

Synthesis of Resins with Ozonized Sunflower Oil and Radiata Pine Tannins

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ABSTRACT: Sunflower oil was subjected to a flow of compressed air containing ozone for different time periods. The addition of α -D-Glucose was used to increase the aldehyde content by reduction of the intermediate ozonides of the ozonation reaction. These new oils were analyzed by FTIR and GC-MS spectrometry, and their relative aldehyde groups content measured by the Henick method. They were then mixed with an aqueous solution of Radiata Pine tannin to form resins, subsequently analyzed by ^{13}C NMR and MALDITOF mass spectrometry. Wood particleboards were then made using some of these resins as the adhesive, and their internal bond (IB) strength measured.

KEYWORDS: Ozone, aldehydes, sunflower oil, tannins, resin

1 INTRODUCTION

Phenol-formaldehyde (PF) and resorcinol-formaldehyde (RF) adhesives are widely used for bonding wood products [1, 2]. However, they are composed of volatile, oil-derived and toxic compounds, which is why the search is on for environmentally friendly alternatives to these resins.

Alternative aldehydes from biosourced materials other than formaldehyde could be used. A way to obtain nonvolatile aldehydes is by ozonolysis of unsaturated carbon chains that are present in vegetable oils [3]. One aldehyde group and a peroxide group are formed by the ozone-induced C=C bond opening. By a subsequent reduction step these peroxide groups are also reduced to aldehyde groups [4, 5]. Ozonolysis has been studied on several vegetal oils such as soybean and sunflower, which contain around 60% of linoleic acid (2 unsaturations) and 30% of oleic acid (1 unsaturation) esterified in triglycerides. These unsaturations (i.e. C=C carbon bonds in aliphatic chains) can react with ozone to form intermediates, "ozonides", according to the Criegee mechanism [6], which can form aldehydes by reduction (Figure 1).

After ozonation, ozonides can produce carboxylic acid groups [7], thus a reduction step is necessary

without delay to obtain stable aldehyde groups. Several reducing agents may be used such as methyl sulfite [8], zinc/acetic acid [9], palladium/ CaCO_3 [10], thiourea [11], and glucose [12]. For the present investigation glucose was chosen for its ease of use, thus avoiding the volatility and bad odour of methyl sulfide, the acid conditions required by zinc, and the relatively high cost of palladium- CaCO_3 systems.

Thus, the ozonolysis of sunflower oil would ideally give different aldehydes, according to the following reaction [4] (Figure 2).

Among natural polyphenolics, condensed flavonoid tannins, extracted from tree barks and wood, have been extensively studied for several years [11–16]. They are interesting because they are relatively inexpensive, they are very reactive with aldehydes, they have a low carbon footprint, and it is possible to make adhesive by reacting them with relatively low proportions of aldehydes.

Recently, work on cashew nut shell liquid (CNSL) has taken such an ozonation approach to produce aldehydes to be reacted first with the natural resorcinol moiety of CNSL [13], and as this did not appear to yield adhesives good enough to satisfy wood panel requirements, with either added resorcinol chemical or, this latter being too expensive, with a commercial flavonoid tannin such as mimosa or quebracho [1, 14, 15]. The results obtained were marginal as regards standard requirements when added resorcinol was used, and insufficient to satisfy standard requirements when commercial flavonoid tannins were used [13]. This is due to the reactivity of these aldehydes being relatively low as well as the reactive

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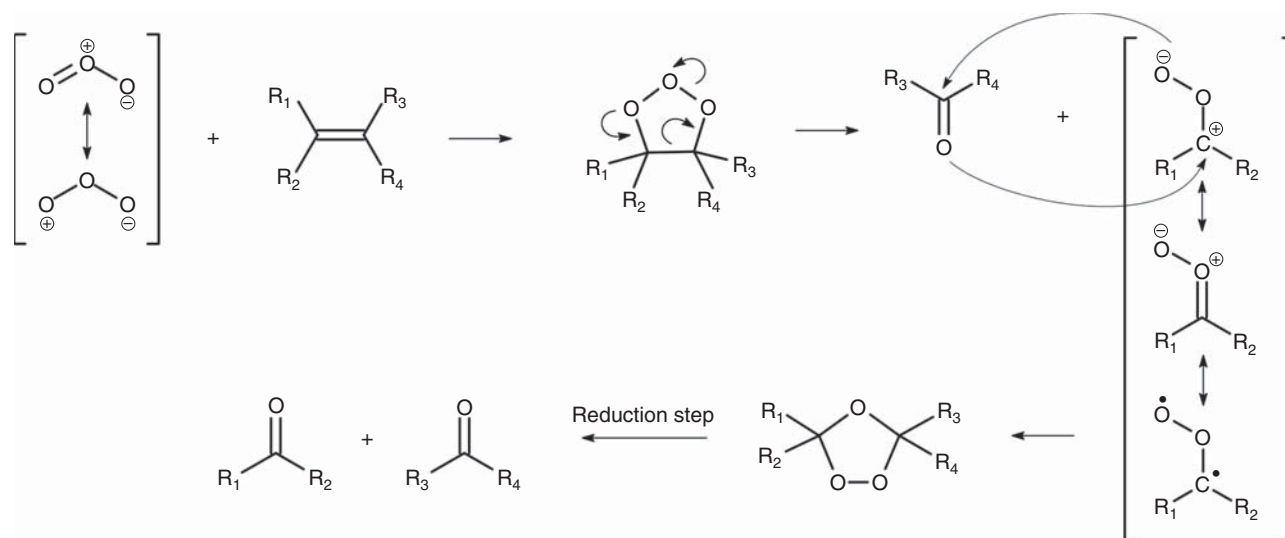


Figure 1 Ozonolysis of an unsaturated carbon chain according to Criegee mechanism.

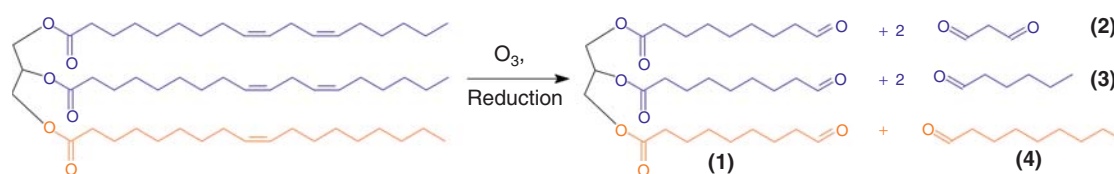


Figure 2 Ozonolysis and reduction of a soybean oil: ideal production of aldehyde oil (1), malonaldehyde (2), caproaldehyde (3) and pelargonaldehyde (4).

sites of the phenols used not being sufficiently reactive to overcome such a shortcoming. Thus, a more reactive phenol may overcome such a problem.

Flavonoid tannins from radiata pine (*Pinus radiata*) bark are mainly procyanidins based on a phloroglucinol A-ring and a catechol or pyrogallol B-ring (Figure 3) with the units linked C4 to C8 with average degree of the polymerization of 5–6 [1]; a limited amount of them are commercially available. The A rings C6 and C8 sites are highly reactive [1–15]. Radiata pine tannins are considerably more reactive than other flavonoid tannins [1], and more reactive than resorcinol chemical [1], thus they should be particularly suitable for such an approach.

The purpose of this work was then to replace formaldehyde by aldehydes obtained by ozonolysis of a more commonly available oil than CNSL, namely sunflower oil, and as phenols the highly reactive tannins from radiata pine. This meant to mix aldehydes less reactive than formaldehyde with a phenolic compound more reactive than resorcinol. It also raised the problem of mixing a hydrophobic oil phase with an aqueous one. In the first part, sunflower oil was analyzed at different steps of ozonolysis by FTIR, GC-MS, and after the α -D-glucose reduction step by UV spectrometry, to analyze the aldehydes content. Following this, the oil-based aldehyde

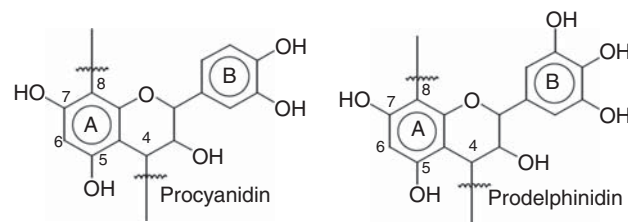


Figure 3 Repeated units of prodelphinidin and procyanidin flavonoid in radiata pine tannins.

mixtures with tannins to give homogenous resins, were analyzed by matrix-assisted laser desorption ionisation time of flight (MALDI-TOF) mass spectrometry and by ^{13}C NMR spectrometry. Finally, wood particleboards were bonded with some of the resins obtained and tested for dry internal bond (IB) strength.

2 EXPERIMENTAL

2.1 Equipment

Commercial sunflower oil was used with a composition of 100% sunflower oil, a total fat content of 92% composed of 10% saturated, 24% monounsaturated

(including oleic acid) and 58% polyunsaturated (including linoleic and linolenic acids) fats. D(+)-Glucose anhydrous ACS reagent and 2,4-dinitrophenylhydrazine were purchased from Thermo Fisher Scientific Inc., Waltham, Massachusetts; ethanol absolute from Sigma-Aldrich Co., St. Louis, Missouri; toluene from VWR International LLC, Radnor, Pennsylvania; potassium hydroxide from Roth Sochiel Eurl, Lauterbourg, France; paraformaldehyde from Merck KGaA, Darmstadt, Germany, and; *Pinus radiata* bark tannin extract from Diteco Ltda, Coronel, Chile. They were dissolved in 45% w/w in water.

Wood particles for making panels were provided by Egger, Rambervilliers, France. The species of wood used are a mix of softwoods, essentially spruce and fir, and hardwoods, essentially beech and oak. Their humidity was controlled at between 2% and 3%.

2.2 Ozonolysis and Reduction

Ozone was produced from the oxygen of a compressed air flow introduced into a 2GLAB model ozonator from A2Z Ozone Systems Inc., Louisville, Kentucky, by corona discharge. The ozone concentration is adjusted to 100% and the flow to 0.2 NL/min on average. At the outlet of the ozone generator, the flow of gas is introduced into a wash bottle containing 200 g of sunflower oil, via a class 1 sintered dip tube. The oil is subjected to continuous mechanical stirring while the ozone-laden air is released through the sintered shaft and bubbled through it. The vial is put in a temperature controlled bath to keep the temperature at 0°C. After passing through the oil, the gas flows through two washing bottles connected in series, each containing a 20 g/L potassium iodide solution: this system eliminates unreacted residual ozone by the reduction of iodide ions to iodine. These solutions are coloured. Thus, it is possible to evaluate the iodine concentration by colorimetric titration or UV spectroscopy, and the ozone content of the gas flow leaving the oil bottle.

Ozonolysis time was adjusted to 30, 60, 90 and 120 minutes for the first analysis. For further applications in particleboards, ozonolysis of oil has been set to 120, 240 and 480 minutes. The ozonized oil was then recovered: it contained peroxide and aldehyde groups. To increase the aldehyde groups content by reducing the peroxide groups, 10% w/w of glucose was mixed under stirring with the oil for 30 minutes.

2.3 Resin Synthesis and Particleboard Making

Ozonized oils were filtered to separate them from glucose. The recovered oils were added to an aqueous

solution of radiata pine tannins (45%w/w); the whole mixtures comprised 10% of ozonized oil and 90% of aqueous tannins.

Duplicate one-layer laboratory particleboard of 350×300×14 mm³ dimension were prepared using a mixture of 10% total solid resin and wood particles at 28 kg/cm² maximum pressure and 190–195°C press temperature [16]. The moisture content of the wood particles prior to resin addition was measured at the same time as the solid content of the resin. The resin solids content on dry wood was 10%. The total pressing time was 7.5 minutes.

Samples of 50mm × 50mm × 14mm cut from the boards were tested for dry internal bond (IB) strength.

2.4 Analysis

2.4.1 Infrared (FTIR) Analysis

Liquid oils at different stages of ozonation were analyzed by Fourier Transform InfraRed (FTIR) spectroscopy with a Shimadzu IRAffinity-1. A blank sample tablet made of potassium bromide from Acros Organics was prepared for the reference spectrum. Then a drop of the test sample was put on this tablet for the sample spectrum.

2.4.2 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

Samples must be derivatized before being injected in the GC-MS apparatus. They were washed with water with sodium sulphate using a filter. Then, they were put into vials according to dosage: 200 µL of pyridine, 100 µL of reagent NO-bis (trimethylsilyl) trifluoroacetamide +1% trimethylsilyl chloride and 5 to 10 µL of test oil sample. The vials were then closed and placed overnight into an oven at 75°C.

One µL of a sample was then injected into a PerkinElmer Clarus 500 model gas chromatograph, the oven of which was initially set at 90°C and temperature of which was steadily raised to 350°C at 7.5°C/min. The carrier gas was helium with a flow of 1mL/min and the column used was an Elite 5-MS of 60 m length, 250 µm of diameter and 0.25 µm of phase width. The chromatograph is connected to a mass spectrometer PerkinElmer Clarus 500 model, which analyzes the different chemicals from the column by a mass scanning from 8 to 60 minutes with an m/z ratio from 20 to 600.

2.4.3 UV Absorbance for Aldehydes Analysis

Studies focused on agro-food fats review the analysis methods to quantify aldehydes relative content in oils [17, 18]. The most accurate and widely used one for the determination of secondary oxidation products

of lipids, carbonyl compounds, is Henick's [19]. This method is based on the reaction of carbonyls with 2,4-dinitrophenylhydrazine under acid conditions and can differentiate saturated from unsaturated aldehydes. This procedure has been criticized because of the formation of new carbonyl compounds due to the decomposition of hydroperoxides under the proposed experimental conditions. In the case of this study, the purpose is to evaluate the maximal capacity for an oil to produce aldehydes, by reduction of peroxides, so this aspect does not constitute a problem. The method is directly inspired by the work of Henick *et al.* [19], with the difference being that benzene, which acts as a solvent for oils and other reagents, is replaced by toluene. These analyses were made with a Shimadzu UV-700 PharmaSpec FTIR spectrometer.

2.4.4 ^{13}C NMR Analysis

Analyses of ^{13}C NMR spectrum were done with a Bruker Avance 300 instrument, with 4 mm rotors turning at 10 kHz, and a contact time of 2 ms.

As comparative elements for interpretation, ^{13}C NMR spectra of radiata pine tannins (Figure 4) and sunflower oil (Figure 5) are shown. On the tannins spectrum, the corresponding carbons from the flavonoid unit have been identified [1].

For the ^{13}C NMR spectrum of sunflower oil before and after ozonization [20], the different groups of bands correspond to the different chemical functions: aliphatic carbon chains between 14 and 35 ppm, glycerol carbons between 60 and 73 ppm, unsaturated carbons in aliphatic chains at 124 and 134 ppm, and carbonates ($-\text{COO}-$) linked by esterification to glycerol between 172 and 173 ppm [20, 21].

After ozonolysis, the spectrum contains the same signal observed in virgin sunflower oil. However new groups of signal were found: aldehydes carbons resonating from 199 to 203 ppm, unsaturated carbons in aliphatic chains with an ozonide ring and/or to an unsaturation and/or to a saturated carbon chain (Table 1).

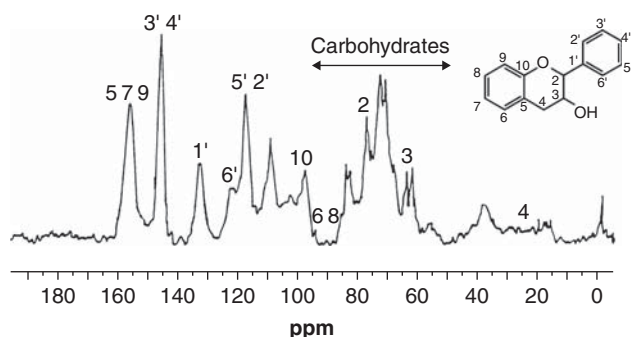


Figure 4 Spectrum of ^{13}C NMR of radiata pine bark tannins.

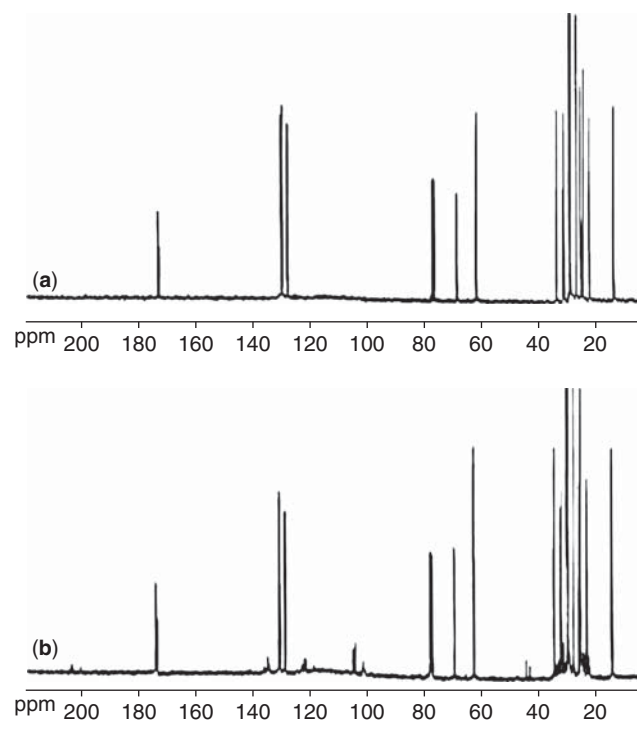


Figure 5 Spectra of ^{13}C NMR of sunflower oil: (a) without; (b) after ozone exposure [20].

2.4.5 MALDI-TOF Mass Spectrometry

MALDI-Tof spectroscopy analysis was performed with Bruker's ultrafleXtreme, with a linear positive mode method from 700 to 2000 Da. The average number of transients was 5000, and the laser intensity was 40%.

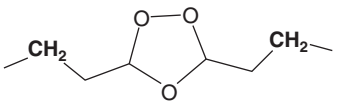
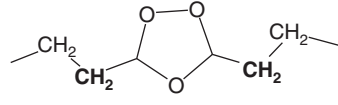
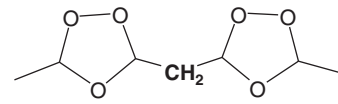
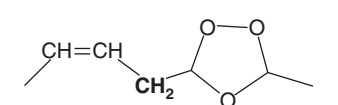
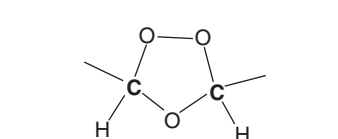
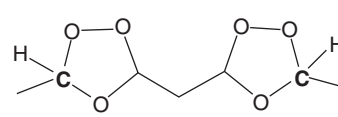
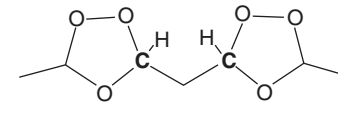
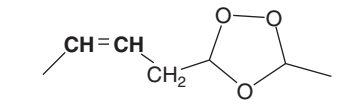
3 RESULTS AND DISCUSSION

3.1 Ozonized Products Analysis

3.1.1 Fourier Transform Infrared Spectrometry (FTIR)

Figure 6 shows the infrared spectra of sunflower oil at different times of ozonation. The main notable difference is the relative increases of the band at 2920 cm^{-1} (broadly representative of aliphatic carbon chains) and those below 1600 cm^{-1} (broadly representative of glycerol and ester bonds with fatty acids). This means that straight carbon chains in the oligomers when treated become proportionally lower than carbonyl and ester groups. Ozonolysis does indeed tend to make scissions of aliphatic carbon chains at the sites of double bonds [5]. The aldehyde group band at 2850 cm^{-1} increases with ozonation time, thus ozonolysis appears to produce carbonyl groups and compounds. However, the presence of bands at 725 cm^{-1} , 1650 cm^{-1} and 3008 cm^{-1} that are representative of $\text{C}=\text{C}$ bonds means that

Table 1 Resonance data of ^{13}C NMR of chemical groups of sunflower oil during ozone treatment [21].

| Moiety | ^{13}C δ (ppm) |
|---|---|
|  | 23.3, 23.4 23.6, 23.7, 23.8 |
|  | 30.6 |
|  | 35.6 |
|  | 41.5 |
|  | 100.2, 100.4 |
|  | 103.4, 104.1, 104.3, 104.4 |
|  | |
|  | 120.8, 120.9, 121.3, 121.4, 133.9, 134.0, 134.2 |

ozonolysis is not complete under the experimental conditions used, not even after 2 hours treatment. This appears to be confirmed by the band at 1100 cm^{-1} corresponding to ozonides, which does not increase enough towards glycerol representative bands [5].

3.1.2 Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS spectra at 0 min, 30 min and 90 min ozonation are shown in Figure 7. The peaks between 36 and 38 minutes of retention time are sterols that are not supposed

to be concerned in ozonolysis. In addition, some low molecular weight molecules at 17.6 min, 21.4 min and 24.5 min of retention time, which are identified as ethoxy oligomers, could be other components of sunflower oil. The unsaturated acids that can react with ozone have retention times of 28 minutes for linoleic acid and 27.5 minutes for oleic acid. These peaks globally decrease with the duration to ozone exposure. The simultaneous progressive increases of signals after 40 minutes, and more precisely between 52 and 58 minutes, may suggest that higher molecular weight species are formed during ozonation. Some ozonolysis intermediates are oligomers of hydroperoxides, thus this wide band at such retention times in the 90 min ozonation spectrum may represent different forms of oligomers obtained from the different possible kinds of hydroperoxides derived from oleic and linoleic acid. Several peaks are still present between 42 and 46 minutes retention, and may be unsaturated 18-carbon chains linked to glycerol, but the MS detector could not identify with enough certainty the compounds they belonged to.

3.1.3 Aldehydes UV Analysis

According to the results from Henick *et al.*, mixtures of 2,4-dinitrophenyl hydrazone with unsaturated aldehydes (crotonaldehyde) give a maximal absorbance close to 460 nm with a molar absorption coefficient of $28,100\text{ cm}^2\text{ mol}^{-1}$, whereas mixtures of saturated aldehydes (hexanal) present maximal absorbance close to 430 nm with a molar absorption coefficient of $16,670\text{ cm}^2\text{ mol}^{-1}$ [19]. As a result, UV analyses of fat samples reveal that the mixture of unknown aldehydes is rather unsaturated or saturated, as the wavelength of the maximal absorbency is closer to 460 nm (globally unsaturated) or 430 nm (globally saturated).

Maximal absorbencies and corresponding wavelengths have been measured from UV spectra of samples of sunflower oil after 0, 120, 240 and 480 min of ozonation and reduction with 10% glucose (Figure 8). To the same wavelength λ , absorbency is proportional to the concentration of the studied substance, according to the Beer-Lambert equation: $A_\lambda = \varepsilon_\lambda \times C \times l$, where C is the concentration of the substance in the solution placed in the spectrometer, λ the corresponding wavelength, l the length of the tank, and $\varepsilon_{\lambda_{\text{max}}}$ the molar absorptivity of the aldehyde at λ .

For untreated sunflower oil, λ_{max} is close to 460 nm, clearly indicating that it contains a very small proportion of aldehydes due to the slow oxidation of unsaturated acids. These carbonyl compounds are still unsaturated, that is why λ_{max} is closer to 460 nm than 430 nm. For ozonized and reduced sunflower oils, λ_{max} are between 445 and 450 nm (Figure 8): there are less unsaturated aldehydes than untreated oil, but the mixture of aldehydes is

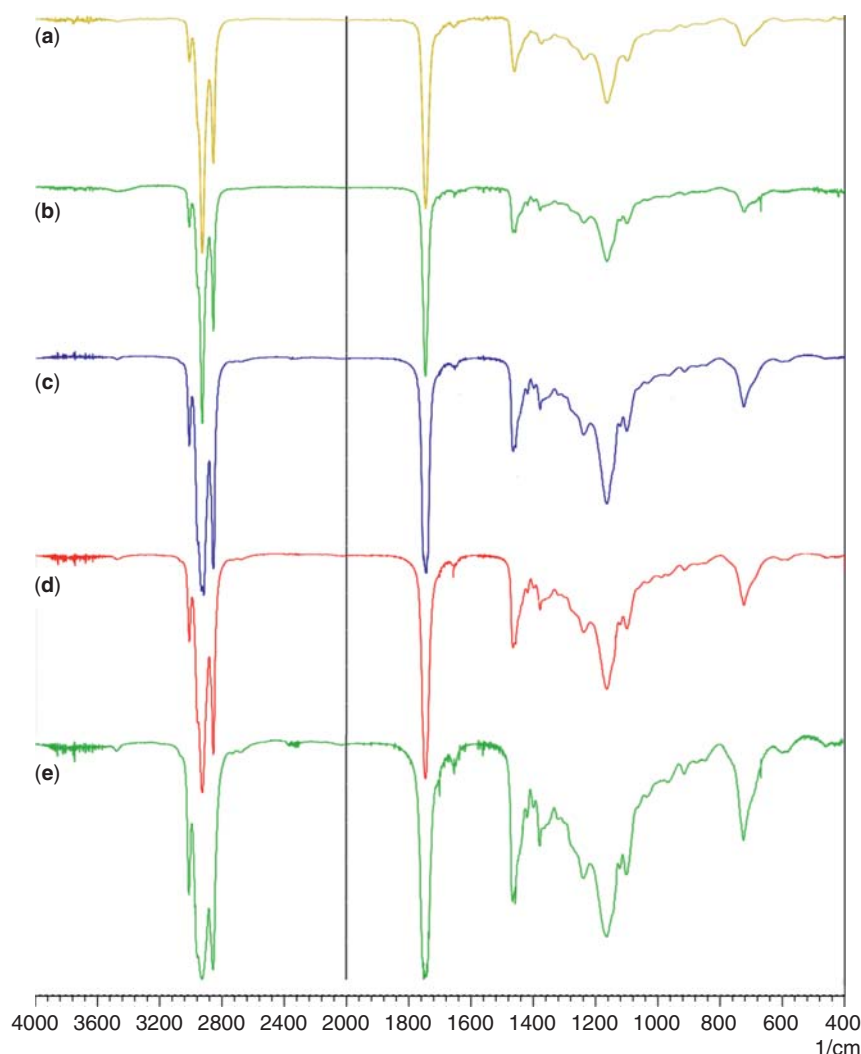


Figure 6 FTIR spectra of sunflower oil: (a) non-ozonated; (b) after 30 minutes of ozone exposure; (c) after 60 minutes of ozone exposure; (d) after 90 minutes of ozone exposure; (e) after 120 minutes of ozone exposure.

not entirely saturated either. Indeed, in one molecule, it seems possible that some carbon double bonds have not been affected by ozonolysis contrary to other ones that produced aldehydes terminations; for example, linoleic acid (Figure 9). This is further evidence that ozonolysis is incomplete even after several hours of ozone exposure under the experimental conditions used. However, it is equally clear that new aldehydes are produced after ozonation and reduction, because of the high values of A_{\max} towards samples masses, in comparison with that for untreated oil (Table 2). Moreover, A_{\max}/m increases with the ozonation time in quasi-linear evolution (Figure 10). Because λ_{\max} is not the same between 0 and 240 minutes of ozonation time (Figure 8), the mixture of aldehydes is evolving and then the global molar absorptivity ϵ_{λ} . So a quantitative estimation of the production of aldehydes cannot be done in this duration. However λ_{\max} is constant between 240 and 480 minutes. Let us suppose that

the global absorptivity ϵ_{λ} stabilized. In this hypothesis, ozonolysis reaction would have reached equilibrium in the composition of the produced mixture of aldehydes at 240 minutes and would start a phase of increasing production next. Thus, between 240 and 480 minutes of ozone exposure, the amount of this stabilized mixture has been doubled (Table 2).

3.2 Resins Analysis

3.2.1 Cross-Polarisation Magic Angle Spinning ^{13}C Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR) Analysis

CP-MAS ^{13}C NMR spectra of resins at different ozone exposure times for sunflower oil are presented in Figure 11.

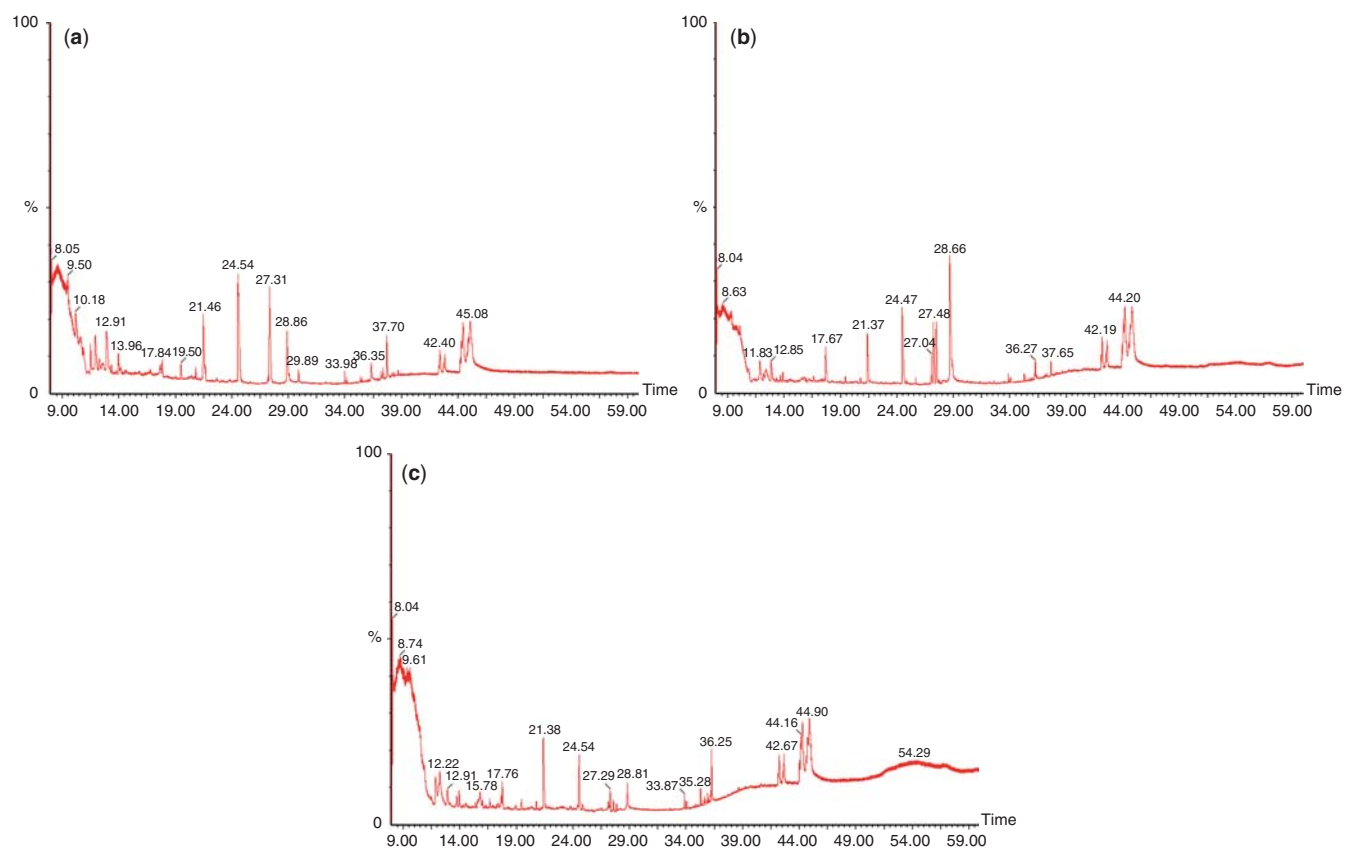


Figure 7 GC-MS spectra of sunflower oil: (a) non-ozonated; (b) after 30 minutes of ozone exposure; (c) after 90 minutes of ozone exposure.

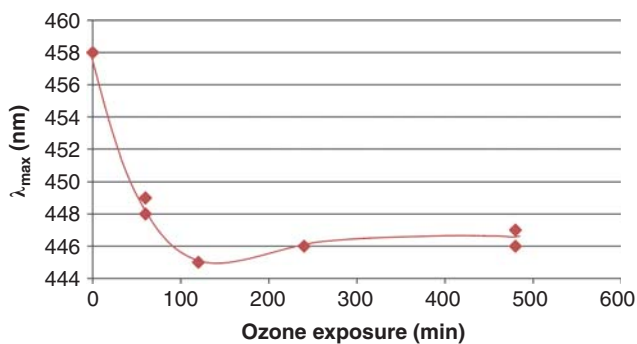


Figure 8 Variation of the wavelength λ_{max} corresponding to the maximal absorbency, with ozone exposure duration.

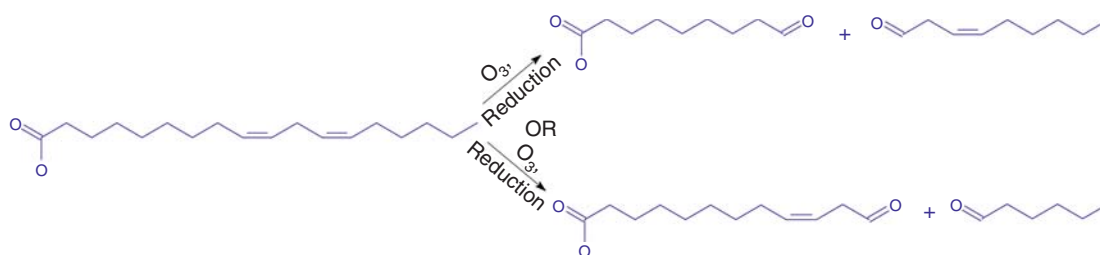
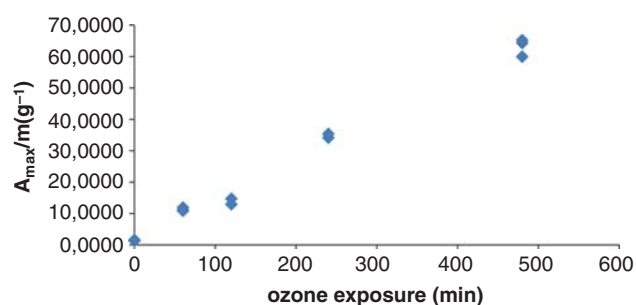
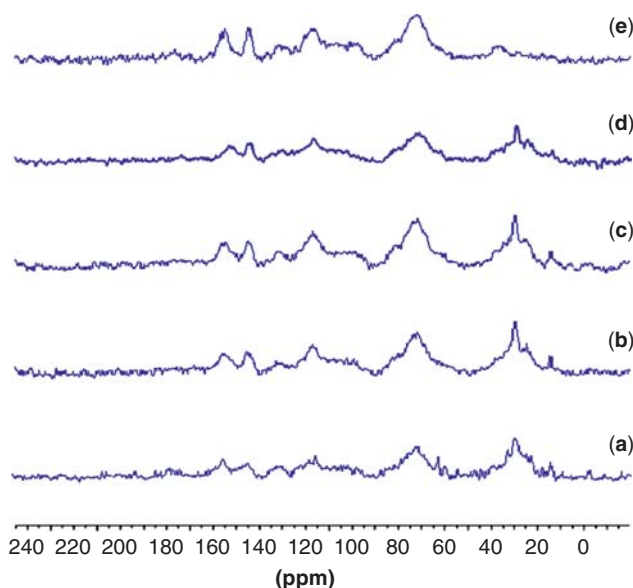


Figure 9 Unsaturated aldehydes produced from uncompleted ozonolysis of linoleic acid.

Table 2 Results of UV-absorbency analyses of test samples according to Henick's method.

| ID | Ozone exposure (min) | Sample mass (g) | λ_{\max} (nm) | A_{\max} | $A_{\max}/\text{sample mass (g}^{-1}\text{)}$ |
|----|----------------------|-----------------|-----------------------|------------|---|
| a. | 0 | 0,2108 | 458 | 0,3110 | 1,47 |
| b. | 60 | 0,0465 | 449 | 0,5252 | 11,30 |
| c. | 120 | 0,0469 | 444 | 0,6497 | 13,86 |
| d. | 240 | 0,0227 | 446 | 0,7874 | 34,77 |
| e. | 480 | 0,0070 | 447 | 0,5546 | 63,20 |

**Figure 10** Variation of maximal absorbency per sample mass A_{\max}/m with the ozone exposure duration of sunflower oil before the reduction step with 10% glucose. Data of the samples masses are listed in Table 2.**Figure 11** CP-MAS ^{13}C NMR spectra of resins made between tannins and sunflower oil ozonated and reduced with 10% glucose: (a) 0 minutes; (b) 30 minutes; (c) 60 minutes; (d) 60 minutes with 1% paraformaldehyde; (e) 90 minutes.

In all of them, some bands are recognizable as part of radiata pine tannins spectrum above 50 ppm: C5, C7 and C9 at 156 ppm, C3' and C4' at 145 ppm, C1 at 131 ppm, C6 at 120 ppm, C5' and C2' at 115–117 ppm, C6, C8 and C10 between 95 and 100 ppm, carbohydrates between 60 and 90 ppm [1]. Below 50 ppm a large band between 20 to 40 ppm that may belong to the oil part is covered by a high one at 29 ppm until 60 minutes of ozone exposure. This high band disappears above 90 minutes of ozonation for the oil; so it enables it to think it belongs to the free C4 tannin site [1] that would be free (i.e. unreacted) with oil aldehydes or other tannins units as long the duration of ozone exposure of oil does not exceed 60 minutes. After 90 minutes, this C4 seems to be polymerized with others chemicals, but not with C6 or C8 whose bands are still present, although slightly higher. The flavonoid C3 band at 67 ppm that is present when sunflower oil has not been exposed to ozone disappears when it has.

Differences between spectra of resins with and without paraformaldehyde show lower intensities for the bands of the flavonoid C6 and C8 sites between 95 and 98 ppm, and carbohydrates at 67–75 ppm, implying that formaldehyde slightly further enhances polymerization.

3.2.2 MALDI-TOF Mass Spectrometry Analysis

The same samples, except the one with non-ozonized oil, have been analyzed by MALDI-TOF MS spectrometry (Figure 12) for 30, 60 and 90 minutes of ozone exposure for oil (Figure 12a,b and d); the spectra show the same compounds with a predominant species at the high mass of 900 Da. Other representative compounds at 375 Da, 550 Da and 877 Da are still represented in these three spectra, with very little variation

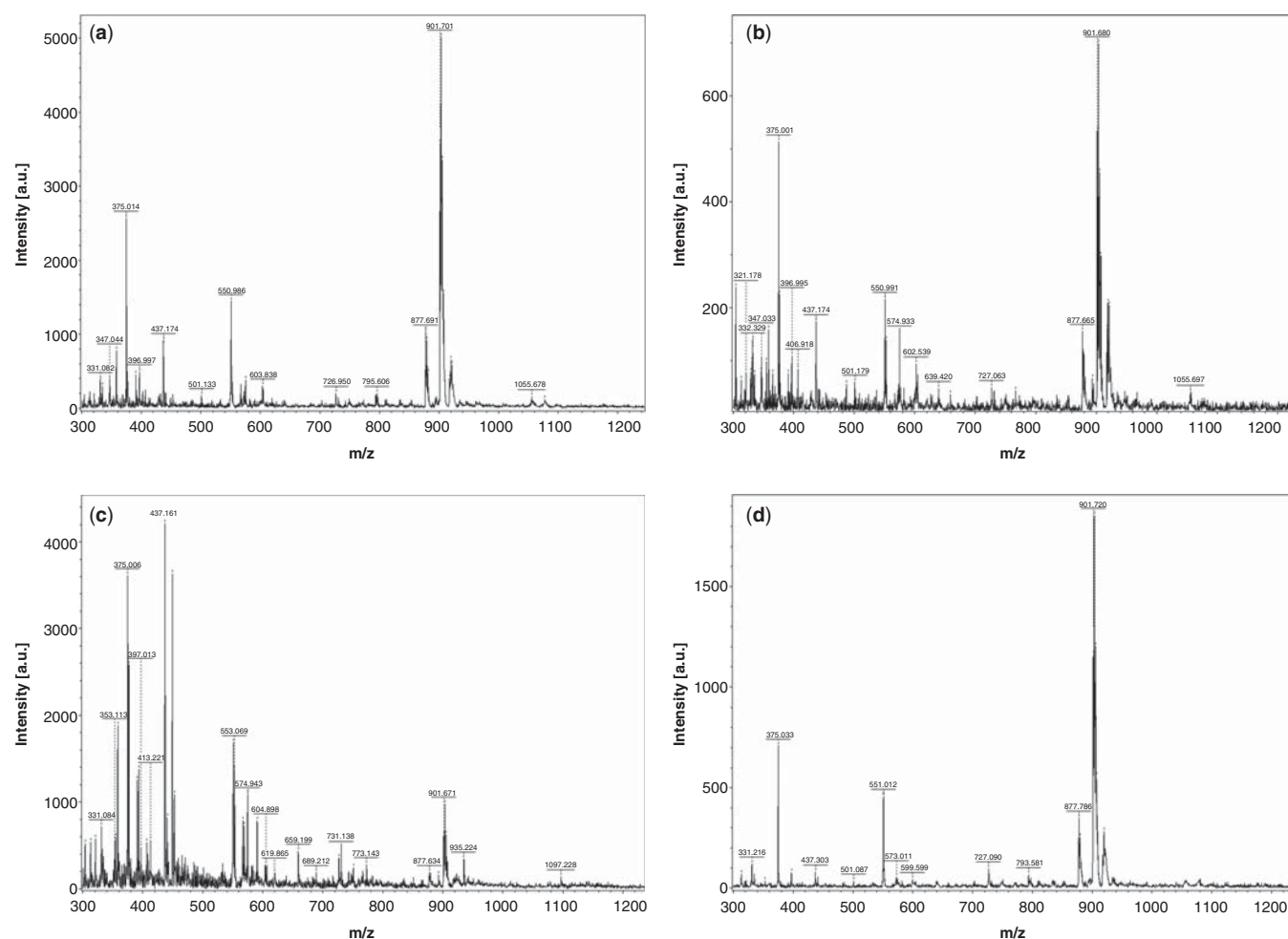


Figure 12 MALDI-TOF SM spectra of resins made between tannins and sunflower oil ozonized and reduced with 10% glucose: (a) 30 minutes; (b) 60 minutes; (c) 60 minutes + 1% paraformaldehyde; (d) 90 minutes.

between them. However, when paraformaldehyde is added to a resin (Figure 12c), the obvious consequence is the decrease of the 900 Da peak compared to several low-weighted peaks like 437 Da. This is due to reaction of the lower molecular weight oligomers with formaldehyde yielding higher oligomers but of lower degree of polymerization than the 900 Da species, the proportions of which then appears to decrease.

3.2.3 Wood Particleboard Panels

Samples of particleboards were tested for dry internal bond (IB) strength according to NF EN 319 B51-250. Experiments were then carried out with a resin with a proportion of 10% ozonized oil/90% aqueous tannins, compared with 100% tannins resin with an addition of 5% paraformaldehyde on tannins (Figure 13, Table 3). Above 10% oil, the mixture with the aqueous tannin solution tends to settle during heating. Sunflower oils were ozonized for 120 and 480 minutes and reduced with 10% w/w glucose.

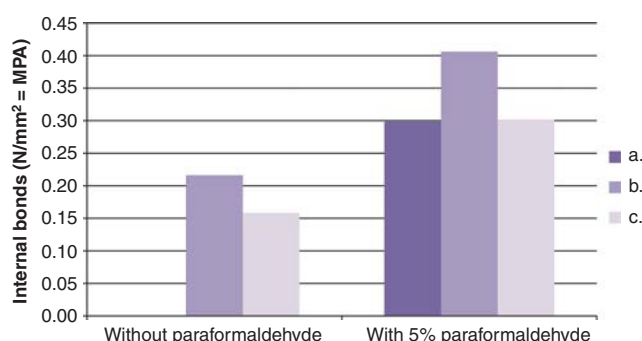


Figure 13 IB dry strength of particleboard made with resin tannins/sunflower oil ozonized: (a) 100% tannins resin; (b) 90% tannins and 10% oil ozonized for 480 minutes; (c) 90% tannins and 10% oil ozonized for 120 minutes.

In these experiments, the addition of paraformaldehyde as hardener significantly improves the mechanical properties of particleboards, as could be expected. Furthermore, the results show that the longer the

Table 3 Density and dry IB strength for the different formulations of resins for particleboards.

| Resin composition | Hardener paraformaldehyde | Particleboards Density (kg/m ³) | Particleboards IB strength (Mpa) |
|---|------------------------------|--|-------------------------------------|
| 100% tannins | + 0% | – | – |
| | + 5% | 708 | 0,30 |
| 90% tannins and 10% oil ozonized for 480 minutes | + 0% | 724 | 0,22 |
| | + 5% | 736 | 0,41 |
| 90% tannins and 10% oil ozonized for 120 minutes | + 0% | 750 | 0,16 |
| | + 5% | 750 | 0,30 |

duration is of ozone exposure of sunflower oil (and thus proportion of oil aldehydes), the higher is the dry IB strength of particleboards. However, most of the IB strength results are below 0.35 Mpa, which is the threshold value for the NF EN 319 B51-250 standard, even with 100% tannin resin which has been presented with better results [22]; this could be due to the wood particles species mix in which hard-to-bond hardwoods predominate.

Studies about resins made of pine tannins and ozonized oils were previously set in patents by Cambridge Biopolymers Ltd [12, 23], but using para-toluene sulfonic acid as catalyst, which cannot be used in wood particleboards preparation as it causes extensive cellulose hydrolysis and thus medium to long-term loss of performance and strength.

4 CONCLUSION

Ozonolysis and reduction of sunflower oil, which is rich in unsaturated triglycerides, produce aldehydes by scission of carbon double bonds of oleic and linoleic acids. Reduction in aldehydes can be done by different ways; α -D-glucose is one of the most simple and convenient ones. By using Henick's analysis method it is possible to verify qualitatively if aldehydes are saturated rather than unsaturated, and if they are broadly more numerous than in virgin oil. Ozonized and reduced sunflower oil can react with radiata pine tannins to form resins that can be used to make particleboards that can be free or with a relatively low charge in formaldehyde.

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