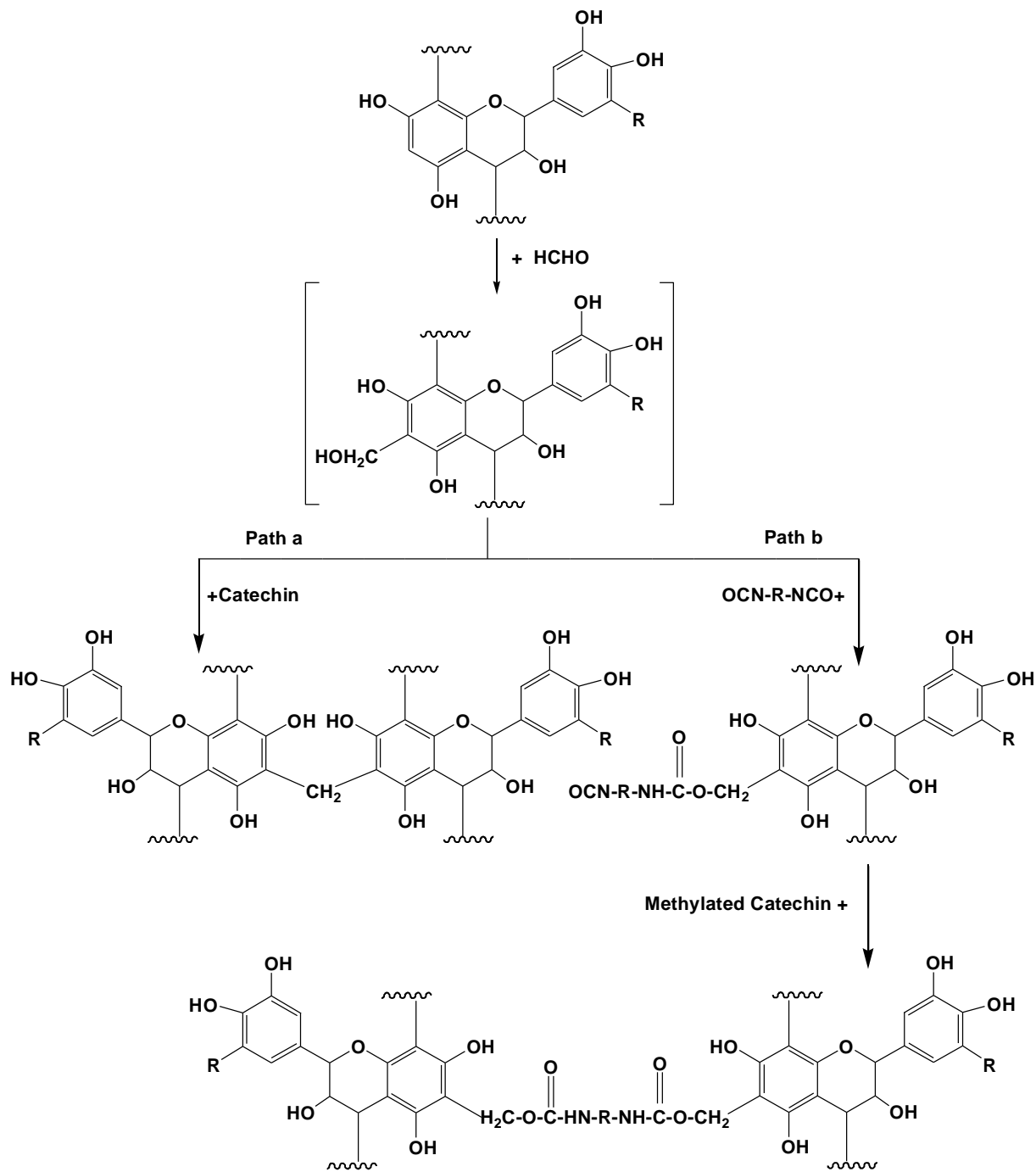


Fig. 5. Underlying mechanisms proposed for the grape pomace tannins adhesive system.

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1 Fig.6. The mechanism proposed for *p*MDI reacted with hydroxyl groups of the carbohydrates.
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