Effect of heat treatment on Pinus pinaster rosin: A study of physico chemical changes and influence on the quality of rosin linseed oil varnish

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Abstract:

The aim of this study was to get a better understanding of the formulation aspect of a new linseed oil – rosin varnish inspired by the antique violin coating, using heat-treated and non-treated rosin. To do so, the heat treatment effect on rosin was studied on both its thermal properties and some of the varnish properties. The rosin without heat treatment was assigned as the reference. The temperature treatments were: 180 °C, 200 °C and 250 °C. The thermal properties were studied using TMA, DSC, ATG and HPLC. A change due to heat treatment was observed, especially on the softening point and the glass transition, which increase with the temperature. Chemical changes were observed, with the apparition of dehydrogenated and oxidised forms of abietane-based acid, which are not present in the reference rosin. As expected, the amount of turpentine decreases with the heat treatment. The varnish properties are also impacted, with a decrease of brightness and solvent resistance with the temperature. A PCA was made in order to have a statistical analysis of the results. Through this, a clear separation of the four groups was graphically observed, with different representative variables. The variables' influence on each other was also clearly identified, as well as the impact of the chemical changes on thermal and varnish properties.

Keywords: rosin, formulation, vegetable oil, maritime pine, varnish, heat treatment

1. Introduction

Pinus pinaster, also known as Maritime pine is present in vast areas of Italy, France, Portugal, Spain and North of Africa. The largest monospecific woodland in south-western Europe extends over the Landes de Gascogne: a 1.5 million hectare maritime pine forest (Rosa et al., 2018). The maritime pine is cultivated for its timber (Pinto et al., 2005; Riesco Muñoz et al., 2014). Historically, it was used to harvest resin (Soliño et al., 2018). Maritime pine contains more resin ducts than other conifers (Wu and Hu, 1997), connected by anastomoses (Rodríguez-García et al., 2014). Conifers in the pine family also have the ability to form new resin ducts following biotic and abiotic attacks (Krokene, 2015). The resin is produced in epithelial cells, and accumulated in resin ducts (Wu and Hu, 1997). The harvest is made by pine tapping, a process based on the defence system of the tree, which secretes resin as a defensive response to external factors (Rodríguez-García et al., 2016). This defence mechanism can come into play as a response to phytopathogenes (Franceschi et al., 2005), abiotic stress (Blanche et al., 1992), chemical stimuli (Moreira et al., 2009), or, in our case, mechanical wounding (Cheniclet, 1987). After distillation, resin is separated into a volatile fraction, the turpentine (30 %), and a solid residue, the rosin (70 %) (Hawley and Palmer, 1912). The rosin is a brittle, glassy solid, with a yellow-brown colour (Coppen and Hone, 1995).

Rosin composition has been investigated for several years. It contains 90 % of diterpenic acids, and its empirical formula is $C_{20}H_{30}O_2$. The composition may vary depending on its source, species and geographical area. There are two main types of acids in the rosin, pimaric-like and abietic-like. The abietic-like includes: abietic, neoabietic, palustric, and dehydroabietic acid. The pimaric-like includes: dextropimaric and isodextropimaric (Baldwin et al., 1958; Joye and Lawrence, 1967). The softening point has been determined with thermomechanical analysis (TMA) developed by Cabaret et al., which could be more precise than the ASTM E28-14 standard, and is between 25 °C to 70 °C (Cabaret et al., 2018). According to Gaillard et al. (2011), rosin does not have a precise glass transition temperature, but a wide temperature range before reaching a liquid state. The thermal decomposition of rosin occurs in a temperature range from 190 °C to 310 °C (Narayanan et al., 2017). Rosin has many applications such as adhesives (Wang et al., 2018), antibacterial polymer (Kanerva et al., 2019) or packaging (Narayanan et al., 2017). It has been widely used from the 16th through to the early 19th

53 century for varnish by violin makers (Echard and Malecki, 2014). There are numerous studies about
54 those varnishes (Chen, 1992; Echard et al., 2010; Invernizzi et al., 2016), which highlight a blend of
55 siccative oil, rosin and siccative additives (lead, aluminium, iron).

56 Previous studies have observed the proportion, preparation and molecular composition of
57 these historical varnishes (Tirat et al., 2017, 2016), revealing the interaction between the triglycerides
58 from the linseed oil and the diterpenic acids ; they most probably react together to form hybrid species,
59 oligomeric diterpenes and/or hybrid glyceride-diterpene species. It is likely that the heat treatment is
60 what causes the formation of acid species. The heat treatment of linseed oil has previously been
61 studied (Byrdwell and Neff, 1999): increasing the temperature results in a higher degree of oxidation
62 and increases the average molecular weight (Berg, 2002). The heat treatment has also been studied for
63 the rosin. The abietic based acids undergo isomerization, due to their two conjugated double bonds,
64 decomposition, dehydrogenation (Chen, 1992; Loeblich et al., 1955) and auto-oxidative
65 polymerization during the heating (Artaki et al., 1992). Those modifications lead to the formation of
66 compounds such as 15-hydroxo-dehydroabietic acid, 7-oxo-15-hydroxy-dehydroabietic acid and 7-
67 oxo-dehydroabietic acid (Cabaret et al., 2019; Scalarone et al., 2002).

68 The objective of this study is to characterize the rosin before and after high-temperature heat
69 treatment (180 °C, 200 °C and 250 °C) with differential scanning calorimetry (DSC),
70 thermogravimetric analysis (TGA), TMA and high-performance liquid chromatography (HPLC), and
71 to qualify the consequences of those treatments in linseed oil – rosin varnishes. A principal component
72 analysis (PCA) was conducted, in order to correlate the rosin results with the varnishes. PCA is a
73 multivariate technique that aims to reduce the number of dimensions in a dataset (Wold et al., 1987).
74 The purpose is to obtain information in order to create a new varnish, inspired by the antique violin
75 coating and using a local resource for our research team localisation, the rosin.

76 ## 2. Materials and methods

77 ### 2.1 Raw materials

The rosin came from a batch obtained after distillation of one resin mixture from various maritime pine trees from the Landes forest, extracted with the Biogemme© eco-process. It was furnished by Holiste, Biscarosse, France. This rosin is used raw as a reference. The distillation, in order to obtain pure rosin, was made by Biolandes, Le Sen, France, at low temperature and low pressure; details of this process are confidential. The raw linseed oil, first pressing and 100 % from linseed, was provided by Onyx, Roche-lez-Beaupré, France. Ôkhra company based in Roussillon, France, supplied the umber powder, containing manganese dioxide and iron oxide, known as driers for linseed oil. Indeed they promote peroxide decomposition and reduce the induction time (de Viguerie et al., 2016).

2.2 Heat treatment

The reference rosin (Holiste, Biscarosse, France) was used without heat treatment. The rosin degradation temperature range starts at 200 °C and ends around 300 °C (Artaki et al., 1992), therefore the heat treatment temperatures were chosen within that range. All the rosin samples were heated for 30 minutes with a stirring hot plate at 180 °C, 200 °C and 250 °C, corresponding respectively to the linseed oil temperature in the varnishes preparation, the onset temperature of rosin degradation and temperature where degradation occurs. It was decided to not test the 300 °C temperature, which is too close to the self-ignition temperature of the rosin, 390 °C (Carson and Mumford, 2002).

2.3 Varnishes preparation

All varnishes were prepared using the same protocol, to ensure reproducibility of the different steps. Linseed oil was first heated in a glass beaker at 180 °C for 220 minutes according to the recipe of the instrument maker Nicolas Gilles (Gilles, 2019). Umber powder was added as a siccative during the heating, at 0,2 % weight of the total varnish mass. After the heating time, the mixture was brought to room temperature. The rosin was grinded in a mortar before sifting at 800 µm, and then added to the mixture with a 20/80 (rosin/linseed oil) w/w ratio at room temperature. The mixture was heated at 180 °C for a duration of 90 minutes under constant stirring. At the end, heating was cut and the varnish

was allowed to cool down to room temperature. The varnish was poured into a UV-protected vial and kept at room temperature.

2.4 Varnish application

Each varnish was applied with a brush on three maritime pine panels, and UV polymerized. The panel dimensions were 150 x 74 x 18 mm. The UV lamp had a wavelength of 340 nm, and an irradiance of 1,55W/m². Each layer of coating required 6 hours of UV exposition in order to polymerize. Three layers were needed, in order to obtain a satisfying homogeneity. The three layers gave a final film thickness between 150 and 200 µm.

2.5 Differential scanning calorimetry (DSC) analysis

Measurements were carried out on a DSC (TA Instruments, Q20) equipped with a rapid cooling system. Individual samples of heat-treated rosin and the reference were weighed (~5 mg) in standard aluminium pans (TA Instruments) and data acquisitions were carried out using the Universal Analysis 2000 program (TA Instruments). Samples were first dried using an isotherm at 105 °C for 1 minute followed by a cooling step at the rate of 10 °C/min. Then, samples were scanned under air atmosphere between 20 °C and 110 °C at a heating rate of 10 °C/min. All experiments were repeated three times. The maximum temperature of 110 °C was chosen from the literature (Coppen and Hone, 1995; Gaillard et al., 2011). The experiment has been tested in a range from 5 °C to 200 °C, but no transition has been observed, as shown in Fig. 1.

Figure 1 : DSC thermogram of reference rosin in a range from 5 °C to 200 °C

2.6 Thermogravimetric analysis (TGA)

Thermal decomposition analysis of heat-treated rosin and the reference sample was performed by TGA (TA Instruments, Q20). Under flow of air at 60 ml/min, samples (10.0 ± 2.0 mg) of rosin were heated under temperature conditions ranging from 30 °C to 600 °C at a heating rate of 10 °C/min. An isotherm was kept for 20 min at 150 °C, in order to determine the turpentine amount in the rosin. All experiments were repeated three times.

2.7 Softening point measurement

According to ATSM E28-14, American standard for measuring this softening point, rosin is liquefied by heating before being cooled and solidified in a ring. This ring is placed in a beaker filled with water, then a ball is placed on the solidified rosin, and the system is heated, until it liquefies. This causes the ball to fall through the rosin. The softening temperature is noted when the ball hits the bottom of the beaker. However, this technique involves a first heat treatment of the rosin, to liquefy it before measuring its softening point. Heat treatment has an influence on its softening properties. This is why we opted to use a technique enhanced by Cabaret et al. (2018), where the softening point of the rosin was measured using TMA. Measurements were carried out using a TMA (Mettler Toledo, SDTA840) and a standard probe. Samples with a thickness of 5 mm of heat-treated rosin and the reference were prepared by breaking small pieces of hard rosin, without heating, and placed between the probe and the support. A constant force of 0.02 N was applied and the sample was scanned at a heating rate of 2 °C/min between 25 °C and 200 °C above the sample softening point. Thickness measurements were performed each second with the shifting of TMA probe according to the thermal gradient. Thickness was measured each second and softening point temperature was determined at 100 µm, after the inflection point where the sample's height begins to quickly decrease due to the penetration of the probe. All experiments were repeated three times.

2.8 High-performance liquid chromatography (HPLC) analysis

All samples (1% w/v in methanol) were analysed by RP-HPLC-DAD (Ultimate 3000, Thermo Scientific) equipped with an Acclaim Polar Advantage II (3 mm x 150 mm, 3 µm, Thermo Scientific), in methanol(A)/water(B) multi-gradient mode at 1 ml/min (injection volume 10 µL). The gradient elution program was set as follows: 0-2 min.: (60%) A, 2-17 min.: (60-80%) A, 17-24 min. (80%) A, 24-35 min. (80-100%) A, 35-44 min. (100%) A. Then, the elution gradient was linearly ramped down to 60% A for 2 min. Finally, this gradient was maintained for 9 min in order to find the initial conditions of the column for the next injection. All experiments were repeated fifteen times.

2.9 Mechanical properties

2.9.1 Thickness

155 The thickness was measured in µm, using an ultrasonic coating thickness-measuring device
156 (PosiTector 200). Three measurements were made on each panel.

157 2.9.2 Colour

158 The measurements were made using a spectrocoloremeter (X-rite, Ci62), according to the NF
159 EN ISO 18314 standard. The colour was expressed using the CIEL*a*b* colour space, which
160 expresses colour as three numerical values: L* for the lightness, a* for the green–red chromatic
161 coordinate and b* for the blue–yellow chromatic coordinate. Three measurements were made on each
162 panel.

163 2.9.3 Brightness

164 The brightness was measured at an angle of 60 °, using a glossmeter (Byk-Gardner, micro-tri-
165 gloss), according to the NF EN ISO 2813 standard. Three measurements were made on each panel.

166 2.9.4 Adhesion

167 The measurements were carried out using a crosscut adhesion test kit (TQC), according to the
168 NF EN ISO 2409 standard. A grip with cutter was used to make two series of parallel cuts cross-
169 angled with each other to obtain a pattern of 25 similar squares. The ruled area was evaluated after a
170 short treatment with adhesive tape, using a table chart from 0 to 5, 0 being the highest score (no
171 varnish removed from the substrate). Three measurements were made on each panel.

172 2.9.5 Solvent resistance

173 The solvent resistance was measured using a sodium hydroxide solution at 5 % mass fraction,
174 according to the ISO 2812-4 standard. The panels were placed at a 30° angle from horizontal, and the
175 solvent drops were applied every one or two seconds for 10 min through a burette. After the solvent
176 application, the blistering was visually evaluated. Not according to the standard, it was decided to
177 evaluate the colour and the brightness after the solvent application. Three measurement were made on
178 each panel.

179 2.10 Principal Component Analysis (PCA) procedure

PCA helps to explain a data set with fewer linear combinations of the original variables, called principal components (PCs). The procedure is to find PCs that explain most of the variation in the data. Extracted PCs are ordered in an increasing explained variance. PCs represent the linear combination of all variables included in the study. PCs are also called loadings because each original variable is associated to weight (coefficient). All PCs are associated with the contribution of samples; a score denotes this contribution.

A 12 x 17 matrix (where 12 is the number of samples, and 17 is the number of variables) was used for the calculation. PCA on mean-scaled data was performed in R 3.6.0 (using RStudio Desktop 1.2.1335 interface) with FactoMineR (Lê et al., 2008) and Factoextra (Kassambara, 2017) packages. The results of the analysis are presented in terms of Biplot.

3. Results and discussion

3.1 Thermal properties

3.1.1 Thermal degradation

The TGA thermograms of the reference and the heat-treated rosin are presented in Fig. 2. The raw rosin is used as a reference.

Figure 2 : TGA thermograms of rosin according to their heat treatment

The weight loss at 150 °C corresponds to the turpentine fraction of the rosin, which will be discussed in the chemical composition part of this paper. For all the samples, the main degradation occurs at about 200 °C and finishes at about 350 °C, as observed by Kanerva et al. (2019). The final mass loss observed with TGA for the reference and the heat-treated rosins are presented in Fig. 3.

Figure 3: Comparison of the final mass loss of rosin according to their heat treatment. The standard deviation is calculated over 3 samples.

This final mass loss appears to be relatively unaffected by the heat treatment, which is confirmed by the student test.

This observation is consistent with the mechanisms proposed by Artaki et al., (1992) at 250 °C. In this study, this degradation observed at 250 °C corresponds to isomerization followed by dimerization, forming a mixture of dimeric diterpenes. In addition, under air, a mechanism of self-oxidation occurs through the formation of hydroperoxides, forming glycols, ketones and esters of varying molecular weights (Artaki et al., 1992). Finally, the degradation observed at 250 °C corresponds to the formation of new compounds through oxidation and isomerization, and not to the formation of small volatile molecules leading to a loss of mass. In our case the degradation caused by heat treatment (below 250 °C) does not lead to a different final mass loss, which is consistent with the study by Artaki et al., (1992). There is no relevant difference in the organic compounds/ashes ratio between the samples. The chemical composition will be checked with HPLC analysis.

3.1.2 Softening point measurement

The softening point is determined at 100 µm after the bending point, which is when the sample thickness begins to shrink, due to the penetration of the TMA probe. Fig. 4 describes the thickness variation of all rosins, according to their heat treatment (raw for the reference, 180 °C, 200 °C and 250 °C).

Figure 4: Thickness variation against temperature for rosins according to their heat treatment

The softening point temperatures, measured with TMA, of all rosins are shown in Fig.5.

Figure 5: Comparison of the rosin softening point temperatures according to their heat treatment. The standard deviation is calculated over 3 samples.

The values are different to the values obtained by Coppen and Hone, using ASTM E28-14, which give softening points rather around 70 – 80 °C (Coppen and Hone, 1995). In addition, it appears that the softening temperature of the rosin increases with the treatment temperature, which is confirmed by the student test.

Reference rosin (raw) has a significantly different softening point from thermally treated rosins. Heat treatment therefore increases the softening temperature of the rosin. This is consistent

with the observations of Cabaret et al. (2018), who showed that the rosin heated at 120 °C for 12 hours might have a softening point 18 °C higher than that of the reference. This may be due to evaporation of residual turpentine and/or chemical transformation of thermally treated rosin (with oxidation, dehydrogenation and isomerization reactions). This will be checked with the turpentine amount analysis by TGA and the composition analysis by HPLC.

3.1.3 Phase transition temperature measurement

Fig. 6 shows the DSC curves obtained for the reference and the heat treated rosin. A phase transition temperature is clearly observed between 45 and 60 °C according to their heat treatment.

Figure 6: DSC curves obtained for rosins according to their heat treatment

This transition had not previously been observed by Gaillard et al. (2011), because, according to this study, the rosin is completely amorphous. In our experiments, the rosin is distilled and purified with the patented process at low temperature and low pressure, which are not the same conditions as Gaillard et al. (2011) experiments and can lead to a more homogeneous product. Its physico-chemical properties can be different. Indeed, this transition has been observed by Cabaret et al. (2018) on industrial rosin and acetone extractived rosin. This study shows that the transition phase temperature, comparable to glass transition according to Schilling (1989), can be observed when the rosin is homogeneous.

The phase transition temperature of all rosins, reference and heat-treated, measured with DSC, are presented in Fig. 7.

Figure 7: Comparison of the rosin glass transition temperature according to their heat treatment. The standard deviation is calculated over 3 samples.

According to the student test, all the phase transition temperatures, which can be compared to the glass transition temperature, are significantly different, except between the 200 °C and 250 °C heat-treated rosins. This confirms the previous results obtained on the softening point of the rosin: the heat treatment induces a softening, and thus a phase transition, at higher temperatures than for the

reference. The following analysis of residual turpentine content and chemical composition may be used to validate the hypothesis of evaporation of residual turpentine, and/or a chemical transformation of the thermally treated rosin (always according to oxidation, dehydrogenation and isomerization mechanisms) leading to this phase transition to higher temperatures.

3.2 Chemical composition

3.2.1 Residual turpentine amount

The residual level of turpentine in the rosin was measured with TGA, where an isotherm at 150 °C was performed for 20 minutes to evaporate residual turpentine. As seen in Fig. 1, the weight loss at 150 °C corresponds to the residual turpentine. The turpentine starts boiling from 150 °C, due to the boiling temperature of its major compounds: α-pinene between 154 °C and 159 °C and β-pinene (between 156 °C and 166 °C) (Hawkins and Armstrong, 1954). Fig. 8 shows the amount of turpentine in the rosin according to their heat treatment. Overall, all the rosin have a low turpentine amount, under 3 %, and even lower with the increased heat treatment. However, these results show that the turpentine loss is not linear, the amount of turpentine being close between the heat-treated rosin.

Figure 8: Comparison of the turpentine amount in rosin according to their heat treatment. The standard deviation is calculated over 3 samples.

These results have been submitted to a student test, in order to evaluate the differences between them. According to this test, the raw rosin is significantly different from the heat-treated ones; the 180 °C heat-treated rosin is significantly different from the 250 °C heat-treated one, while the others heat-treated are not significantly different. Obviously, the residual turpentine is much lower after treatment at 180 °C and above, as its boiling point is between 150 °C and 180 °C. The small difference between 180, 200 and 250 °C can be explained by the difficulty to remove all the turpentine in the rosin (Cbaret et al., 2019).

The results obtained confirm the hypothesis of a lower level of turpentine for higher softening and phase transition temperatures. Glass transition temperature and softening point increase with heat treatment, and do not vary much for high processing temperatures, 200 °C and 250 °C. The opposite

trend is observed with residual turpentine: it decreases with heat treatment, and does not vary much for high treatment temperatures. However, the residual turpentine amount of the 180 °C treated rosin is very close to the ones of the 200 and 250 °C treated rosins, whereas the phase transition temperatures of the 180 °C rosin is significantly different from the ones of the 200 and 250 °C treated rosins. Thus, the differences observed between the phase transition temperatures cannot be explained only by the evaporation of the turpentine. Indeed, heat treatment can also be affected by the chemical composition (Cabaret et al., 2018).

3.2.2 Abietane-based acids composition

All the rosin samples were analysed by HPLC, the raw rosin used as a reference, and the heat-treated ones (at 180 °C, 200 °C and 250 °C). The chromatograms are presented in Fig. 9.

Figure 9: HPLC chromatograms at 254 nm wavelength absorption of rosins according to their heat treatment. (1) 7-oxo-dehydroabietic acid (7–oxo–DHA), (2) Abietane-based dehydroabietic acid (DHABA), (3) Dehydroabietic acid (DHA), (4) Palustric acid, (5) Abietic acid, (6) Neoabietic acid

Previous work by Cabaret et al., (2019) on rosin analysis by HPLC-MS, coupled with a comparison of UV profiles of compounds based on results from Kersten et al. (2007), allows the identification of the abietane-based acids and derivatives. Dehydroabietic acid (DHA) peak was assigned based on the study by Kersten et al. (2007). A second abietane-based dehydrogenic acid (DHABA) was also detected but could not be identified precisely. According to Cabaret et al. (2019) and (Pastorova et al., 1997), 7-oxo-dehydrobietic acid (7-oxo-DHA) was identified.

According to Ren et al. (2015), the hydroxyl group is formed first through the attack of oxygen, resulting in the isomerization of the conjugated band. At the same time, the methylene is converted to a hydroxyl intermediate by an oxygen atom.

In order to compare the different rosin samples, the surfaces of the different peaks, normalized to 100, are calculated. With this technique, the concentration variation can be compared. The surfaces are presented in table 1.

Table 1: Comparison of abietane-based acids and derivatives contents in rosins according to their heat treatment. The standard deviation is calculated over 15 samples.

An apparition of dehydrogenated forms of abietane-based acids is noticed in heat-treated rosins. For the DHA, this dehydrogenation leads to an aromatisation, and for the 7-oxo-DHA, it occurs along with an oxidation. This has not been observed before, previous results presented by Cabaret et al. (2018) only show heat-treated rosins, and the results presented by Kersten et al. (2006) show the presence of DHA in reference rosin. Resin samples tested in Kersten et al. paper were obtained after industrial distillation process during purification of Tall oil, which is a waste obtained from Kraft pulp. This process might have been done at higher temperature than Biolandes process, and could be at the origin of isomerization and degradation.

The presence of levopimaric acid was not observed. Classical acid portion of commercial pine oleoresin contains from 23 to 40 % levopimaric acid, which is completely isomerized to other resin acids during distillation (Loeblich et al., 1955). According to our study, this is probably due to the isomerization of levopimaric acid into palustric, abietic and neoabietic acids during the distillation process. The chromatogram obtained from levopimaric acid after heating at 155 °C for 3 hours by Loeblich et al. (1955) is presented in Fig. 10.

Figure 10: Chromatogram of levopimaric acid, heated at 155 °C for 3 hours, obtained by Loeblich, (1) palustric acid; (2) abietic acid; (3) neoabietic acid

The chromatogram closely resembles the one obtained in this study if we compare the reference and heat-treated rosins, with the same elution order. The palustric, abietic and neoabietic acids obtained here are therefore derived from the isomerization of levopimaric acid, which occurs during the hydrodistillation of the resin.

Cabaret et al., (2019) showed the presence of levopimaric, abietic and neoabietic acids in rosin obtained directly by heating the maritime pine resin at 60 °C and 90 °C, rosin that has not been hydrodistilled. In this study, the proportion of neoabietic acid is greater than the proportion of abietic and levopimaric acids, while palustric acid does not appear. We used a similar HPLC analysis

program as was used by Cabaret et al. (2019). We were therefore able to compare the results. The hypothetical order of isomerization may be the following: levopimaric acid isomerises to abietic acid and neoabietic acid. At higher temperatures, that of hydrodistillation, levopimaric acid also isomerises to palustric acid, which, with neoabietic acid, isomerise in abietic acid, resulting in the disappearance of levopimaric acid and a higher proportion of abietic acid. The isomerisation pathways could be checked by comparing the spectra of pure palustric, abietic and neoabietic acids with the spectra of pure levopimaric acid heated at different temperatures.

These results also show that the Biogemme® hydrodistillation process, at low pressure and low temperature, could have been done at a temperature higher than 90 °C.

The appearance of dehydrogenated and oxidized compounds of abietane-based acids, observed in thermally treated rosins, is associated with a decrease of abietane-based acids. Heat treatment can therefore cause dehydrogenation of the palustric, neoabietic and abietic acids in DHA and DHABA, lowering their proportions. Dehydrogenic acids also undergo oxidation, leading to the 7-oxo-DHA formation.

This analysis confirms the chemical transformation of rosin, which can affect phase transitions at higher temperatures observed in TMA and DSC.

3.3 Varnish properties

3.3.1 Physical properties

The film thickness, measured in the reference and the heat-treated rosins, is presented in table 2. The test is performed to ensure the homogeneity of the batch. According to the student test, the raw rosin is different from the heat-treated ones. It can be explained by the small standard deviation of this sample.

Table 2 : Varnish colours according to the rosin heat treatment expressed using the CIELAB colour space. Three measurements were made on each of the three panels. The standard deviation is calculated over 9 measurements.

These results show that the film thickness is homogeneous with brush application.

The colours' measurements are presented in Fig. 11. No relevant difference is noticed, which is confirmed by the student test.

Figure 11: Varnish colours according to the rosin heat treatment expressed using the CIELAB colour space. Three measurements were made on each of the three panels. The standard deviation is calculated over 9 measurements.

Only one coordinate is different: the b* value is different for the varnish formulated if compared with the reference. The varnishes formulated with the heat-treated rosins are more yellow, which might be due to the rosin oxidation with heat treatment (observed with HPLC). Also, rosin is known for having a yellowing effect (Domene-López et al., 2018).

The brightness is presented in Fig. 12. It seems to decrease with the heat treatment, but, according to the student test, only the raw rosin is significantly different from the other ones. It means that in order to obtain a less brightening coating, rosin has to undergo heat treatment.

Figure 12: Brightness variation at 60 ° for varnishes according to the rosin heat treatment. Three measurements were made on each of the three panels. The standard deviation is calculated over 9 measurements.

3.3.2. Mechanical properties

The adhesion performances are presented in Fig. 13. All varnishes present good adherence on wood, with no grade above 2. According to the student test, there is no significant difference between the samples.

Figure 13: Comparison of varnish adhesion on wood for varnishes according to the rosin heat treatment. Three measurements were made on each of the three panels. The standard deviation is calculated over 9 measurements.

The solvent resistance, according to the standard, is evaluated with the apparition of blistering. No blistering is noticed on the film, but a loss of brightness and a deepening is observed. The results are presented in table 3.

Table 3: Comparison of brightness and colour loss after a solvent test for varnishes according to the rosin heat treatment. Three measurements were made on each of the three panels. The standard deviation is calculated over 9 measurements.

A noticeable loss of brightness and a change of colour are observed for every varnishes. For all the samples, the varnish is deeper, less green and less yellow. The difference in L* and a* is more important for the heat-treated rosin, while the difference in b* and brightness is similar for all rosins. These results show a lower solvent resistance for the heat-treated rosin, which may be due to a higher solvent sensibility of the dehydrogenated and oxidized compounds of abietane-based acids.

3.4 PCA analysis

From thermal analysis, chemical analysis and varnish properties, and using the R Studio software, a PCA was performed. The aim was to investigate some similarities and differences between the samples, according to the rosin heat treatment, and the influence of the variables on each other.

PC1 and PC2 together represent 78 % of the total variability. The PC1 is mainly representative (64,6 %), and is based on the chemical differences in abietane-based acids and derivatives, the thermal properties and some varnish properties (brightness, brightness loss, L* loss and b*). The PC2 is representative of some colour characteristics (L*, a*). The representation of PC1 vs. PC2 shows the variable position and their corresponding correlations. In fact, the variable position from one to another can be correlated: their opposition means that these variables are inversely proportional.

The PCA biplot is presented in Fig. 14. The three representative values of the groups (non-treated rosin, 180 °C, 200 °C and 250 °C treated rosin) are represented in the same graphic as the variables.

Figure 14: Biplot: Projection of variables and samples onto the first two PCs. (1, 2, 3) for reference rosin; (4, 5, 6), (7,8,9) and (10, 11, 12), respectively for 180 °C, 200 °C and 250 °C heat-treated rosin

The PC1 allows a good separation of the samples according to their heat treatment, with 64,6 % of the total variance: G1 (represented by the yellow point) is the raw rosin group, G2 (represented by the green point) is the 180 °C heat-treated rosin, G3 (represented by the blue point) is the 200 °C heat-treated rosin and G4 (represented by the deep blue point) is the 250 °C heat-treated rosin. This spatial distribution demonstrates the influence of the heat treatment on both the rosin properties and the varnish properties.

The first group (G1) is characterized by the presence of abietane-based acids without degradations, the varnish brightness and the high amount of turpentine left in the rosin. It is also characterized by a low softening point and a low glass transition temperature, along with a small amount of abietane-based acids with degradations. G2 is characterized by the same variables as G1, but less marked than G1. The characteristic variables of G3 are the softening point, the Tg and the presence of dehydrogenated and oxidized compounds of abietane-based acids. G4 has the same characteristic, but stronger than G3.

The PCA also shows the influence of the variables on each other. It is clear on the PC1 that the turpentine amount seems to have an impact on the glass transition and the softening point; when the amount of turpentine increases, the temperatures decrease. This allows a visual observation of the results obtained with the thermal analysis of the rosin. The dehydrogenated and oxidized form of abietic-based acid seems to have an influence on the brightness and the solvent resistance (brightness loss). Their presence causes a lower brightness, and a more important loss of brightness in the presence of solvent, which also allows a visual observation of the varnishes properties' results.

4. Conclusion

The heat treatment has an impact on thermal properties, as the softening point and a phase transition temperature, which can be compared to the glass transition temperature, increase with the temperature. The turpentine amount, as expected, is lower when rosins are heated. The heat treatment also causes the apparition of dehydrogenated and oxidised forms of abietane-based acid. For the first time, we have shown the presence of abietane-based acid only, without their degraded form in non-treated rosin, probably due to the innovative Biogemme® distillation process at low temperature. However, the chemical composition changes could be further confirmed with elementary analysis for the C, O and H content.

This study shows the relevance of the rosin heat treatment for varnish formulation. The varnish films are less bright when formulated with heat-treated rosin. It can be interesting for the customer demand, which can change from a very bright to a natural aspect coating. However, the solvent resistance seems to decrease with the heat treatment, probably due to a higher sensibility of the dehydrogenated and oxidised forms of abietane-based acid to the sodium hydroxide solution.

The PCA allows us to have a spatial repartition of the samples groups, according to their results. In addition, some variables affect each other. Thanks to the PCA, the impact of the heat treatment on the thermal and the varnish properties, through the chemical composition change, can be observed visually.

From this study, a better understanding of the formulation aspect of bio-based varnishes with rosin can be expected.

Acknowledgements

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573

Table 1: Comparison of abietane based acids and derivatives contents in rosins according to their heat treatment. The standard deviation is calculated over 15 samples.

#	Molecule	Absorption max (nm)	Peak area ratio for Raw rosin	Peak area ration for 180 °C rosin	Peak area ration for 200 °C rosin	Peak area ration for 250 °C rosin
(1)	7-oxo-DHA	255.6	0	1.6±0.4	2.0±1.1	6.5±4.6
(2)	DHABA	243.5	0	0.8±0.1	1.1±0.4	1.6±0.6
(3)	DHA	225.3/252/268	0	3.8±0.4	4.5±1.7	7.0±1.6
(4)	Palustric	268	11.4±1.8	9.9±1.8	9.5±2.0	9.0±2.5
(5)	Abietic	240.8	84.3±1.6	85.8±3.9	81.5±2.7	73.1±7.6
(6)	Neoabietic	252	4.1±2.3	5.0±0.8	3.4±0.8	1.1±1.4

Table 2 : Varnish colours according to the rosin heat treatment expressed using the CIELAB colour space. Three measurements were made on each three panels. The standard deviation is calculated over 9 measurements.

Value	Raw	180 °C	200 °C	250 °C
L*	54.30±3.76	54.33±1.86	55.92±0.91	54.79±2.43
a*	17.26±2.85	16.78±1.04	16.07±0.71	16.81±1.17
b*	52.55±1.34	48.09±1.90	47.56±2.98	47.63±3.19

Table 3: Comparison of brightness and colour loss after a solvent test for varnishes according to the rosin heat treatment. Three measurements were made on each three panels. The standard deviation is calculated over 9 measurements.

Value	Raw	180 °C	200 °C	250 °C

L*	-7.3±2.4 %	-13.0±4.0 %	-15.1±0.6 %	-19.2±1.7 %
a*	+5.4±9.2 %	+9.8±4.3 %	+32.1±5.5 %	+15.0±5.9 %
b*	-26.9±1.1 %	-21.3±3.6 %	-19.3±2.1 %	-24.9±2.5 %
Brightness	-89.2±5.3 %	-92.2±7.2 %	-95.7±8.1 %	-96.2±16.1 %

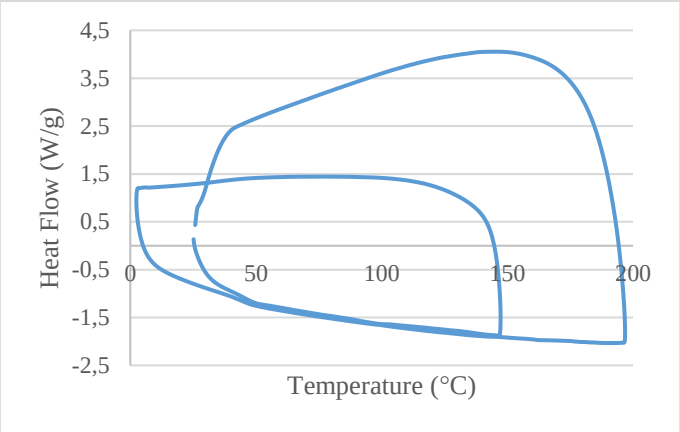


Figure 1 : DSC thermogram of reference rosin in a range from 5 °C to 200 °C

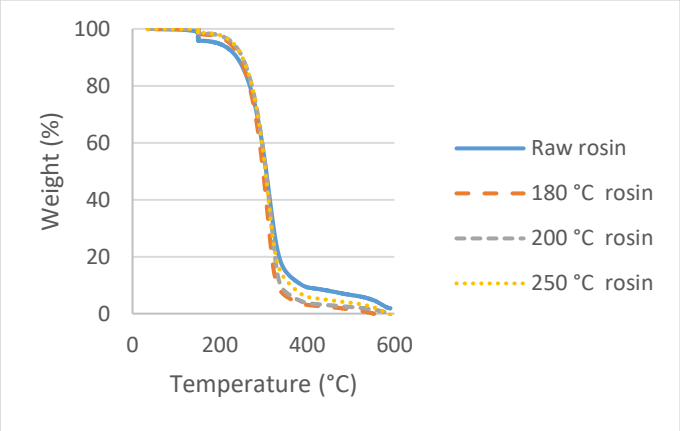


Figure 2 : TGA thermograms of rosin according to their heat treatment

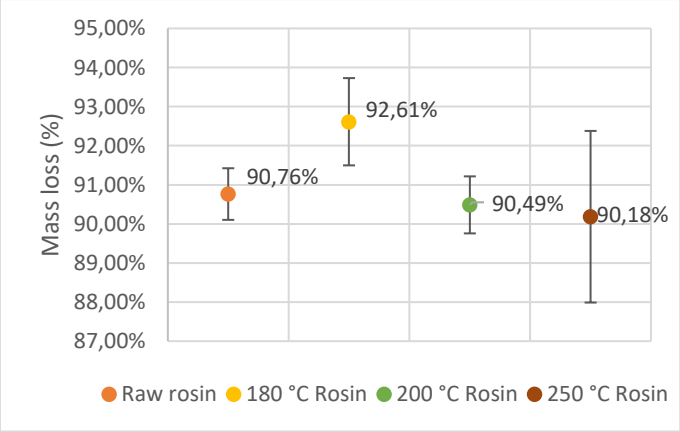


Figure 3: Comparison of the final mass loss of rosin according to their heat treatment. The standard deviation is calculated over 3 samples.

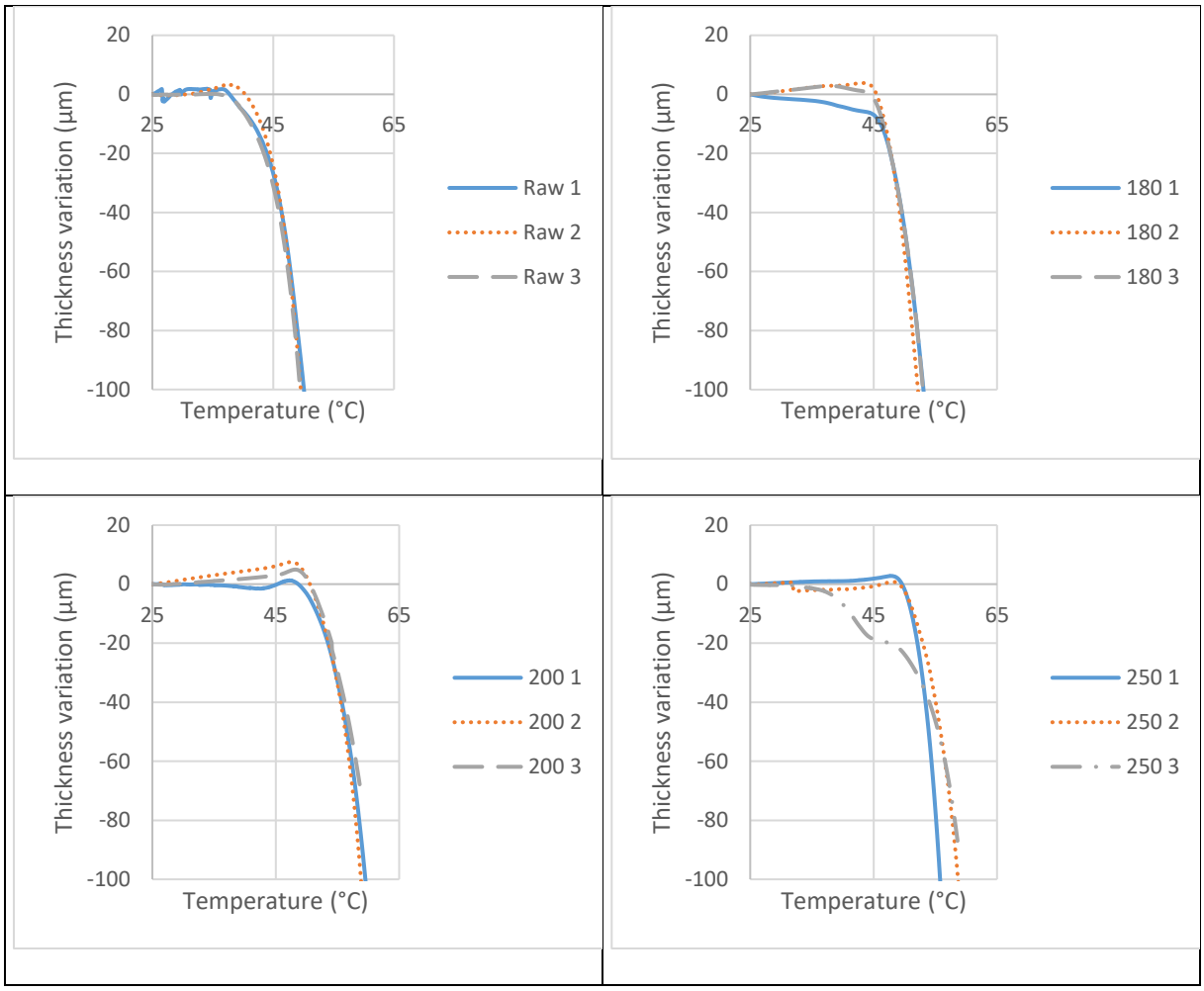


Figure 4: Thickness variation against temperature for rosins according to their heat treatment

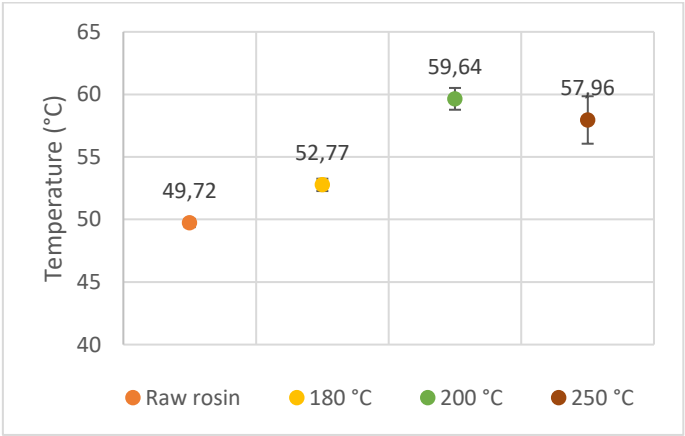


Figure 5: Comparison of the rosin softening point temperature according to their heat treatment. The standard deviation is calculated over 3 samples.

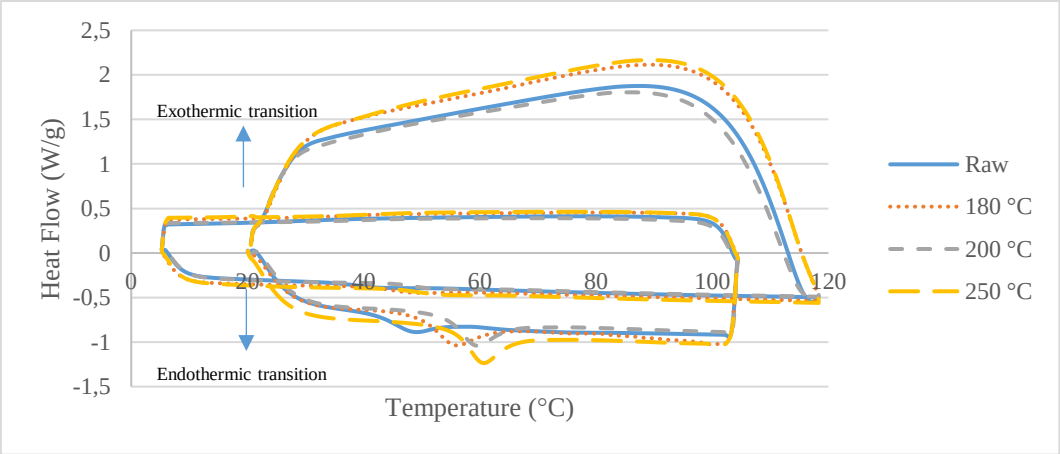


Figure 6 : DSC curves obtained for rosins according to their heat treatment

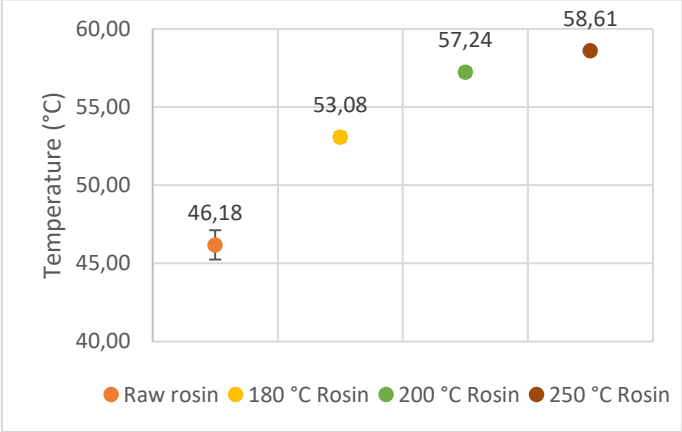


Figure 7: Comparison of the rosin glass transition temperature according to their heat treatment. The standard deviation is calculated over 3 samples.

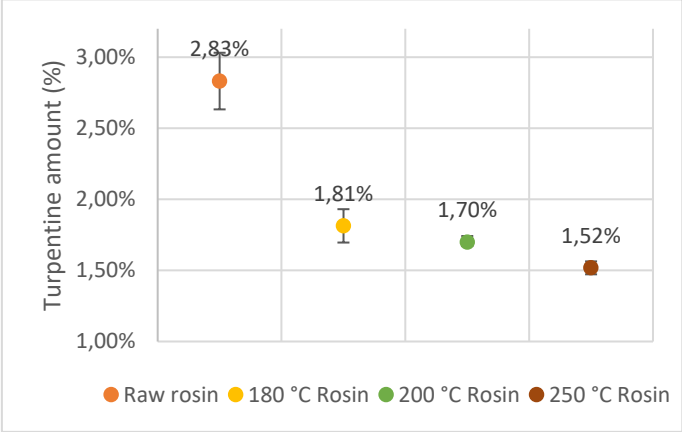


Figure 8: Comparison of the turpentine amount in rosin according to their heat treatment. The standard deviation is calculated over 3 samples.

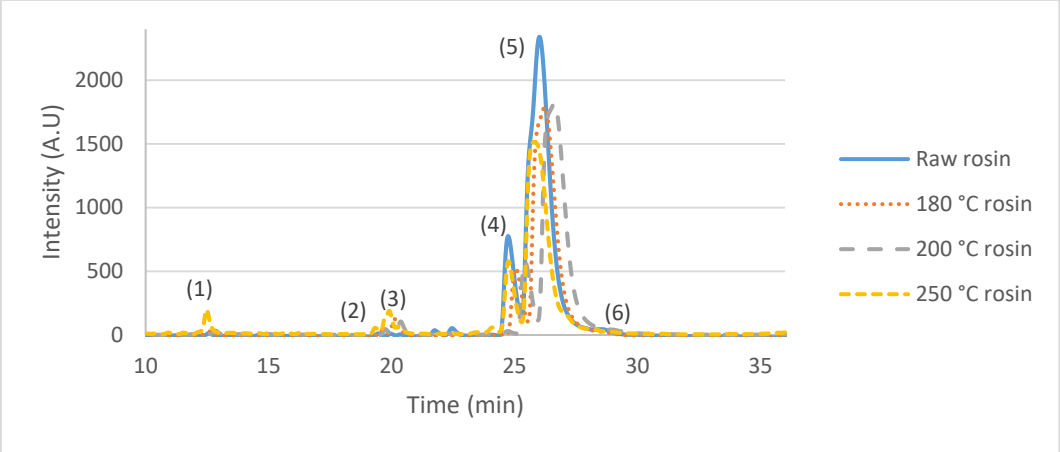


Figure 9: HPLC chromatograms at 254 nm wavelength absorption of rosins according to their heat treatment. (1) 7-oxo-dehydroabietic acid (7–oxo–DHA), (2) Abietane-based dehydroabietic acid (DHABA), (3) Dehydroabietic acid (DHA), (4) Palustric acid, (5) Abietic acid, (6) Neoabietic acid

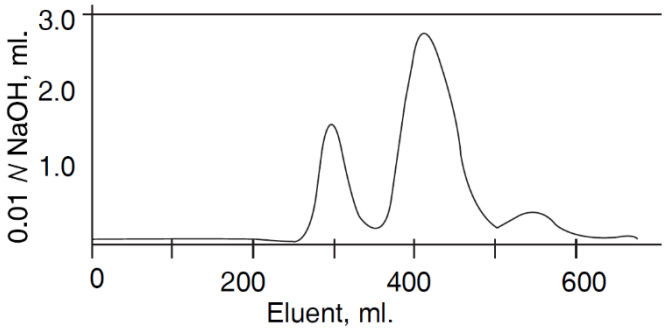


Figure 10: Chromatogram of levopimaric acid, heated at 155 °C during 3 hours, obtains by Loeblich, (1) palustric acid; (2) abietic acid; (3) neoabietic acid

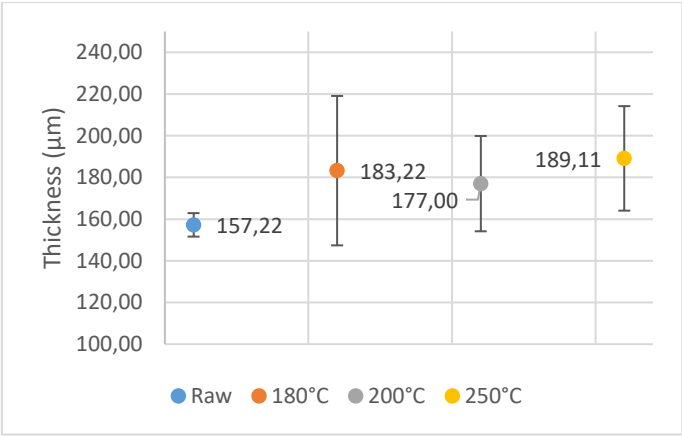


Figure 11: Thickness variation for varnishes according to the rosin heat treatment. Three measurements were made on each three panels. The standard deviation is calculated over 9 measurements.

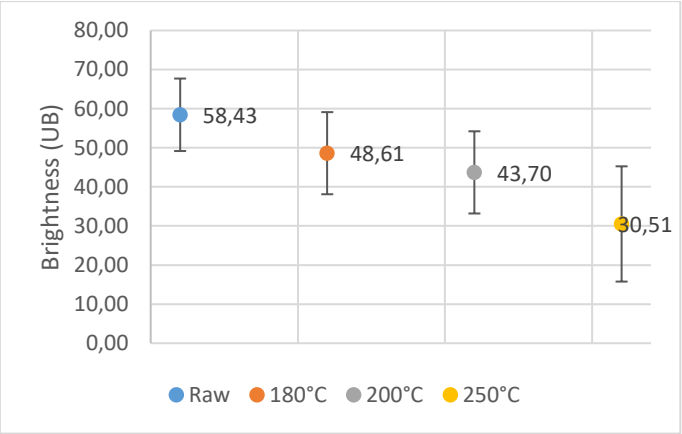


Figure 12: Brightness variation at 60 ° for varnishes according to the rosin heat treatment. Three measurements were made on each three panels. The standard deviation is calculated over 9 measurements.

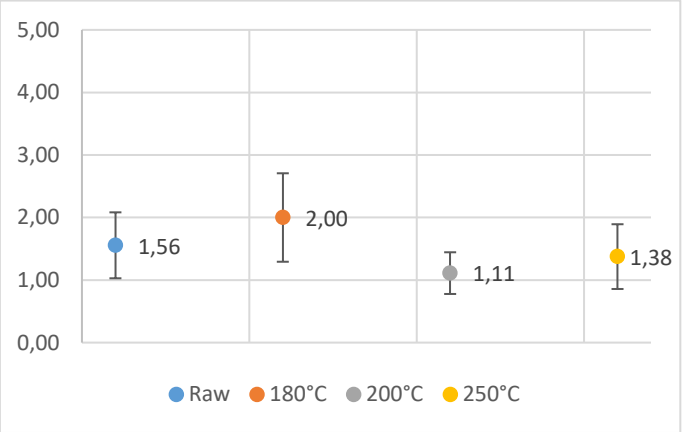


Figure 13: Comparison of varnish adhesion on wood for varnishes according to the rosin heat treatment. Three measurements were made on each three panels. The standard deviation is calculated over 9 measurements.

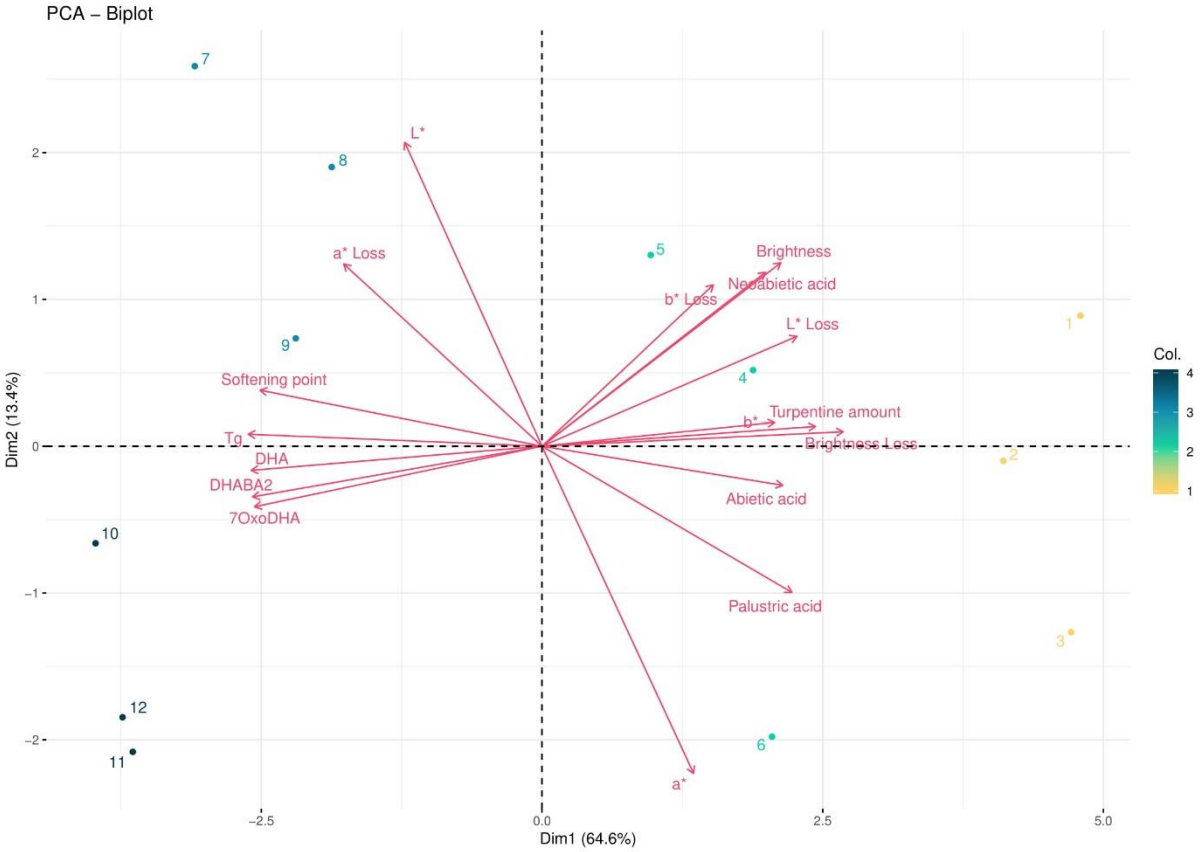
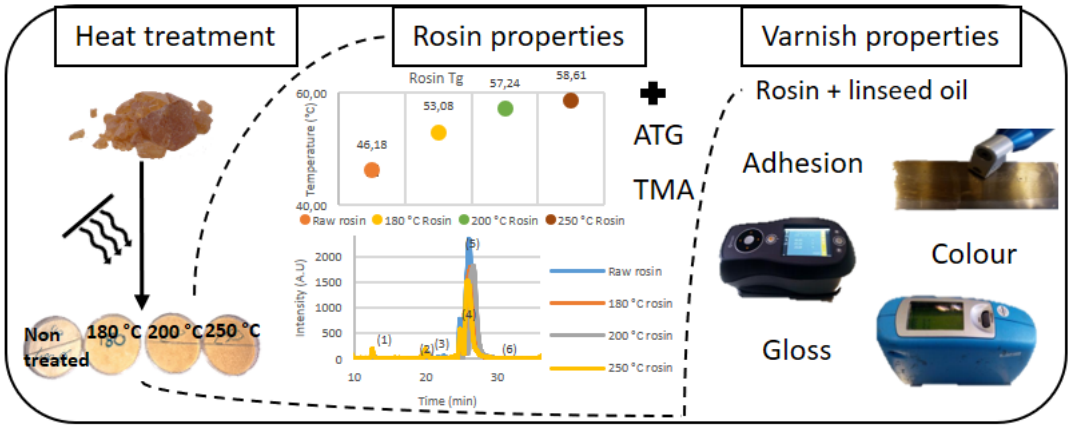


Figure 14: Biplot : Projection of variables and samples onto the first two PCs. (1, 2, 3) for reference rosin; (4, 5, 6), (7,8,9) and (10, 11, 12), respectively for 180 °C, 200 °C and 250 °C heat-treated rosin


Heat treatment
Rosin properties
Varnish properties
Non treated
180 °C
200 °C
250 °C
Rosin Tg
60,00
40,00
Temperature (°C)
46,18
53,08
57,24
58,61
Raw rosin
180 °C Rosin
200 °C Rosin
250 °C Rosin
ATG
TMA
Intensity (A.U)
2000
1500
1000
500
0
10
20
30
Time (min)
(1)
(2)
(3)
(4)
(5)
(6)
Raw rosin
180 °C rosin
200 °C rosin
250 °C rosin
Rosin + linseed oil
Adhesion
Colour
Gloss