

Valorization of Tunisian Pomegranate Peel Tannins in Green Adhesives Formulation

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ABSTRACT: The possible use of Tunisian pomegranate tannins in wood adhesive formulation was studied for the first time. Colorimetric tests, Fourier transformed infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were used to examine pomegranate tannins. Analysis showed that pomegranate peels are rich in hydrolyzable tannins. The Stiasny number tests showed the low reactivity of pomegranate tannin extract to formaldehyde and thus the difficulty of using it in wood adhesive formulation. Thermomechanical analysis (TMA) and strength analysis of pomegranate tannin/hexamine-based resin showed weak bonding properties.

KEYWORDS: Pomegranate tannin, wood adhesives, NMR, FTIR, TMA, shear strength

1 INTRODUCTION

Pomegranate (*Punica granatum L.*) belongs to the Punicaceae family. The cultivation of pomegranate is native to the Middle East and was later known in the Mediterranean. Pomegranate grows well in semi-arid, mild-temperate to subtropical climates [1,2] Tunisia is one of the native lands of pomegranate. The cultivation occupies more than 11,000 ha and extends to all areas, except high level areas. More than 60 local varieties have been denominated (Jbeli, Tounsi, Zehri, Mekki, etc.). Production was estimated to be 71,597 tons of pomegranate fruits in 2010 compared with 67,000 tons in 2009 [3–5]. The fruit peels represent approximately 50% by weight of fruit. So, about 37,500 tons of pomegranate peels are rejected annually. Pomegranate peels are rich in tannins [6], they have been used traditionally for their medicinal properties and for other purposes such as tanning, dyeing and heavy metal removal [7–9]. Recently, there has been a growing interest in tannin-based resins, which contribute to the tannins' structure, suggesting that

they can be used as substitutes for phenol in phenol-formaldehyde resins, which are known for their toxicity [10]. Tannins can be divided into two categories: hydrolyzable tannins and condensed tannins. Hydrolyzable tannins have low reactivity toward formaldehyde due to lack of macromolecular structures and also low nucleophilicity, which limits their usage in worldwide adhesive production. Condensed tannins contain complex chemical structures of polyphenolic compounds, which have higher reactivity toward formaldehyde than phenol. The most common commercial tannins are mimosa (*Acacia mearnsii*) bark tannin; quebracho (*Schinopsis balansae* and *Schinopsis lorentzii*) wood tannin, pine bark tannin and eucalyptus species bark tannin [11–14]. Based on their abundance and tannin content, pomegranate peels could be used as raw material for wood adhesive production.

In this study, the polyphenolics, hydrolyzable tannins and condensed tannins of Tunisian pomegranate peels were analyzed using colorimetric tests and spectrometric (NMR, FTIR, MALDI-TOF) methods. Pomegranate tannin extraction was optimized. Then, pomegranate tannin-based adhesive

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was characterized using mechanical and thermo-mechanical tests in order to test its possible use as a wood adhesive.

2 EXPERIMENTAL

Pomegranate fruits of 'Jbeli' cultivar were collected from the Dharoufa site (Cap Bon) of Tunisia. The peels were separated manually from the fruit, dried in shade until reaching a moisture content of 10% and then kept at room temperature for further study.

The peels were ground using a grinder (Retsch SK1 rotating knife) to conduct the following analyses.

To estimate the polyphenolics of the condensed tannin and hydrolyzable tannin contents in pomegranate peels, we exploited colorimetric methods commonly used in the study and determination of the polyphenolic composition of plants [15,16].

2.1 Extraction of Polyphenols

Peel powder (0.5 g) was extracted three times with 10 mL of 80% methanol solution using a homogenizer at room temperature (3×2 h). The supernatant was collected after each extraction by filtering through Whatman Paper No. 1. The methanol was evaporated under reduced pressure and then two drops of HCl (6 N) were added. The resulting solution was extracted with diethyl ether (3×5 mL). After drying over sodium sulfate, the diethyl ether was removed and the residue was dissolved in 5 mL of methanol. The volume of the aqueous extract was adjusted to 10 mL [16].

The experiment was carried out in triplicate.

2.2 Determination of Total Polyphenolic Content

The total polyphenolic content of the ether and aqueous extract was determined by colorimetric test according to the method of Scalbert *et al.* [16]. Briefly, 0.5 mL of a 200-fold diluted aqueous extract (or 0.5 mL of a 20-fold diluted ether extract) was mixed with 2.5 mL of 10-fold diluted Folin-Ciocalteu's phenol reagent and incubated for 1 min, before 2 mL of 7.5% Na₂CO₃ was added. The mixture was allowed to stand for 5 min at 50°C in a water bath and then transferred into cold water. The absorbance versus prepared blank was monitored at 760 nm. A gallic acid aqueous solution (80 µg/mL) was used for calibration. The final results were expressed as mg gallic acid equivalent (GAE) per g of dry weight (DW). We note that the aqueous extract was diluted with water while ether extract was diluted with absolute methanol [16].

The experiment was carried out in triplicate. The result was expressed as means±SD.

2.3 Determination of Condensed Tannins (by Colorimetric Tests)

2.3.1 Catechin Equivalent Content

Determination of condensed tannins by the vanillin test was based on the procedure reported by Broadhurst and Jones [17]. First, 0.5 mL of aqueous extract, contained in a test tube covered with aluminum foil, was mixed with 3 mL of 4% vanillin-methanol solution and then with 1.5 mL of hydrochloric acid. The mixture was allowed to stand for 15 min at 20°C in the dark. The absorbance of the mixture was measured at 500 nm. A catechin aqueous solution (30 mg/L) was used for calibration. The final results were expressed as mg catechin equivalent (CE) per g of dry weight (DW).

The experiment was carried out in triplicate. The result was expressed as means±SD.

2.3.2 Cyanidin Equivalent Content

An aqueous extract of 0.5 mL was added to 5 mL of an acid solution of ferrous sulfate (77 mg of FeSO₄·7H₂O in 500 mL of 2:3 (HCl d=1.18/n-BuOH)). The tubes were loosely covered and placed in a water bath at 95°C for 15 min. The absorbance was read at 530 nm and results were expressed as cyanidin g equivalent (Cya) per g of dry weight (DW) [16].

The condensed tannins content was calculated using the formula given in Equation 1.

$$[CT] = A \times V \times Df \times V' \times M / (\epsilon \times v \times m) \quad (1)$$

Where [CT] is the condensed tannin content (mg Cya/g DW); A is the absorbance of the sample; V is the volume of the reaction medium; V' is the volume of the aqueous extract recovered after extraction with diethyl ether; v is 0.5 mL; Df is the dilution factor; M is the molecular weight of cyanidin; m is the weight of the dry matter and ϵ is the molar extinction coefficient (34,700 M⁻¹cm⁻¹).

The experiment was carried out in triplicate. The result was expressed as means±SD.

2.4 Determination of Hydrolyzable Tannins Content

Hydrolyzable tannins were determined by a colorimetric test according to the method of Bossu *et al.* [18] with slight modifications. In the test, 0.25 g of the ground sample was extracted with 50 mL of methanol (80%) using a homogenizer at room temperature

for 6 h. After centrifugation (10 min, 2000 rpm), the final extract was diluted 3 times with water before determination. Next, 5 mL of KIO_3 aqueous solution (2.5%, w/v) was heated for 7 min at 30°C, and then 1 mL of the diluted sample was added. After an additional 2 min of tempering at 30°C, the absorbance was measured at 550 nm. A calibration curve was obtained using tannic acid solution (5000 mg/L) prepared by solubilization of 0.25 g of tannic acid in 50 mL of methanol (80%). The analytical standard solutions of tannic acid were prepared by aqueous dilution. Results were expressed as mg tannic acid equivalent (TAE) per g of dry weight (DW).

The experiment was carried out in triplicate. The result was expressed as means \pm SD.

2.5 Extraction of Tannins for FTIR and NMR Analysis

Tannin extraction from pomegranate peels was carried out in water containing 2% of sodium bisulfite and 0.5% of sodium bicarbonat, with a sample-to-water ratio equal to 1/5. The bark powder was immersed in water under continuous magnetic stirring for 6 h at 70°C. The tannins extract so obtained, was filtered and dried in an oven at 50°C to yield tannins.

2.5.1 FTIR Spectra Analysis

Infrared analysis was performed using a Perkin Elmer Spectrum One equipped with an ATR-FTIR module. A few milligrams of milled product were deposited on the crystal (Diamond/ZnSe). The sample was crushed using the module for 10 scans and the scanning wavelength of infrared was 4000-600 cm^{-1} at a resolution of 4 cm^{-1} .

2.5.2 NMR Analysis

The NMR analysis was carried out on the ^{13}C carbon atom, in liquid phase. The spectra were recorded on a Brüker Avance 400MHz spectrometer. The chemical shifts were calculated relative to TMS (tetramethylsilan). The spectra appear at 100.6 MHz. The number of scans and the acquisition time were 1.36 s and 12000 respectively.

Tannin extract was dissolved in DMSO-d₆ (deuterated dimethyl sulfoxid).

2.6 Extraction of Tannins for MALDI-TOF Analysis

The extraction of tannins from pomegranate peels was conducted as described by Saad *et al.* [19]. It was carried out in water containing 2% of sodium sulfite and

0.5% of sodium bicarbonat, with sample-to-water ratio equal to 1/5. The ground sample was immersed in water under continuous magnetic stirring for 7 h at 80 \pm 5 °C. The extract so obtained, after spray drying, was used for analysis.

2.6.1 MALDI-TOF Mass Spectrometry

The spectra were recorded on a KRATOS Kompact MALDI AXIMA TOF 2 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive (alternatively negative), flight pathlinear, 20 kV acceleration voltages, and 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

2.6.2 MALDI-TOF Sample Preparation

The sample was dissolved in acetone (4 mg/mL, 50% acetone solution volume). The sample solutions were mixed with an acetone solution containing 10 mg/mL of the matrix, 2,5 dihydroxybenzoic acid. For the enhancement of ion formation, NaCl solution of 10 mg/mL in water was added. The solutions of the sample and the matrix were mixed in the proportions: 3 parts matrix solution + 3 parts polymer solution + 1 part NaCl solution. Then 0.5–1 μL of the resulting solution mix was placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer. Due to the addition of sodium salt in the positive mode all mass peaks correspond to $[\text{M}+\text{Na}]^+$. To obtain the molecular weight of the chemical species of the peak, 23 Da for sodium must be subtracted. For negative mode measurements, Harmin (7-methoxy-1-methyl-9H-pyrido[3,4-b]indol) was used as matrix. A solution of 10 mg/mL Harmin in tetrahydrofuran was mixed with the polymer solution in volume proportion 1/1. No sodium salt was added for these MALDI measurements in order to get proton abstracted anions in the spectra.

2.7 Optimization of Pomegranate Tannins Extraction

Extraction was performed using a process commonly used in industry to produce tannin extracts for adhesive formulations and leather tanning. The extraction is conducted in a hot water solution containing sodium bisulfite and sodium bicarbonat [20].

For this study, we have considered only the influence of experimental conditions on the

tannin extraction yield. Based on the study results of Saad *et al.* [11], we have considered the following parameters:

- Temperature: 60°C,
- Extraction time: 2 h,
- Solid-to-liquid ratio: 1/20, 1/10, 1/5.

Tannin extraction was carried out in water, containing 2% of sodium bisulfite and 0.5% of sodium bicarbonate, under continuous magnetic stirring for various combinations of the studied parameters. The extract obtained was filtered and dried in an oven at 50°C to constant weight. The extraction rate was calculated according to Equation 2 and is the average of three extractions:

$$\text{Extraction rate (\%)} = \frac{\text{oven-dried weight of precipitate} \times 100}{\text{extracted sample dry weight}} \quad (2)$$

2.8 Determination of Extract Properties (Determination of Reactive Tannin)

The Stiasny number reaction was used to determine the reactivity of tannins (obtained for the different extraction conditions) towards formaldehyde. According to Hoong *et al.* [21], fifty milliliters of sample (0.4%, w/w) tannin solution were pipetted into a 150 ml flask. Aqueous formaldehyde (37%, 5 ml) and hydrochloric acid solution (10 M, 5 ml) were then added and the mixture was heated under reflux for 30 min. At the end of this reaction, the mixture was filtered through a sintered glass filter (filter n°3) while it was still hot. The precipitate was dried to a constant weight in an oven at 105°C. The Stiasny number was performed in triplicate and determined as follows (Eq. 3):

$$\text{Stiasny number (\%)} = \frac{\text{Oven-dried weight of precipitate} \times 100}{((\text{Dissolved solid content}/100) \times 50)} \quad (3)$$

2.9 Resin Formulation

For the resin formulation, we have used the tannin extract obtained in the optimum conditions.

A tannin solution in water was prepared (30%). Its pH was adjusted to 10 with a NaOH solution (33%), and then 6% of hexamine solution (30%) was added (on solid tannin-containing base). In general, the hexamine solution is used for tannin solution pH equal to 10 in accordance with the best performance at such a pH [22].

Formulations based on quebracho tannins and mimosa tannins provided by the Rolkem and Silvateam companies, respectively, were prepared under the same conditions and for a tannin solution in water concentration equal to 45%, to use as controls. We cannot operate with a pomegranate tannin solution in water concentration equal to 45%, since a very viscous solution is obtained.

2.10 Resin Modulus of Elasticity Analysis (E')

Modulus of elasticity (E') of the pomegranate tannin-based adhesive was studied using thermal mechanical analysis (TMA), by monitoring the rigidity of a bonded wood joint as a function of temperature. Triplicate samples of two beech wood plies, each 0.6 mm thick, bonded with each formulation for a total sample dimension of 17 mm × 5 mm × 1.2 mm, were tested between 25°C and 250°C at a heating rate of 10°C/min and for 30 mg of resin using a Mettler Toledo SDTA840 apparatus in three-point bending. A force varying continuously between 0.1 N, 0.5 N and back to 0.1 N was applied on the specimens with each force cycle of 12 s (6 s/6 s).

2.11 Resin Strength Analysis

2.11.1 Two-Ply Wood Composite Preparation and Testing

According to Moubarik *et al.* [23], maritime pine veneer with a thickness of 3 mm was cut into rectangular specimens of 2.5 × 11.5 cm². For each resin formulation, the adhesive was applied to one side of each piece of veneer. The application area was 2.5 × 2.5 cm² for each veneer. The spread rate of hexamine-tannin adhesive was 120–150 g/m² on a dry weight basis. Two adhesive-coated veneer boards were lapped together with the grain parallel to each other and then pressed using a handscrew vice. The press temperature and press time were fixed at 180°C and 5 min, respectively. After bonding, the assemblies were conditioned at 25°C and 65% of relative humidity for 24 h. Five samples were prepared for the mechanical test.

2.11.2 Evaluation of Mechanical Properties of Two-Ply Wood Composites

The shear strength of the two-ply wood composites was determined on a Zwick/Roell Z010 traction machine. The crosshead speed was 2 mm/min. The load at fraction was measured and reported as shear strength.

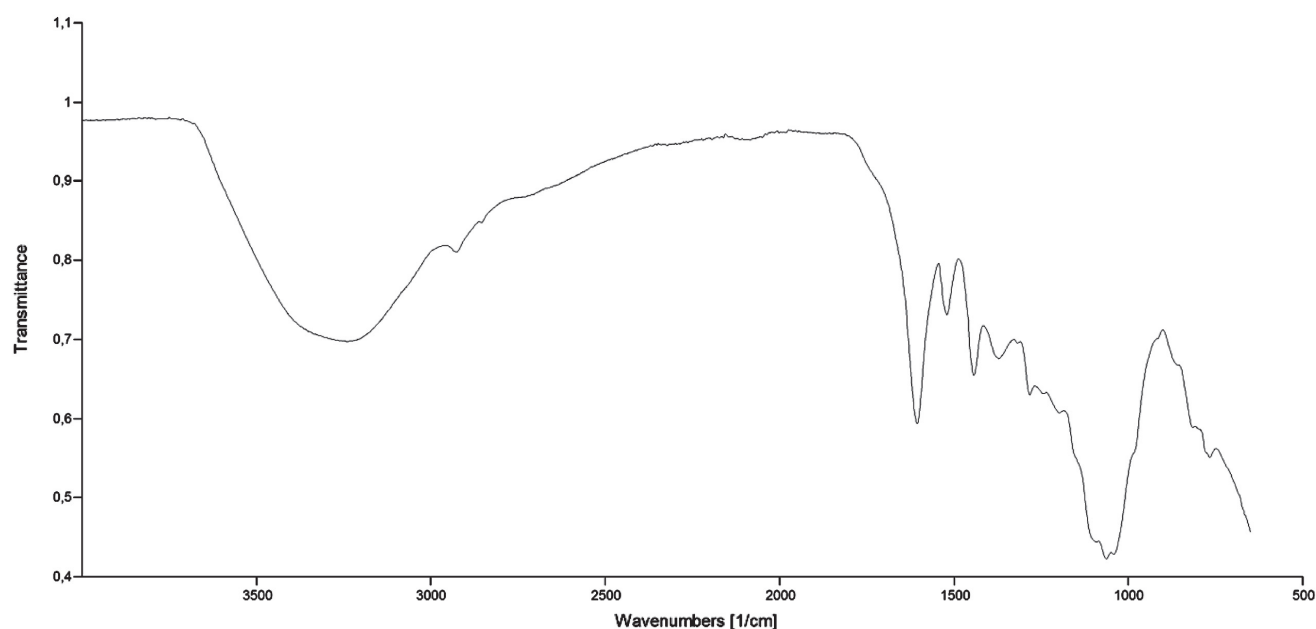


Figure 1 FTIR spectrum of 'Jbeli' pomegranate peels extract.

3 RESULTS AND DISCUSSION

3.1 Total Polyphenolic Content

The total polyphenolic content determined for 'Jbeli' pomegranate cultivar peels extract is equal to 181 ± 3 , mg GAE/DW. Compared to other Tunisian pomegranate cultivars, as reported in a previous study, we have observed differences between cultivars for the total polyphenolic levels [19]. These variations were explained essentially by the pomegranate age, the mean annual precipitation, the agro-climatic and environmental conditions and the degree of sun exposure of the selected fruit [24,25,19].

Pomegranate peels constitute an important source of polyphenols compared to Tunisian Aleppo pine barks ($64,5$ mgGAE/gDW) [11], *Cedrus atlantica* wood ($8,2$ mgGAE/gDW) and *Quercus robur* bark ($28,7$ mgGAE/gDW) [16].

The calculation of the partition coefficient of polyphenolic compounds between the aqueous and the ether phases gives a value equal to 27, justifying that 'Jbeli' pomegranate peels are richer in water-soluble phenols than in diethyl ether-soluble phenols.

3.2 Condensed Tannin and Hydrolyzable Tannin Contents

The hydrolyzable tannins level determined for 'Jbeli' pomegranate peels is equal to 505 ± 46 mg TAE/gDW, while the condensed tannin levels determined

by vanillin test and butanol-HCl test are 8 ± 1 mg CE/gDW and 3 ± 1 mg cya/gDW respectively. We note that hydrolyzable tannins concentration is around 160 times higher than condensed tannins concentration, which clearly shows the more important part of hydrolyzable tannins in pomegranate peels. These results are detailed and discussed in a previous study [19].

3.3 FTIR Analysis of Pomegranate Tannin Extract

The IR spectrum of pomegranate tannins extract is recorded in the $600\text{--}4000$ cm^{-1} region and is presented in Figure 1. The 3277 cm^{-1} absorption band is attributed to -OH stretching vibration [26]. The band at 2930 cm^{-1} is due to -CH and -CH₂ vibration of aliphatic hydrocarbon [27,28]. The bands at 1610 cm^{-1} , 1520 cm^{-1} and 1444 cm^{-1} are assigned to aromatic ring stretching vibration. The $1030\text{--}1225$ cm^{-1} absorption bands include the C-O-C symmetrically stretching vibration, the aromatic CH in-plane bending vibrations and the glucose ring vibration [27]. The band at 920 cm^{-1} is attributed to the bending vibration of aromatic CH out of plane [28]. According to Falcão and Araújo [29], hydrolyzable tannins, gallo- and ellagitannins, present two characteristic intense bands at $1731\text{--}1704$ cm^{-1} and $1325\text{--}1317$ cm^{-1} , the former assigned to the stretching vibration of the carbonyl function and the latter to the symmetric stretching of the C-O bond of the ester function. The bands present between 778 and 870 cm^{-1} are considered as marker bands for the presence of

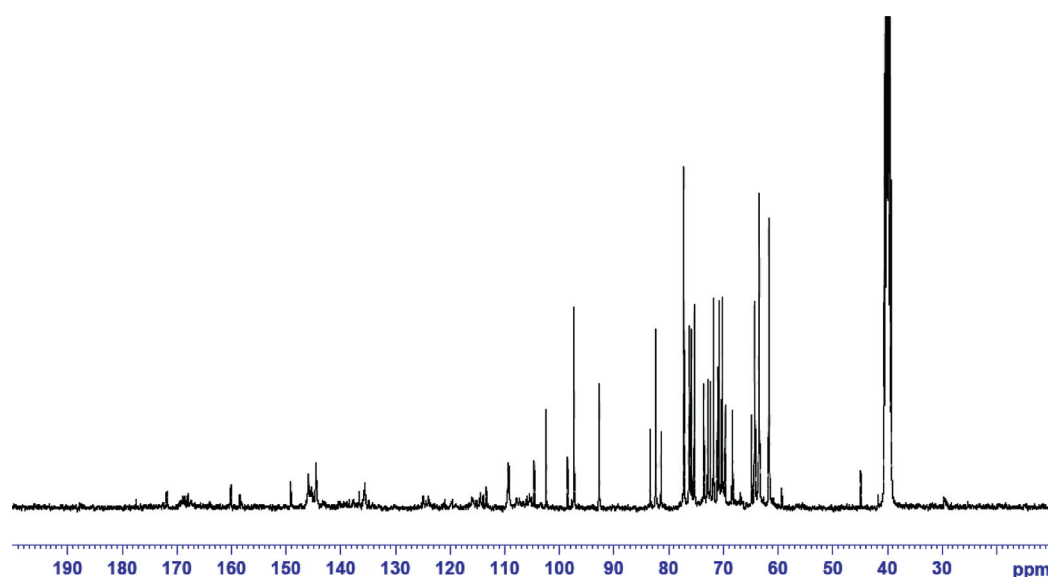


Figure 2 The ^{13}C NMR spectrum of 'Jbeli' pomegranate peel tannins extract in DMSO-d_6 .

gallotannins subclass. Bands at 1110 cm^{-1} and 1283 cm^{-1} that characterize the presence of condensed tannins [29] are not noticeable in the pomegranate tannins IR spectrum. These results confirm the colorimetric tests' results showing the richness of pomegranate peel in hydrolyzable tannins.

3.4 NMR Analysis

The ^{13}C NMR spectrum (Figure 2) was interpreted according to Fu *et al.* [30] and Zhang *et al.* [31]. The typical signals of condensed tannins are practically null. However, we noted a small peak at 145,8 ppm characterizing the presence of condensed tannins with procyanidin units. Strong peaks appear between 90 ppm and 110 ppm and between 60 ppm and 65 ppm, justifying the high amount of carbohydrates in the pomegranate extract. The high intensity of peaks appearing between 60 ppm and 100 ppm suggest that a significant amount of carbohydrate units was detected. According to Castillo-Muñoz *et al.* [32] and Gutzeit *et al.* [33], the sugar moieties are detected at 101,8~102,8 ppm (C1), 71,4~77,1 ppm (C2, C3 and C5), 68,7~71,4 ppm (C4) and 60,6~61,1 ppm (C6). This result seems logical, since we have already proven the high content of hydrolyzable tannins in pomegranate peel. And we know that these tannins are esters of carbohydrates, which are generally glucose.

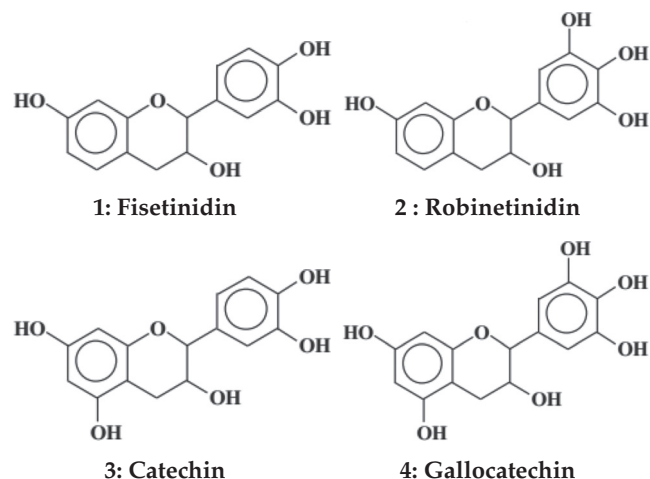
3.3 MALDI-TOF Analysis

MALDI-TOF analysis results have already been detailed and discussed in an earlier study on

the characterization of pomegranate peel tannin extractives [19].

The main findings revealed from this analysis are:

- The presence of 4 relevant monomers in the tannin oligomer, whose structures are:



- The most abundant oligomers are those of flavonoid tetramers,
- The presence of flavonoids linked to carbohydrates, be it glucose or rhamnose or other monomeric carbohydrates,
- The presence of hydrolyzable tannins.

2.6 Extraction Yield and Stiasny Number

Table 1 shows the extraction yields and Stiasny number values determined for the different extraction conditions.

Extraction rate results are comprised between 39% and 54%. The maximum extraction yield of Tunisian pomegranate tannins (54%) is considered very important compared to rates found with Tunisian Aleppo pine (29,9%) [11], maritime pine (24,9%) [34], quebracho (26–29%) and mimosa (30–33%) [20].

It is observed in this study that the extraction efficiency is more important for the less concentrated solutions. Onem *et al.* [35] and Saad *et al.* [11] reported the same observation in their study on optimization of acorn tannins extraction and Tunisian Aleppo pine tannins extraction, respectively. In fact, they found that maximum extraction yield is found for lower solid-to-liquid ratio. This could be justified by an inadequate stirring and a poor contact between the extraction solvent and the matter particles in a concentrated medium. Taking into account the industrial interest in the extraction process, we

Table 1 Tannin extraction yield and Stiasny number results for different solid-to-liquid ratios (time: 2h, temperature:70°C).

Ratio (S/L)	Pomegranate tannin extract	
	Yield (%)	Stiasny number (%)
1/20	54 ± 1	< 10%
1/10	54 ± 1	< 10%
1/5	39 ± 2	< 1%

could assume that 70°C, 2 h and 1/10 are the optimal extraction conditions of Tunisian pomegranate tannins' peels.

The Stiasny number provides information about the reactivity of a tannin extract toward formaldehyde; this information can help to determine if the extract can be used as adhesive [36].

According to Yazaki and Collins [34], at least a 65% Stiasny number is needed for a typical wood adhesive application. The Stiasny number relieved from this study is lower than 10% for solid-to-liquid ratios equal to 1/20 and 1/10 and is lower than 1% for solid-to-liquid ratio equal to 1/5. In all cases, pomegranate tannin extracts are not suitable for wood adhesive application, contrary to mimosa tannins, quebracho tannins, pine tannins and acacia tannins characterized by their high Stiasny number values [37,38,21,39]. The low values of the Stiasny number are basically assigned to the hydrolyzable character of pomegranate tannins [13], as well as to the presence of carbohydrates in the pomegranate extract [34].

2.7 Modulus of Elasticity Analysis

Curves giving elasticity modulus (E') as a function of temperature for the formulated resins are given in Figure 3.

Results of E' obtained for the different formulations at 180°C (to be used later in tensile tests) are shown in Table 2.

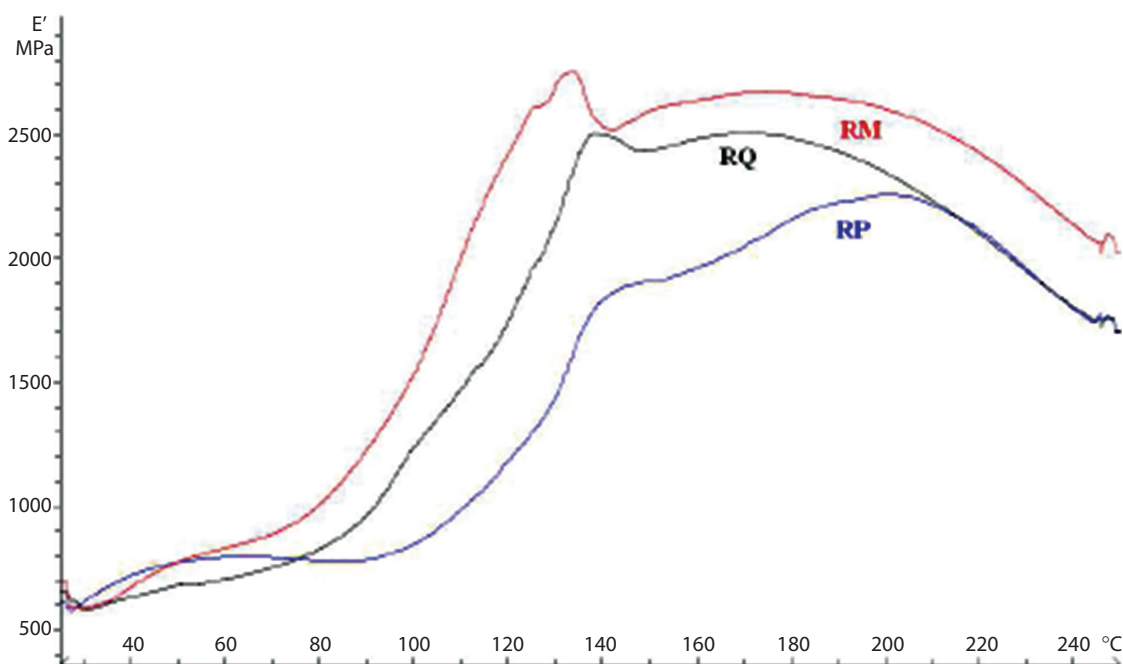


Figure 3 TMA measuring MOE as a function of temperature to describe the curing of resins of mimosa tannins (RM), quebracho tannins (RQ) and pomegranate tannins (RP)/hexamine.

Table 2 MOE values (at $T^\circ = 180^\circ\text{C}$) and shear strength results (for $T^\circ = 180^\circ\text{C}$ and $t = 5$ min) of the studied adhesive formulations.

Formulation	Composition	E' at 180°C (MPa)	Shear strength (MPa)
Pomegranate	6% hexamine + 30% pomegranate tannin (pH=10)	2100	Null
Mimosa	6% hexamine + 45% mimosa tannin (pH=10)	2665	0.76 (± 0.14)
Quebracho	6% hexamine + 45% quebracho tannin (pH=10)	2464	0.64 (± 0.14)

Mimosa resin formulation presents the highest E' and is followed by quebracho resin formulation and then by pomegranate resin formulation. Curing of tannin resin results in several parameters that overlap and that are related to the complexity of the studied systems. Thus, several factors could influence the tannins' reactivity with hardener, like the presence of branched or linear polymers, the degree of polymerization, the type and the structure of flavonoid units, the number of free reactive sites, the natural variability of tannins and the steric hindrance [20,34]. Based on MALDI-TOF analysis results, pomegranate condensed oligomers are characterized by a weight average degree of polymerization of approximately 3.5 and an average reactive sites number of 4.5 [19]. Nevertheless, the number average degree of polymerization calculated for quebracho and mimosa tannins is 6.25 and 5.5 respectively [40].

From Figure 3, it appears that the E' of mimosa resin keeps a stable value in the range of temperatures that correspond to wood panel press conditions ($180^\circ\text{C} < T < 200^\circ\text{C}$). In the case of pomegranate, we noted that the E' increased from 180°C to 200°C with a maximum at the latter temperature, whereas for quebracho resin, we observed a decrease in this range of temperatures. Early decrease in quebracho resin E' could be characteristic of quebracho tannin depolymerization reaction. In fact, the interflavonoid link in quebracho tannin (profisetinidin/prorobinétidin) is particularly labile and therefore is subject to a depolymerization reaction under heat action [41]. It appears from the TMA curves that mimosa resin and quebracho resin curing begins around 120 – 130°C . However for pomegranate, resin curing begins around 140°C . The delayed curing of pomegranate resin and the weak density and E' of the final network could be explained as follows: it has been demonstrated from the colorimetric test as well as from Stiasny number calculation that pomegranate extract is very rich in hydrolyzable tannins, which limits its reactivity towards formaldehyde. However, based on TMA results, it can be seen that the resulting network from pomegranate resin curing, in the presence of hexamine, presents a rigidity of 2100 MPa at

the temperature range of 180 – 200°C . This observation could be justified by the fact that hydrolyzable tannins are a mixture of simple sugars, like glucose, of phenolic acid (gallic acid, ellagic acid...) and of their combined substances. Thus, under heating, gallic acid, for example, can readily undergo a decarboxylation, so giving pyrogallol, which is reactive toward formaldehyde in alkaline medium. Sugars are also reactive toward formaldehyde [42]. In this way, hydrolyzable tannins could participate in the polymerization of pomegranate tannins-based adhesive. However, this polymerization will not have the same performance as that of condensed tannins with formaldehyde (or hexamine).

3.8 Resin Strength Analysis

The results of the shear strength tests conducted for the various formulations (Table 2) reconfirm the results of the thermomechanical analysis.

These results clearly indicate the predominance of hydrolyzable tannins rather than condensed tannins in pomegranate peel extract. In this study, a formulation approach, used mainly with condensed tannins such as mimosa tannins and quebracho tannins, was tested with pomegranate tannins. The lower reactivity of gallic acid-like nuclei in hydrolyzable tannins precludes the direct use of such tannin with classical condensed tannin adhesive technology approach. Yet, excellent adhesives can still be obtained with hydrolyzable tannins, as the tannins described in this research work, by co-condensing them with phenol to form phenol-hydrotannin-aldehyde resins in which hydrolyzable tannins are in a proportion of 80% hydrolyzable tannins to 20% synthetic phenol, or other phenols. This approach has been shown to be successful with chestnut hydrolyzable tannins [43] and even when used industrially for a 50/50 phenol/hydrotannin proportion [44].

4. CONCLUSION

We have analyzed for the first time the tanniferous composition of Tunisian pomegranate peels for wood adhesive application. Colorimetric tests showed that Tunisian pomegranate peels are richer in hydrolyzable tannins than in condensed tannins. This result has been confirmed by FTIR and ^{13}C NMR analyses. We have observed by MALDI-TOF analysis that the abundant oligomers in pomegranate extract are of flavonoid tetramers, as well as the presence of flavonoids linked to sugars. Optimization of tannins extraction showed that conducting an extraction at 70°C , for 2 hours and for a solid-to-liquid ratio equal to 1/10, allows a maximum yield of 53,7%, but with a reactive tannin rate lower than 10%. E' and resin strength analyses of pomegranate tannins/hexamine-based adhesive showed poor performance compared to mimosa and quebracho tannins/hexamine-based adhesives, which is basically explained by the high amount of hydrolyzable tannins. It would be interesting to study and evaluate the use of these tannins as substituent for synthetic phenol in phenol-formaldehyde resin, as has been reported for chestnut hydrolyzable tannins.

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