Isocyanate-Free Polyurethanes by Coreaction of Condensed Tannins with Aminated Tannins

M. Thébault[1,2], A. Pizzi[1,3]*, F.J. Santiago-Medina[1], F.M. Al-Marzouki[3] and S. Abdalla[3]

[1]*Laboratory of Studies and Research on Wood Material (LERMAB), University of Lorraine, 88000 Epinal, France*
[2]*Kompetenzzentrum Holz (WoodKPlus), 9300 Sankt Veit-an-der-Glan, Austria*
[3]*Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia*

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ABSTRACT: Isocyanate-free polyurethane resins biosourced to a very high percentage level were prepared by the reaction of aminated mimosa tannin extract with commercial mimosa tannin extract prereacted with dimethyl carbonate. The reaction took place with ease at ambient temperature. Indications were that the polyurethanes obtained formed a hard film when cured at a temperature higher than 100 °C. Furthermore, the carbohydrate fraction of the tannin extract also appeared to be carbonated and reacted to generate isocyanate-free polyurethane linkages with the aminated tannins. This indicated that not only the polyphenolic fraction of the tannin extract, but also its other major component, can be used to prepare polyurethane resins. Flavonoid monomers and oligomers carbonated at different levels, both unreacted and urethane-linked to aminated flavonoid monomers and oligomers, were identified by FTIR and MALDI-TOF spectrometry.

KEYWORDS: Flavonoid tannins, non-isocyanate polyurethanes, MALDI-TOF, FTIR, aminated tannins, carbohydrate polyurethanes

1 INTRODUCTION

The strong research trend on resins, adhesives and plastics derived for renewable, biosourced materials has being gaining momentum as interest in such materials continues to grow. In the case of polyurethanes (PUR), considerable literature now exists on the use of biosourced polyols, this approach leading to PURs partially biosourced up to around 50% [1–6]. This approach works well but its shortcoming is the severe limit in biosourced materials which can be used. In reality, it is not the number of eligible biosourced polyols that are lacking, but an adequate alternative to the use of the other major and essential reagents, namely reactive isocyanates. Isocyanates are the materials which have rendered possible the dominance of polyurethanes in many fields today. However, they are now classified as toxic, thus under pressure by new and upcoming government regulations. Moreover, isocyanates are mainly synthesized in industry through the phosgene ($COCl_2$) route, a hazardous route that needs specific precautions [7]. Some research was carried out several decades ago to synthesize new kinds of isocyanates by using fatty acids in vegetable oils [8–9] and furan derivatives [10–12]. These chemicals, however, are still isocyanates, thus potentially toxic materials, and in part are not issued from biosourced materials.

An alternative approach to the preparation of polyurethanes without any use of isocyanates does exist [13–15]. In a first step, a synthetic polyol, generally propylene glycol, is reacted with either a cyclic carbonate [16] or dimethyl carbonate [17]. This is followed by a second step where the carbonated polyol is reacted with a diamine, generally hexamethylene diamine, to form the isocyanate-free polyurethane. This approach has again relied on the use of synthetic, non-biosourced materials [18] or the use of vegetable oils as polyol reagents [14, 19]. Recently, this same approach was used to prepare isocyanate-free urethanes based on hydrolyzable and condensed tannins [20, 21], these materials being biosourced forestry waste. These polyurethanes, however, although being biosourced up to 45–50%, contained as reagents not only the biosourced tannin extracts, but also a synthetic diamine, the latter being the second major reagent involved. Thus, to have an isocyanate-free urethane of much higher biosourced origin, it would be necessary to substitute a biosourced

**Corresponding author*: antonio.pizzi@univ-lorraine.fr

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material for one of the other two main reagents, namely the diamine [3, 4, 13, 18, 20, 21].

2 MATERIALS AND METHODS

2.1 Materials

Mimosa (*Acacia mearnsii* formerly *mollissima*, de Wildt) bark tannin extract was provided by Silvachimica (San Michele Mondovi, Italy). It contained 80–82% actual flavonoid monomers and oligomers, 1% of amino and imino acids, the balance being composed mainly of oligomeric carbohydrates, mainly hemicellulose fragments, and some carbohydrate monomers.

The majority of the flavonoid part of mimosa tannin extract is composed of robinetinidin and fisetinidin but also includes 10–15% of catechin and delphinidin (Figure 1), each of these monomers forming the repeating units of the tannin, the units being respectively linked by C4-C6 or C4-C8 [22]. The tannins enchainments formed by these units are respectively called prorobinetinidin, profisetinidin, procyanidin and prodelphinidin. The average number of units varies from monomers to octamers with an average DPn between 4 and 5 [23] which are otherwise too difficult to determine by other techniques. It has been possible to determine by MALDI-TOF for the two major industrial polyflavonoid tannins which exist, namely mimosa and quebracho tannins, and some of their modified derivatives that: (i. Dimethyl carbonate (99%) was purchased at Acros Organics (Geel, Belgium) and the ammonium hydroxide solution (28%) from Sigma-Aldrich (St. Louis, Missouri).

2.2 Procedure

Five grams of tannins were reacted with 5,6 g of a 28% ammonia hydroxide water solution for approximately ten minutes at ambient temperature (22–23 °C). The solution became viscous rather rapidly due to the alkaline condition brought by the ammonia solution. This type of solution, after stirring for 1 h at ambient temperature, tends to increase in viscosity if left at ambient temperature for up to 1 day, due to further tannin condensation under basic conditions and formation of =N- bridges between flavonoids [24].

The reactions were carried out at ambient temperature. First, 5 g Mimosa tannin extract were added to 10.5 g dimethyl carbonate and mixed under mechanical stirring for two h [21]. At this stage, tannins are only solvated into the carbonate solvent; the pH then being around 5. This was added to the aminated tannins and stirred vigorously for a few minutes. Carboxymethylation of phenolic hydroxyl groups by dimethyl carbonate group, which is generally observed at temperatures around 90 °C for phenol, has been reported to be a bimolecular nucleophilic substitution, acyl-cleaving in basic catalysis ($B_{AC}2$) [17]. Due to the basic conditions of the aminated tannins mixture, a condensation reaction is expected to occur according to the following mechanism (Figure 2):

The reaction mixture so obtained was left to gel at ambient temperature (between 20 and 25 °C) for at least 24 h. Under these conditions, only oligomers of urethanes could be expected. Their solubility in a solvent such as acetone/water rendered possible their characterization by MALDI-TOF. To verify these can cure into a thermoset resin if heated at high temperature, a part of this material was placed in an oven at

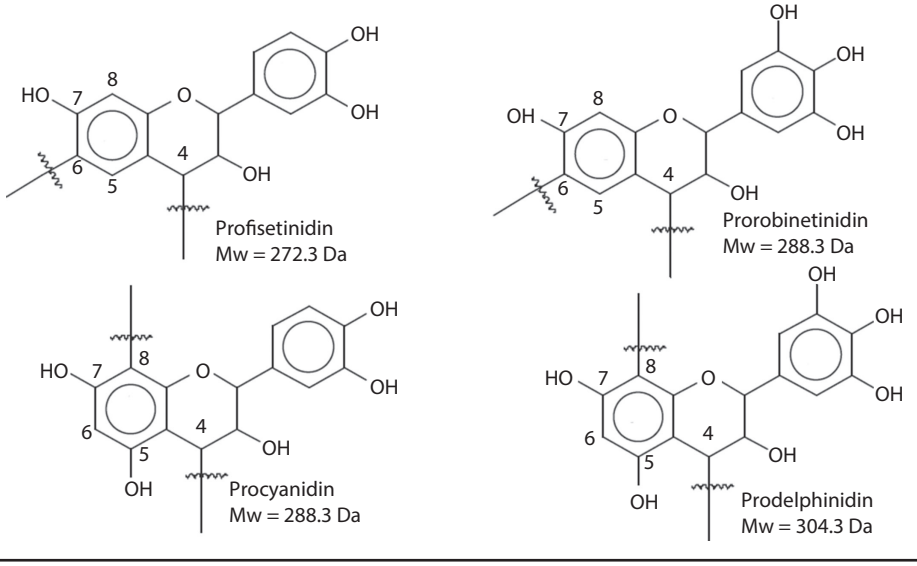

Figure 1 The four main structures in commercial flavonoid tannins.

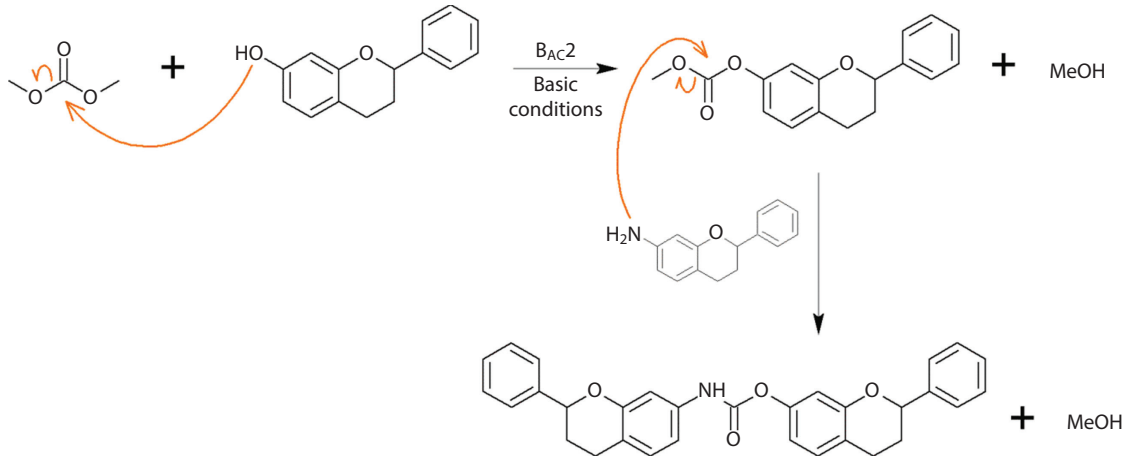

Figure 2 Bimolecular nucleophilic substitution, acyl-cleaving in basic catalysis ($B_{AC}2$) mechanism between dimethyl carbonate and a flavonoid tannin molecule.

103 °C for 24 h. A hard solid, insoluble in acetone/water, was then obtained.

2.3 Analysis

2.3.1 *Fourier Transform Infrared (FTIR) Analysis*

To confirm the presence of urethane structures, Fourier transform infrared (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer (Shimadzu France, Marne-la Vallée, France). A blank sample tablet of potassium bromide, ACS reagent from Acros Organics (Geel, Belgium), was prepared for the reference spectrum. A similar tablet was prepared by mixing potassium bromide with 5% w/w of the sample powder to analyze. The spectrum was obtained in absorbance measurement by combining 32 scans with a resolution of 2.0.

2.3.2 *MALDI-TOF Analysis*

Matrix-assisted laser desorption/ionization with time-of-flight (MALDI-TOF) characterization is a high resolution mass spectrometry technique which can analyze oligomers and pre-polymers distribution. The samples to analyze are mixed with a matrix consisting of crystallized molecules such as 2,5-dihydroxy benzoic acid (DHB). For this reason, they must be dissolved in a solvent in order to be efficiently associated with the matrix.

Samples for MALDI-TOF analysis were prepared by first dissolving 5 mg of sample powder in 1 mL of a 50:50 v/v acetone/water solution. Then 10 mg of this solution is added to 10 µL of the 2,5-dihydroxy benzoic acid (DHB) matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 µL of a NaCl solution 0.1M in 2:1 v/v methanol/water, and predried. Then 1 µL of the sample solution was placed on its dedicated location and the plaque was dried again. MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical, Shimadzu Europe Ltd., Manchester, UK) using a linear polarity-positive tuning mode after calibrating the instrument with red phosphorous standard. The measurements were carried out making 1000 profiles per sample with 2 shots accumulated per profile. The spectrum precision is of +1Da.

3 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectrometry (FTIR) Analysis

Figure 3 shows the FTIR spectra of the original mimosa tannins extracts (a), these tannin extracts reacted with an ammonia solution (b), and the product obtained by reaction of the carbonated mimosa tannin extract with the aminated tannin extract (c).

Actually, several peaks in the reaction material spectrum (c) could be relevant for the presence of urethane linkages, namely at 3400 cm^{-1}, 1700 cm^{-1}, 1507 cm^{-1}, 1296 cm^{-1} (the urethane peak being generally in the range of 1200–1300 cm^{-1}), and 1072 cm^{-1}. However, these peaks can also be relevant for other linkage types present in (a) and (b), such as C-O and C-N respectively. The characteristic bands of aromatic nuclei at 1600 cm^{-1}, 1500 cm^{-1} and 1460 cm^{-1} are present in the three materials spectra, although two of them seem to be covered by a large band at 1630 cm^{-1}, relevant for $–NH_2$ and/or C=N deformation. Aromatic moieties remain dominant in reaction

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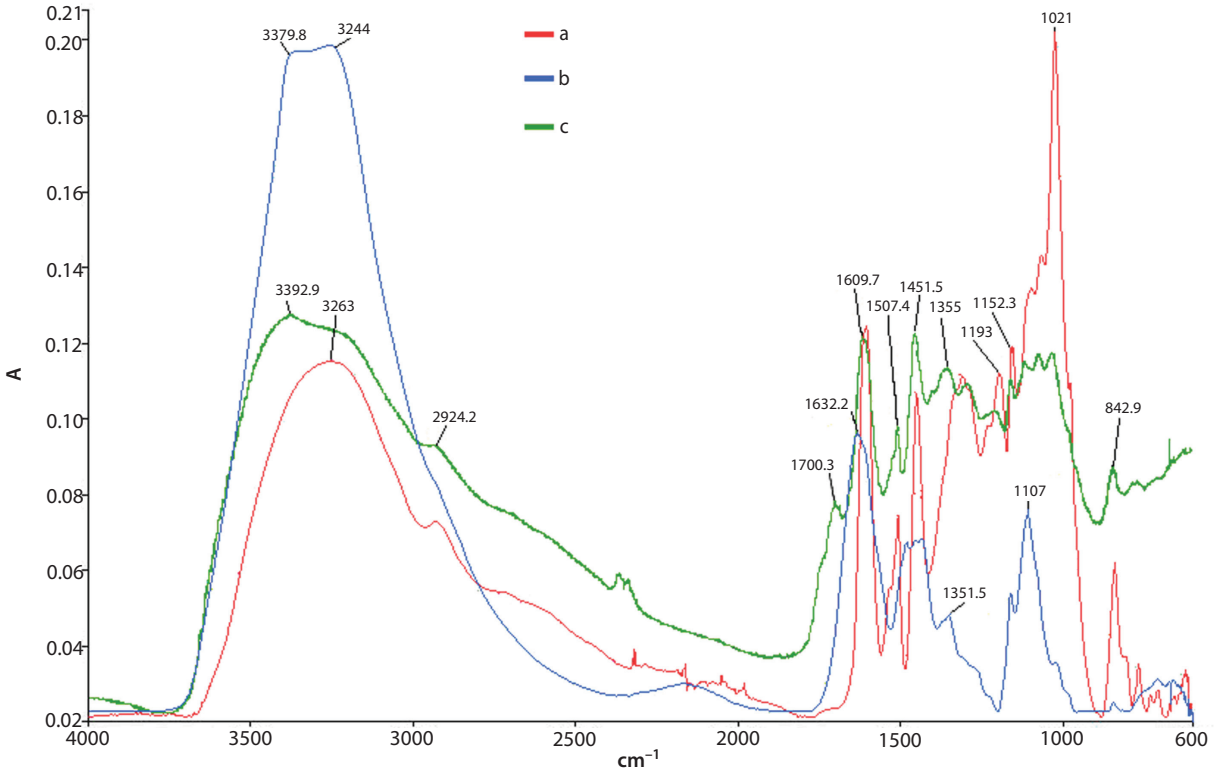


Figure 3 FTIR spectra of (**a**) Mimosa tannins extract; (**b**) Mimosa tannins extract reacted with an ammonia solution; (**c**) the product mixture obtained by reaction of mimosa tannin extract in dimethyl carbonate with the aminated tannin extract.

material (c), meaning that urethane bonds would not be significant enough compared to flavonoids polyphenolic structures. There are, however, some clues that let us suppose that some urethane bonds could have been actually formed in the reaction material (c).

In the original tannin extracts spectrum (a), a major peak at 1020 cm^{-1} can be attributed to the C-O-C ether of the heterocyclic ring of the flavonoid. This is small in (c), indicating opening of the heterocyclic ring, a fairly common occurrence in flavonoids. Alternatively, it could be assigned to either a carbohydrate primary hydroxyl stretching or, alternatively, to the C-O stretching of the only alcohol –OH on the C3 site of the flavonoid. In either of these last two cases its decrease in (c) would indicate that either the –OH in C3 of the flavonoids has reacted and/or that –OH groups on the carbohydrates have also reacted.

In the aminated tannins material (b), two bands between 3240 and 3400 cm^{-1} attest to the presence of primary amines, and the width of the band between 3500 and 3000 cm^{-1} shows that not all the hydroxyl groups have been aminated. The major peak at 1632 cm^{-1} is relevant for $–NH_2$ and/or C=N deformation. The presence of –C=N- groups has been demonstrated by ^{13}C NMR in aminated tannins obtained in the manner described here [24]. However, in the reaction material (c), this peak is less represented as it is probably covered by the more dominant band at 1610 cm^{-1} of aromatic nuclei. However, a major band at 3340 cm^{-1} remains in the spectrum, relevant for secondary amines, partly masked by the wide –OH peak. This is due to the tannin residual hydroxyl groups, the methanol produced during carbonatation, or possible residual water.

In the aminated tannins (b), the most relevant peak for the amine groups is at 3380 cm^{-1}, whereas it is situated at 3340 cm^{-1} in (c) due to a greater level of substitution on the carbons in alpha positions: for instance, the C=O of urethane bond. Concerning the remaining phenolic –OH groups, their vibrational band is usually approximately situated between 3700 and 3125 cm^{-1}. However, for tannin extracts alone (a), this band is rather symmetric and centered at 3250 cm^{-1}. This is typical of the intermolecular interactions of the -OH groups (between 3400 and 3200 cm^{-1}), this being common between flavonoid monomer units. Concerning the -NH vibration, the bands are generally narrower, which on spectra is characterized by particular peaks besides the large vibration of the remaining –OH groups [(b) and (c)]. Finally, the appearance of the 1700 cm^{-1} band in (c) is characteristic of urethanes, this when it is coupled with the 1220–1230 cm^{-1} band (with the caution that this could also be interpreted as the C-O

stretching of phenolic groups) and the small band at 1020–1035 cm^{-1} (also described above for other possible interpretations).

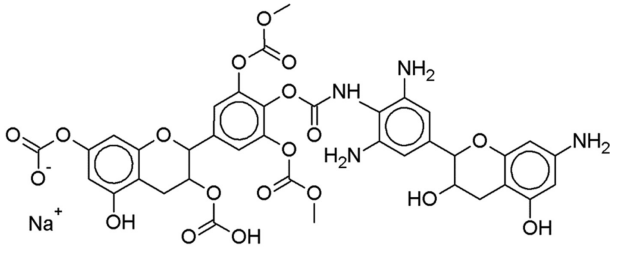
3.2 MALDI-TOF Analysis

At this early stage of reaction, the material prepared at ambient temperature is not expected to be a fully crosslinked network. However, the pre-polymerized moieties soluble in acetone/water and likely to contain some urethane linkages could be characterized by MALDI-TOF spectrometry. In this way, possible urethane/polyurethane moieties could be compared in molecular weight to the main peaks and patterns that were obtained in the spectrum in the range of 400–1500 Da.

The MALDI spectrum of the material prepared at ambient temperature is presented in Figure 4(c) to compare it with the original mimosa tannins extract (a) and the aminated mimosa tannins extracts (b). Interpretations of these last two spectra were already done in previous works on mimosa tannins chemistry [23–25] prorobinetinidin (PR and tannins reacted with ammonia [24]. A first assessment that can be made, comparing these three spectra, is that the main signals and repeating patterns are different. It indicates, on the one hand, that the basic monomer unit of the reaction material (c) is not the same as in either the raw material or in the initial materials. Thus, the mass difference between the main signal of 889 Da in the original tannins (a), which can correspond to a procyanidin trimer for instance, and the main signal of 1113 Da in the reaction material (c), is of 224 Da, which is lower than a flavonoid unit. This is probably due to a complex combination of carbonation with dimethyl carbonate and formation of urethane linkages. Conversely, while the main repeating patterns of the original tannin (a) are separated by a mass differential of 288 Da, the reaction material's (c) are of approximately 286 ± 2Da, which supposes that the additional monomers are tannins original units in which some hydroxyl groups have been substituted by amine groups, resulting in the slight loss of mass observed.

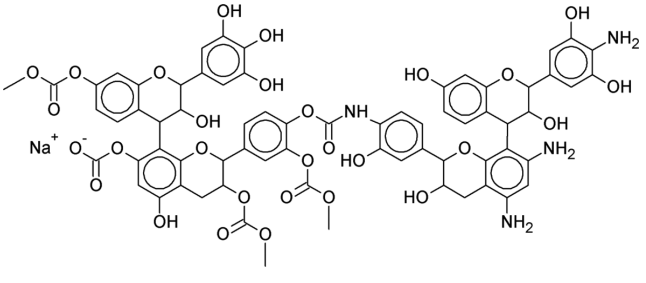
Thus, a list of possible oligomers interpreted from Figure 4 is shown in Table 1. In the reacted mix, one can find multicarbonated flavonoid oligomers, several carbonated at different levels, and carbonated and aminated flavonoid monomers and oligomers linked by urethane linkages. Aminated flavonoid species reacted through a urethane bridge with carbohydrate monomers contained in the extract are also present. First, it must be pointed out that the identical molecular weight of catechin and robinetinidin does not allow distinguishing which of the two structures is present. Thus, in the discussion that follows and in Table 1 wherever catechin is indicated it can be robinetinidin instead, and vice versa. While in the type of tannin used (mimosa), where robinetinidin is in the majority, the higher potential reactivity of catechin could indicate that in the structure described below both exist with the two types of flavonoid.

Examples of urethane-linked flavonoids are those at 796 Da, 812 Da, 827 Da, 861 Da, 1084 Da, 1100 Da, 1112 Da, 1117 Da, 1130 Da, 1381 Da, 1397 Da and 1413 Da. It is possible that these types of species have structures of the type observed for the 861 Da peak, for instance, namely:

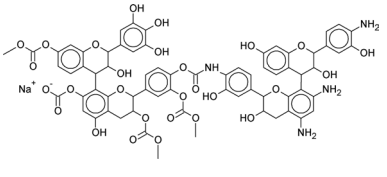


with a variable number of carbonated and aminated flavonoids.

One can observe species in which two flavonoid monomers are linked by a urethane such as those represented by the peaks at 796 Da, 812 Da and 861 Da, and species in which flavonoid oligomers are linked through a single urethane bridge to a flavonoid monomer or oligomers such as the peaks at 1084 Da, 1100 Da, 1112 Da, 1130 Da, 1381 Da, 1397 Da and 1413 Da, such as one of the representations of the peak at 1413 Da:



And the peak at 1397 Da which can be represented as:



On top of these species there are species where flavonoid monomers are linked through a urethane bridge to a carbohydrate monomer such as the peaks

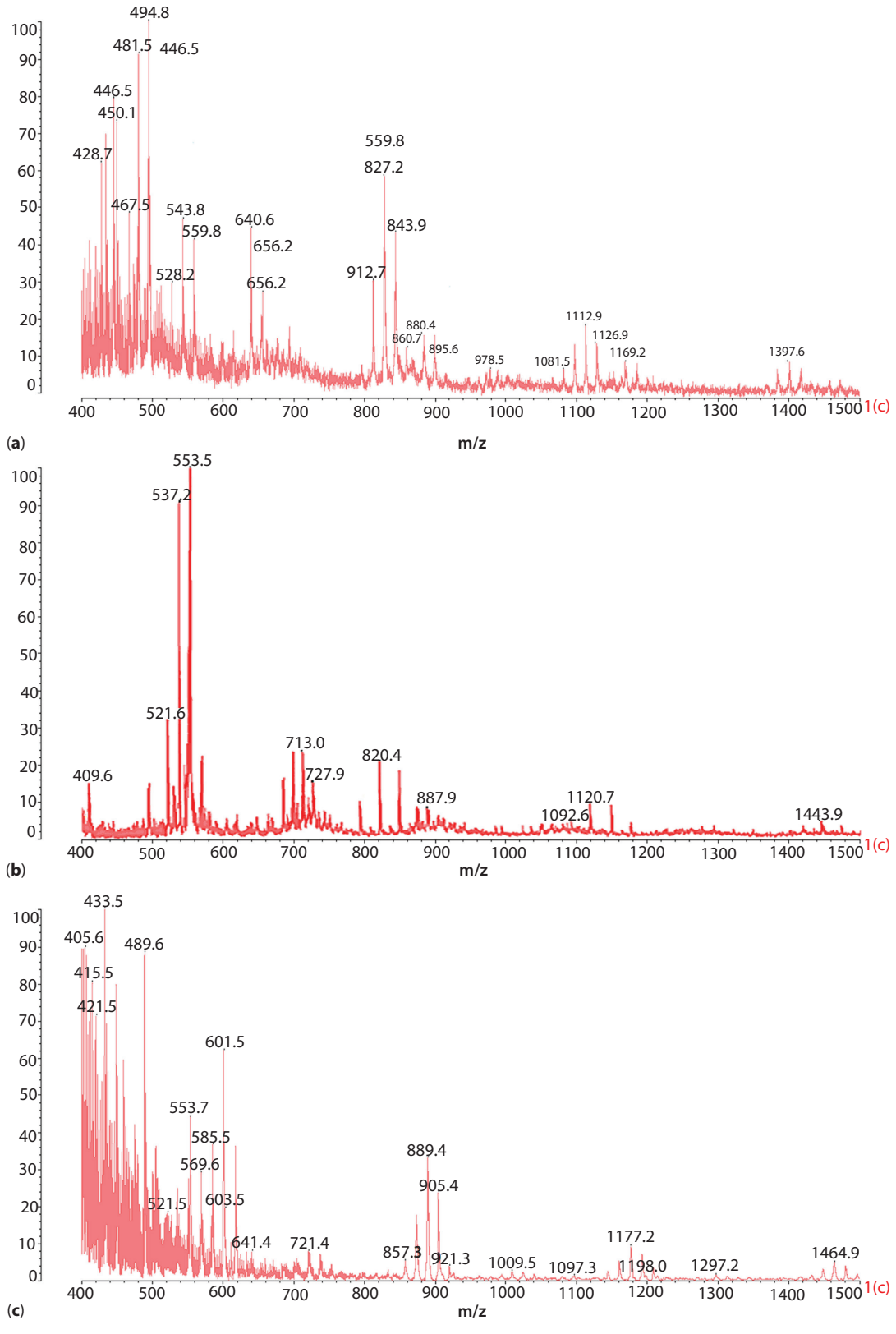
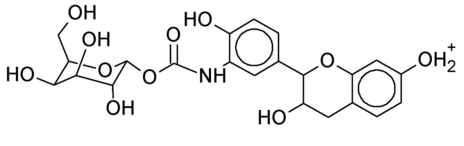


Figure 4 MALDI-TOF spectra of (**a**) Mimosa tannins extract [23–25] which are otherwise too difficult to determine by other techniques. It has been possible to determine by MALDI-TOF for the two major industrial polyflavonoid tannins which exist, namely mimosa and quebracho tannins, and some of their modified derivatives that: (i; (**b**) Mimosa tannins extract reacted with an ammonia solution [24]; (**c**) the product mixture obtained by reaction of mimosa tannin extract in dimethyl carbonate with the aminated tannin extract.

Table 1 Interpreted possible oligomer species identified by MALDI-TOF for the mixture of carbonated mimosa tannin extract reacted at ambient temperature with aminated mimosa tannin extract. The urethane linkage between flavonoid units is indicated as "URETHANE."

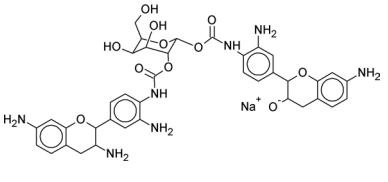
Moiety	Corresponding description possibilities
481 Da	Urethane aminated fisetinidin-carbohydrate monomer
495-496 Da	Urethane aminated catechin-carbohydrate monomer (or robinetinidin-sugar)
529 Da	Fisetinidin tetracarbonated, sodium
543 Da	Catechine and/or robinetinidin tetracarbonated OR unprotonated monocarbonated carbohydrate monomer-URETHANE-diaminated fisetinidin
559 Da	Delphinidin tetracarbonated OR unprotonated monocarbonated carbohydrate monomer-URETHANE-triaminated robinetinidin
640 Da	Monocarbonated catechin/robinetinidin dimer OR unprotonated monocarbonated fisetinidin-URETHANE-fisetinidin
655 Da	Monocarbonated delphinidin dimer OR unprotonated monocarbonated robinetinidin-URETHANE-fisetinidin
796 Da	Unprotonated tricarbonated catechin-URETHANE-tetraamminated catechin OR diaminated catechin-URETHANE-carbohydrate monomer-URETHANE-protonated triaminated fisetinidin
812-813 Da	Unprotonated tricarbonated catechin-URETHANE-pentaaminated delphinidin OR protonated catechin-URETHANE-carbohydrate monomer-URETHANE-protonated robinetinidin
827-830 Da	Unprotonated tetracarbonated robinetinidin-URETHANE-triaminated delphinidin
843 Da	Unprotonated tetracarbonated delphinidin dimer OR unprotonated tetracarbonated catechin-URETHANE-tetraaminated delphinidin
861 Da	Unprotonated tetratacarbonated delphinidin-URETHANE-triaminated delphinidin
880 Da	Diaminated [(robinetinidin)$_2$ delphinidin] trimer
895 Da	Triaminated [(delphinidin)$_2$-robinetinidin] trimer
1081 Da	Tricarbonated (catechin)$_2$ dimer-URETHANE-triaminated delphinidin
1097 Da	Tricarbonated catechin-delphinidin dimer-URETHANE-triaminated delphinidin
1113 Da	Unprotonated tetracarbonated (catechin)$_2$ dimer-URETHANE-pentaaminated delphinidin OR triaminated robinetinidin-URETHANE-unprotonated tricarbonated delphinidin-URETHANE-triaminated robinetinidin
1126 Da	Pentaaminated delphinidin-URETHANE-unprotonated tricarbonated delphinidin-URETHANE-tetraaminated robinetinidin
1381 Da	Tetracarbonated monoaminated fisetinidin-catechin dimer-URETHANE-monoaminated fisetinid-robinet dimer
1397 Da	Unprotonated tetracarbonated robinetinidin-catechin dimer-URETHANE-triaminated fisetinidin-catechin dimer
1413 Da	Unprotonated tetracarbonated robinetinidin-catechin dimer-URETHANE-triaminated robinetinidin-catechin dimer

at 481 Da, 496 Da, such as the 481 Da peak represented as:

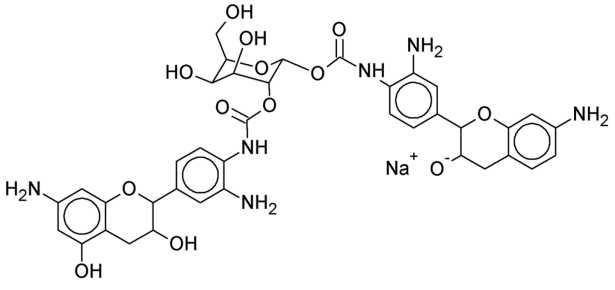


And even species in which two urethane bridges link a monomeric carbohydrate to two different flavonoid monomers such as for the peaks at 796 Da and 813 Da, for example:

796Da



And
813 Da



The presence of these two species implies that in carbonating the polyphenolic part of the tannin extract, the carbohydrate monomers, and possibly also carbohydrate oligomers, present in the commercial extract can get carbonated as well. This then renders possible their reaction with aminated flavonoids to form species like those belonging to the 796 Da and 813 Da peaks. Reaction of carbohydrates with dimethyl carbonate and the reaction which follows with aminated compounds were already observed in the case of the reaction of hydrolyzable tannins with hexamethylenediamine to form urethanes [20].

4 CONCLUSION

- The preparation of more than 70% biosourced isocyanate-free polyurethane resins for adhesives and surface finishes obtained by the reaction of carbonated condensed flavonoid tannin extracts by reaction with aminated tannin extracts of the same nature seems to be possible.
- The reaction to obtain the intermediate resins in solution, finally applicable and curable at 103 °C, occurs with ease at ambient temperature. Furthermore, if dimethyl carbonate is also considered as biosourced, then the composition of these polyurethanes is well over 80–90% biosourced.
- The carbohydrate fraction of the tannin extracts can also be carbonated and reacted to generate isocyanate-free polyurethane linkages with aminated tannins. The carbohydrates in tannin extracts are in general either carbohydrate monomers or short carbohydrate oligomers, both originating from hydrolysis of hemicelluloses during tannin extraction.

These findings show that the entire tannin extract and not only its polyphenolic components can be used to prepare polyurethanes. It opens up the possibility of producing the same starting exclusively from carbohydrates, a possibility that must still be checked.

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