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ARTICLE

Synthesis of Green Adhesive with Tannin Extracted from Eucalyptus Bark for Potential Use in Wood Composites

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ABSTRACT

Recently, the exploitation of renewable plant resources in the formulation of adhesives is very promising for their availability at low coast, as well as their richness in biomolecules such as polyphenols. In this way, many research studies tannins extracted from different sources such as mimosa, quebracho, and pine have been the subject of very satisfactory recent studies. In this paper, a new complete characterization of the tannins extracted from the bark of *eucalyptus globulus* harvested from two regions in Algeria was achieved. The structural characterization enabled us to confirm the richness in condensed tannins, particularly in *procyanidin* and *prodelphinidin* units. The most reactive tannins obtained during extraction at 70°C (yield: 27.1%) have a Stiasny number of 75.92%. This extract was used for the formulation of adhesives (tannin/hexamine). The thermal characterizaction of the adhesives showed higher stability for the tannin formulation of eucalyptus/hexamine as well as an excellent mechanical performance with a MOE of 2807 MPa at 180°C and shear strength of 689.4 N/mm^2.

KEYWORDS

E. globulus; tannins; resin; adhesives; FTIR; NMR

1 Introduction

Eucalyptus is the most planted species in the word after *Pinus and Cunninghamia* with more than 500 species [1,2]. The most cultivated species in the subtropical and Mediterranean regions is *E. globulus* [3] because it meets the growing need for a paper being an ideal ingredient for paper pulp since its fast-growing species. A tree usually produced every 80 to 100 years while Eucalyptus produced every 15 years with 3 times more than Aleppo pine.

Eucalyptus globulus belongs to the *Myrtaceae* family, it is native to Australia. Ramel introduced it to Algeria in 1854 [4]. Not characterized by its rapid growth, it was therefore chosen to constitute plantations whose production covers the needs of pulp mills.

Around 1975, a eucalyptus reforestation program was started in Algeria, particularly in the regions of Annaba (16.310 ha), Tizi-Ouzou (6070 ha), Guelma (3940 ha) and Skikda (2845 ha) covering a total of 43.235 ha. These plantations produce 144.800 m^3/year [5]. *Eucalyptus globulus* is currently widely

distributed in Algeria, plantations increased from 30 000 ha in 1990 to 39 000 ha in 1995 and today it represents well over 44 000 ha of the country's forest wealth [6] making it a widely available local bio-source. However, Eucalyptus forests can play a key role in the timber industry.

Eucalyptus forests are mostly exploited for pulp production, and the possibility of producing wood adhesives could be considered by exploiting eucalyptus bark as a raw material. Thus, many scientific studies have been carried out on the development of biodegradable materials to reduce greenhouse gas emissions. Studies on the production of wood adhesives began in the 1990s [7] in the southern hemisphere, then in Asia in 2006 [8] and recently in some European countries [9,10].

Extensive studies were conducted to develop numerous industrial applications of tannins, be they natural phenolic compounds [11] that are present in plants, leaves, fruits, wood, and the majority of trees [12,13]. Bate-Smith and Swain have described tannins as water-soluble phenolic compounds with molecular weights between 500 and 3000. They precipitate alkaloid, gelatin, and other proteins in addition to the usual phenolic reactions [14]. The most commonly used sources of tannin are bark of quebracho (*Schinopsisbalansae* and *Schinopsislorentzii*), mimosa (*Acacia mearnsii*), different pine species bark [15,16] and different species of eucalyptus [17,18].

Extraction conditions such as water temperature have a direct effect on the yield and properties of extracts [19,20]. The climate conditions as well as forest activities varying from one area to next also affect the extract properties [21].

In this paper, the extraction of eucalyptus bark tannins from Algeria has been optimized. The tree populations studied are aged between 15 and 20 years, the solvent used was water to reduce the toxicity to human health as well as the environmental impact during the transition to the industrial process.

A detailed spectral (FTIR –^{13}C NMR) and thermal characterization (TGA/DTG) of the tannins extracted from the Algerian *E. globulus* bark was studied for the first time. A resin of eucalyptus tannin/hexamine and mimosa tannin/hexamine has been formulated to study the possibility of using it as a wood adhesive. And finally, the thermal stability and the mechanical properties of this resin and composite were studied using TMA and TGA analysis and shear strength.

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2 Materials and Methods

2.1 Materials

The *E. globulus* bark was harvested during the year of 2019 in two different Algerian Wilaya which are:

- M'Sila (Forest of Ain Ghrab-Djebel Messaade): Latitude 35°02'19"N, longitude 4°08'45"E, 1346 m.a.s.l;
- Algiers (Polytechnical Military School–Bordj El Bahri): Latitude 36°47'20"N, longitude 3°15'42"E, 35 m.a.s.l.

called in this work EU. R1 and EU. R2, respectively. They contain 16% of moisture.

The commercial tannin extract of mimosa is supplied by the company "Chimie Algérie" and which is intended for tannins companies.

2.2 Extraction

The *E. globulus* was air-dried until a stable moisture level, grounded, and sieved to 0.4 mm (40 Mesh) using a grinder (Universal. Grinder Ika M20) to prepare the polyphenol extracts.

The method used to extract polyphenol from the eucalyptus bark was the high-temperature infusion (ratio 1/20 w/v). The extractions were carried out in 1L glass beaker under reflux with controlled

temperature and with mechanical stirring. Sodium hydroxide, sodium sulphite, and sodium carbonate are used in aqueous solutions with determined concentration for extraction in an alkaline solution. The extraction temperature was varied between 70°C and 90°C.

After extraction, the solution was first filtered then, the volume of the extract was reduced under low pressure using a rotary evaporator (BuchiRotavapor). The solid obtained was then lyophilized (Christ Martin ALPHALYOPHILIZER) the extract is stored at a temperature of 5°C, to maintain very low and constant moisture content and also to avoid any reaction between polyphenols and light. The extract obtained was weighed and the yield was calculated. The determination was done in triplicate. The yield of extraction was calculated using the following Eq. (1):

$$Extraction\ yield\ \% = \frac{W_e}{W_b} \times 100 \tag{1}$$

where W_e: Oven-dry weight of extract, g; W_b: Oven-dry weight of bark, g.

The reactivity of the extracts obtained is determined by calculating the Stiasny number as described by Voulgaridis et al. [22] according to the following Eq. (2):

$$Stiasny\ number\ \% = \frac{Oven\ -dried\ weight\ precipitate\ \times 100}{(Dissolved\ solid\ content/100) \times 50} \tag{2}$$

2.3 Eucalyptus Extract Characterization

The most reactive extract was maintained for the rest of the study, to be characterized by FTIR, ^{13}C NMR, and TGA/DTG.

FTIR analyses were performed using a Perkin Elmer spectrum device, which is provided with an ATR-FTIR unit, was used to perform infrared analysis, a few milligrams of extract were deposited on the crystal (Diamond/ZnSe) after milled. The scanning tongue was between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and a scan number of 10.

NMR analysis was performed using a 400 MHz spectrometer. The analysis was performed on the ^{13}C atom, in the liquid phase. Chemical shifts were calculated based on Tetramethylsilane (TMS). The number of analyzes and the duration of acquisition are 1.36 s and 12000, respectively, Deuterated dimethyl sulfoxide (DMSO-d6) was used to dissolve the extract. The spectra appear at 100.6 MHz.

The thermal decomposition study of the eucalyptus tannin extract was made using an SDT A600 TA instrument with a thermal cycle of 25–600°C and the heating rate was 10°C/min. The analysis was carried out under static air nitrogen with a gas flow rate of 100 mL/min.

2.4 Resin Formulation

The tannin extracted and characterized was used to prepare the resin. For comparison of the resin (ER) properties, another resin using mimosa tannin (MT) was formulated using the same method.

Briefly, the formulation was carried out as follows: 45% of an aqueous solution of tannin was prepared. Then, 30% of NaOH solution was added to adjust the PH at 10 [8] and next, 6% of hexamine solution (30%) was added (on solid tannin contain base).

2.5 Resin Characterization

The properties of resins formulated using mimosa and eucalyptus tannins extracted from Algerian bark were studied. The thermal decomposition analysis was achieved using an SDT A600 TA instrument, with a thermal cycle from 25 to 600°C and the heating rate of 10°C/min. the analysis was carried out under nitrogen (40 ml/min).

The thermal-mechanical analysis (TMA) was applied to study the modulus of elasticity (MOE) of the mimosa and eucalyptus tannin-based resins using Mettler-Toledo SDTA840 apparatus. The rigidity of the bonded wood joint as a function of temperature was monitored.

Two beechwood ply 0.6 mm thick, with each formulation (ER and MR) bonded together. the total sample size was: 17 mm × 5 mm× 1.2 mm, and the test conditions were: Temperature between 25°C and 250°C with 10°C/min for the heating rate.

2.6 Mechanical Tests of the Two-Ply Wood

Plywood composite shear strength was determined using traction machine (Zwick/Roell Z010), crosshead speed was 2 min/min. the load at fraction was estimated by a fraction and reported as shear strength.

3 Results and Discussion

3.1 Extraction

The infusion at high temperature was used to extract tannin from Algerian *E. globulus* bark from two regions. The extraction yield for each method is presented in Tab. 1. The highest yield obtained is 29.4% for a EU. R1 bark at 90°C. A slightly lower yield was obtained for the same bark under lower extraction temperature. The maximum yield of tannin's extraction from Algerian *E. globulus* is similar to rates found with a mimosa (30–33%) and quebracho (26–29%) [23]; and is higher than Scots pine (10.5%) and maritime pine (24.9%) [24].

Table 1: Yield and reactivity of extract

Temperature (°C)	Bark region	Yield (%)	Stiasny number (%)
70°C	EU. R1	27.1 ± 4.46	74.60 ± 12.92
	EU. R2	17.9 ± 5.42	49.86 ± 9.56
90°C	EU. R1	29.4 ± 7.79	63.78 ± 12.48
	EU. R2	23.8 ± 6.52	37.43 ± 9.49

Concerning the EU. R2 bark, the extraction yield is lower than the EU. R1 bark with a value of 17.9% and 23.8% at 70°C and 90°C, respectively (see Tab. 1).

The nature of species, the age of the tree, the period of storage, and the method of extraction are parameters influencing the yield of the extraction as well as the quality of the obtained tannin [25].

According to the extraction study of Xavier et al., when the extraction temperature increased, a higher extraction yield is obtained, and in that way, higher yields are observed during extraction at 90°C [26].

3.2 Stiasny Number

The Stiasny number provides information on the reactivity of the extracts obtained, and this information will allow us to decide whether or not the extracts obtained can be used to formulate wood adhesives [27]. For wood adhesives formulation, a Stiasny number of at least 65% is needed [24].

The Stiasny number obtained for our extracts is between 37.43% and 74.60% (Tab. 1). the extract obtained from the EU. R1 bark is the most reactive with a Stiasny number of 74.60% (70°C) and 63.78% (90°C). However, the extract obtained from the EU. R2 bark is less reactive: 49.86% (70°C) and 37.43% (90°C) which is less interesting for the formulation of wood adhesives. This decrease can be explained by the work of Zanetti et al. [28], where they observed that increasing the extraction temperature does not systematically increase the level of reactive tannin, but often it influences by increasing the extraction of

non-phenolic compounds. Sometimes it causes structural changes in tannin and therefore a decrease in their performance as adhesive. The reactivity of other species is summarized in Tab. 2.

Table 2: Stiasny number of extracts from other species

Species	Stiasny Number (%)	Reference
Tanzania mimosa	92.2	Kueny [29]
Brutia pine	88.80	Gönültaş et al. [30]
Quebracho	88.32	Gerengi and Sahin [31]
Aleppo pine (Tunisian)	82.5	Saad et al. [32]
Aleppo pine (Greece)	80.30	Voulgaridis et al. [22]
Aleppo pine (Algeria)	78.50	Voulgaridis et al. [22]
Stone pine	78.31–83.14	Gönültaş et al. [30]
Pine tannins	70.77	Gönültaş et al. [30]
Acacia manguim	70.1–94.2	Hoong et al. [33]
Maritime pine	68.7	Yazaki et al. [24]
Radiata pine	56.2	Yazaki et al. [24]
Scots pine	43.8	Yazaki et al. [24]

The Algerian eucalyptus tannin is more reactive than other species, but it remains much less reactive than the mimosa and quebracho tannin with a maximum reactivity of 74.60%, but it remains interesting for the formulation of wood adhesive.

The extract obtained at 70°C for the EU. R1 bark was maintained for the rest of the study because of its high reactivity and its good yield.

3.3 Spectral Characterization of Eucalyptus Extract

In Fig. 1 is illustrated the eucalyptus extract spectrum FT-IR within the range of 400 to 4000 cm^{-1}. However, the discussion of the different bands observed is summarized in Tab. 3.

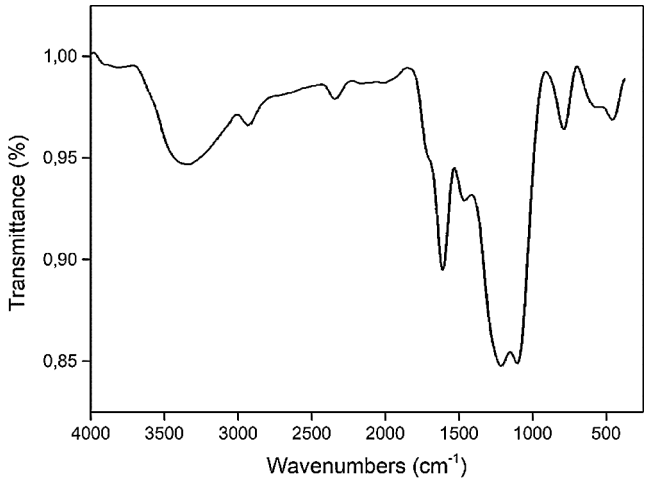

Figure 1: FT-IR spectrum of Algerian eucalyptus bark extract

Table 3: Interpretation of the FT-IR spectrum of the *E. globulus* extract

Band (cm^{-1})	Assignments	References
3277	–OH stretching	Ping et al. [34]
2939	–CH and –CH2 aliphatic hydrocarbon vibration	Lee et al.; Ping et al. [34,35]
	–CH stretch vibration in aromatic methoxyl groups and methyl and methylene groups of side chains	Chaupin et al. [27]
	Aromatic and non-aromatic –CH deformation	Soto et al. [36]
1610–1520; 1444	Aromatic ring stretching vibration	Lee et al. [35]
1370	Phenolic stretch vibration of –OH Aliphatic –CH deformation in methyl groups Lignins	
1110; 1283	Ethereal CO asymmetric stretching vibration arising from the pyran-derived ring structure of condensed tannins	Chaupin et al. [27]
880–835	Hydrolyzable tannins	Soto et al. [36]

The FT-IR spectrum of the Algerian eucalyptus (*E. globulus*) extract is similar to the spectrum of *Pinus radiata* barks in the study produced by Soto et al. [36], in which, the bands located at 1400–2000 cm^{-1} and below 900 cm^{-1} confirmed the aromatic nature of the condensed tannin structure.

Fig. 2 shows the ^{13}C NMR spectrum, its interpretation (Tab. 4) was based on research conducted by [37–40].

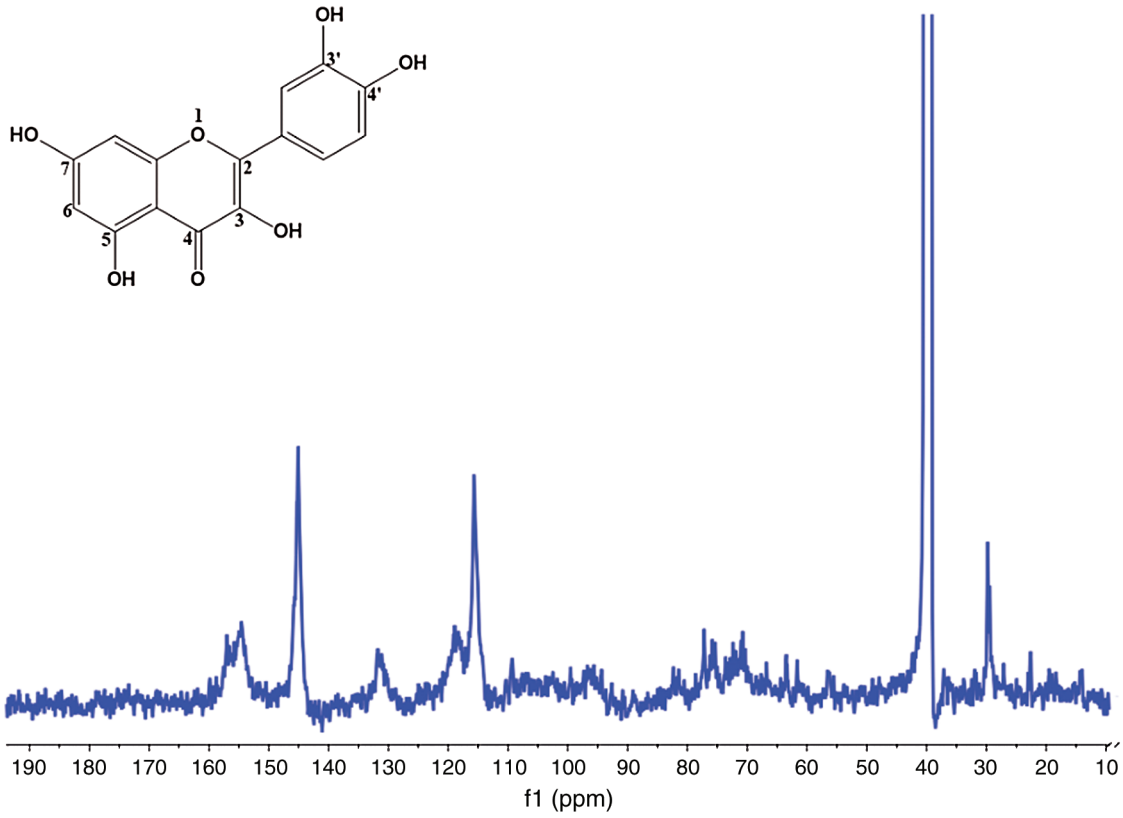

Figure 2: ^{13}C NMR of Algerian eucalyptus bark extract in DMSO-d6

Table 4: Interpretation of the ^{13}C NMR spectrum of the *E. globulus* extract

Signal (ppm)	Assignments
Procyanidin units	
115–120	C2′, C5′ and C6′
131.4	C4′ units
145	C3′ and C4′
150–160	C5, C7 and C8a
75–76	C2 Cis
82	C2 Trans
Prodelphinidin units	
130.8	C4′ overlapping the chemical shift of C1
90–110	C8, C6, C6′ and C2′
36.6	C4 of expansion units
29.4	Terminal C4
Other	
29.4	Catechin C4 or terminal flavanol unit when neighbouring C3 carries a hydroxyl group
60–85	Carbohydrates

The ^{13}C NMR spectrum of Algerian eucalyptus tannins is unlike pomegranate that is rich in hydrolysable tannins which shows strong signals between 60 and 100 ppm [41], while it is close to that of *pinus brutia* with a predominance in tannins condensed as well as *Kandelia candel* species with a predominance of the isomer cis [39,42]

3.4 Thermogravimetric Analysis of Eucalyptus Extract

The thermogram analysis was carried out on the Algerian eucalyptus tannins under nitrogen atmosphere. Fig. 3 shows two typical mass loss of thermal phenomena.

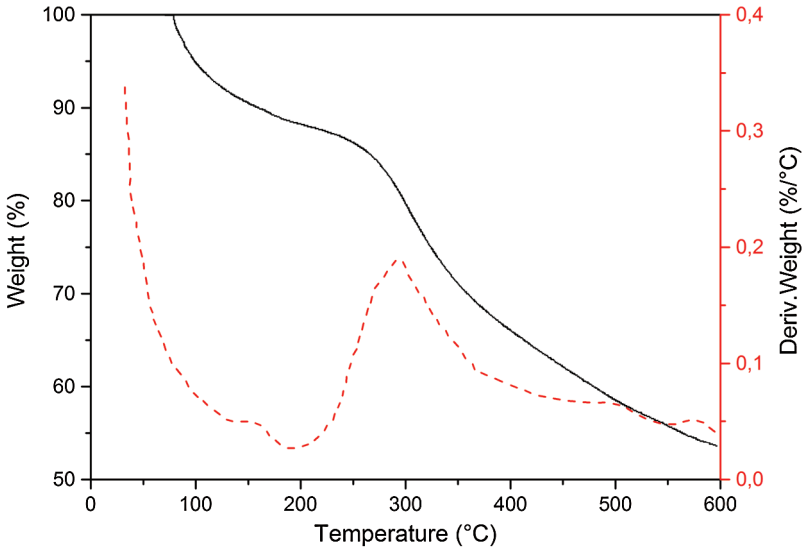

Figure 3: The TGA and DTGA thermograms of Algerian eucalyptus tannins heated at 10 °C/min under nitrogen

The first is attributed to the loss of absorbed moisture mass and is equivalent to 10%. The second loss, which is more significant, corresponds to the decomposition of the tannins. The decomposition of the eucalyptus tannins begins at 169°C, the peak of this latter appears at 275°C. the residue is equal to 53% at the end of the decomposition.

Eucalyptus tannins are, also, more steady than the condensed tannins of radiata pine, which starts degradation at 150°C [43].

Unlike pomegranate peels hydrolysable tannins [44] which begin degradation at 149°C and have a decomposition peak at 190°C with a residue rate of 36.4%, the analysis of eucalyptus tannins shows that they are more stable under the same circumstances. This result is explained in the work of Saad [41], as being caused by the presence of a large amount of carbohydrate in the pomegranate peel extract, mainly due to the presence of sugar in the structure of the hydrolysable tannins.

Algerian eucalyptus tannins are thermally stable compared to quebracho tannins, which has a decomposition peak at 249.9°C with a residue level of 55.29% [45].

Fig. 4 shows the thermal behavior of Algerian eucalyptus tannins under air. The degradation begins at 156°C. The TGA thermograms show three decompositions (156, 350, and 470°C). the formation of catechin and catechol moiety, that characterize the degradation of condensed tannins can be driven by pyrolysis [46].

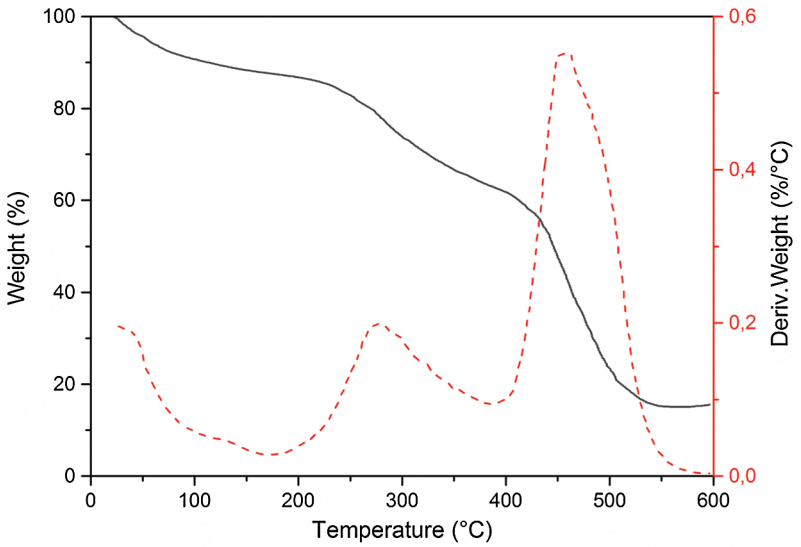

Figure 4: The TGA and DTGA thermograms of Algerian eucalyptus tannins heated at 10 °C/min under air

Galvez et al. [47] during a study on the thermal decomposition of gallic acid, observed a decomposition in three stages: the first corresponding to decarboxylation (release of carbon dioxide) during heating at 260°C (26.27%); the second may be caused by additional loss of hydroxyl at 308°C (29%), and the last at 503°C (45%) is due to the significant oxidation of the residual carbon (CO_2, H_2O, CO).

In our study, the different stages of the thermal decomposition depend essentially on the structure, the decomposition, the degree of polymerization as well as the nature of the inter-flavonoid bond.

3.5 Thermogravimetric Analysis of Formulated Resin

The thermal behavior of the resin formulated from both: the tannin of *eucalyptus globulus* (ER) and the tannin of mimosa (MR) is represented in Fig. 5 by the thermogram obtained under nitrogen. Thermogravimetry allows us to study the stability and thermal decomposition levels of the new ER resin.

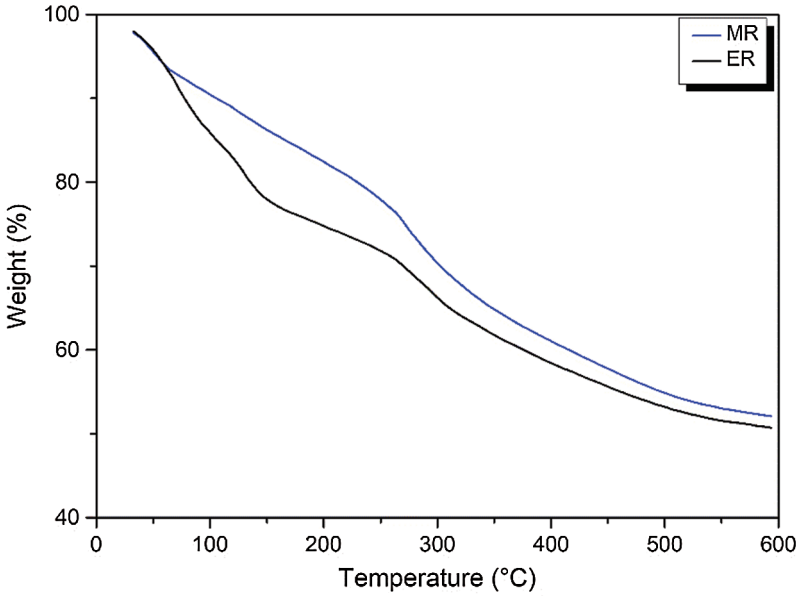

Figure 5: The TGA thermograms of tannins/hexamine resins (MR: Mimosa resin and ER: Eucalyptus resin) heated at 10 °C/min under nitrogen

According to Moubarik et al. [48], it is only after the absorption of a certain amount of thermal energy that decomposition begins which initiates degradation by breaking down the molecular chains.

Three stages are observed in the degradation of the resins (ER and MR). according to Sekaran et al. [49], the first step corresponds to the elimination of residual water; the second between 100 and 300°C is attributed to the partial degradation of the intermolecular bonds. Finally, between 300 and 600°C, we observe the third step which could correspond to the fragmentation of intermolecular bonds.

The nature of the tannins, type of intermolecular bonds, and the rigidity of the network following the crosslinking of hexamine with the tannins, influence the thermal behavior of the resins.

3.6 The Module of Elasticity Analysis of Formulated Resin

Fig. 6 presents the elasticity modulus (MOE) as a function of temperature for the formulated resins, based on commercial mimosa tannins (MR) and *E. globulus* tannins extracted (ER). The results of the MOE of the two resins at 180°C are 2505 MPa for the resin-based on tannins of mimosa and 2807 MPa for the resin-based on *E. globulus*.

The resin ER has a higher MOE (2807 MPa) than the MR (2505 MPa). the complexity of the systems studied is one of the factors which have a considerable impact on the hardening of the resin. However, according to Pizzi et al. [23,24], several parameters could influence on the reactivity of the tannins with the hardener, those include the existence of branched or linear polymers, the composition and form of flavonoid groups, the arrangement of the aromatic rings A and B (their reactivities, the amount of reactive free sites), and interflavonoic bond type.

The reaction of the hardener, formaldehyde in the case of the study carried by Garnier [50], is faster with the phloroglucinol rings in pine tannins that with the A ring of resorcinol type in the tannins of mimosa.

In Fig. 6 it is observed that the ER exhibits stability of MOE over a greater temperature range than the MR. the MOE value of the MR (≈2600 MPa) reported in the literature is slightly greater than the value recorded in this work [32,51]. This may be due to the nature of the hardener used as well as the operating

conditions during the preparation of the resin or the extraction conditions of the mimosa tannins. For the value of the MOE of ER, we did not have a basis of comparison because the formulation of resin-based tannins extracted from Algerian eucalyptus is carried out for the first time in this study.

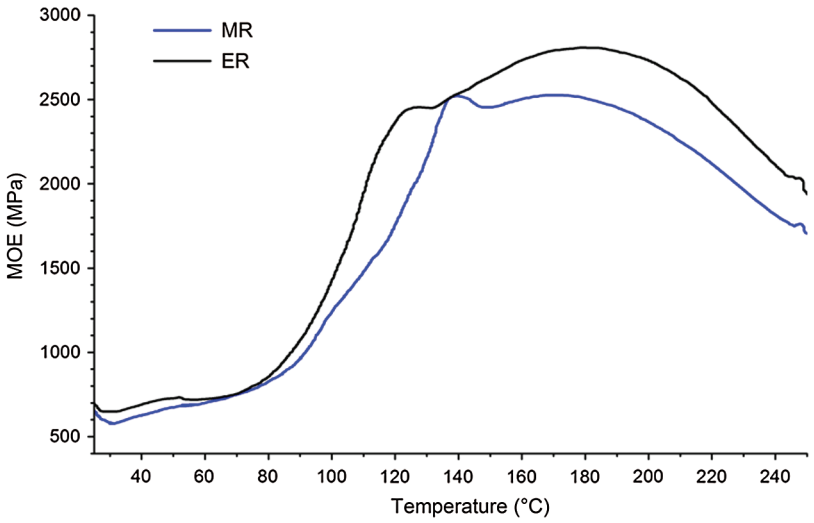

Figure 6: TMA measuring MOE as a function of temperature to describe the curing of mimosa resin (MR) and eucalyptus resin (ER)

3.7 Mechanical Properties of Composite

The results obtained for the shear resistance tests carried out for the ER and MR formulation confirm and support the results of the thermomechanical analysis. With a shear strength of 759.6 N/mm^2 and 689.4 N/mm^2 for MR.

4 Conclusion

In this paper, the characterization of tannins extracted from the bark of Algerian *E. globulus* has been performed for the first time to be used for the formulation of wood resin adhesive. FT-IR analysis allowed us to determine the predominance of condensed tannins over hydrolysable tannins in the bark of Algerian *E. globulus*.

Moreover, the ^{13}C NMR analysis indicated that the tannins extracted are of the *procyanidin* and *prodelphinidin* type. The thermal behavior studied by gravimetric analysis release interesting thermal stability compared to the tannins of pine, mimosa, and quebracho.

The tannins extracted from the bark of M'Sila (EU. R1) at 70°C was found to be more reactive than the tannins extracted from the bark of the Algiers region (EU. R2) with a Stiasny number of 74.60% at 70°C. It is concluded that increasing the extraction temperature does not increase the reactivity of extracts, but increase the extraction of non-phenolic compounds. It is found that the highest extraction yield was obtained for the EU. R1 at 90°C which is 29.4%. Moreover, it is discovered that the maximum yield of tannins extraction from Algerian *E. globulus* is similar to rates found with a mimosa (30–33%) and quebracho (26–29%) [23], and is higher than scots pine (10.5%) and maritime pine (24.9%) [24].

Thermal analysis of the prepared resin (tannins/ hexamine) showed more interesting thermal stability compared to that of mimosa. MOE results illustrate that the produced resin (2807 MPa) presents interesting performances compared to mimosa (2505 MPa), which was confirmed by the shear strength test of plywood.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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