Improving Water Repellence and Friability of Tannin-Furanic Foams by Oil-Grafted Flavonoid Tannins

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Tannin-furanic biobased foams, based on the co-reaction of bark-derived condensed tannins and thermoset furanic polymers, have low thermal conductivity, are self-extinguishing, and have high fire resistance, which allows their development for several industrial uses. One of their main drawbacks, however, is the absorption of water within the foam itself. Another problem is the rather friable surface, which is a definite drawback for some potential applications. In this work, these two problems are minimized or eliminated by introducing a component of oil-grafted tannin in the foam formulation. The incorporation of fatty chains markedly decreased foam friability and increased water repellency in the body of the foams. These properties and the compounds formed by fatty acids grafting onto the tannin flavonoids were extensively tested.

Keywords: Foam; Oil-grafted tannin; Water repellency; Flavonoids.

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INTRODUCTION

Recent work on resins derived from natural products has led to the development of biobased rigid foams with excellent performance and characteristics based on polyflavonoid tannin-furfuryl alcohol copolymerization (Meikleham and Pizzi 1994; Pizzi *et al.* 2008; Tondi *et al.* 2008, 2009a,b; Tondi and Pizzi 2009; Li *et al*. 2012; Basso *et al.* 2013a,b,c; Lacoste *et al.* 2013a,b,c).

The technology developed for such tannin-based foams is based on self-blowing because the very mild exothermic reaction of the self-condensation of furfuryl alcohol under acidic conditions causes the rapid evaporation of an organic volatile solvent during hardening. This process takes place at ambient temperature, although foams at mild induction temperatures have also been developed (Basso *et al.* 2014). Even though several applications are already in the initial phases of industrialization, two properties of interest need attention to further improve these materials. These are their surface friability and, in particular, their water repellence. Untreated tannin-based foams are solid but friable materials, which means that they are easily crumbled and yield a lot of powder (small fragments). Their surfaces are friable to the touch. Improvement of the water repellence and friability has been observed in the past by surface treating such foams with a vegetable oil (Basso, unpublished results 2013). However, these were only surface treatments, thus unusable to render the whole foam body water repellent and non-friable. If the foam block was cut, the newly exposed face would not be water repellent and would remain friable.

Recently, fatty acids or amines have been grafted onto various flavonoids, such as catechin, naringenin, and mesquitol, to obtain amphiphilic or lipophilic anti-oxidants for diverse applications such as surfactants or gelators (Sahmim, unpublished results 2015). The same approach has been used to successfully graft fatty acids onto flavonoid tannins to lead to oil-grafted tannins.

While advanced formulations without any formaldehyde or solvent have already been developed, a basic formulation has been used here simply to establish the principle of the use of oil-grafted tannins in these foams. This paper deals with the introduction of small proportions of the oil-grafted tannins into the formulations of standard tannin-furanic foams to improve both their friability and their water repellence.

EXPERIMENTAL

Synthesis of Oil-grafted Tannins

To a commercial tannin extract from mimosa (5 g) in suspension in chloroform (30 mL) in a 100-mL flask under an inert atmosphere were successively added triethylamine (Et_3N) (12.5 mL), 4-diméthylaminopyridine (DMAP) (0.350 g), and then, dropwise, palmitoyl chloride (20 mL). The reaction mixture was magnetically stirred at room temperature for 12 h. The medium was then evaporated until dry under reduced pressure, keeping the temperature below 40 °C. The residue was then added to 50 mL of methanol / water (9:1), which allows precipitation of the product. The mixture was stirred for 1 h at room temperature and filtered; the resulting solid was transferred to a 250-mL flask and suspended again in 50 mL of methanol with stirring at room temperature. Finally, the solid was washed with acetone and allowed to dry overnight in a vacuum desiccator. A total of 43 mg of esterified tannin was obtained as a brown solid. Such oil-grafted tannins were analyzed by infrared (IR) spectroscopy using a Perkin-Elmer (France) FTIR "spectrum one" equipment in ATR mode and compared to natural mimosa tannin spectra.

Matrix Assisted Laser Desorption Ionization - Time of Flight (MALDI-TOF) Analysis

The tannin samples were dissolved in water/acetone for analysis (Merck, supplied by VWR, France) (4 mg/mL, 50/50 volume), and the solutions were mixed with the matrix solution (10 mg/mL in acetone). The matrix, which facilitates the deposition of the sample in the instrument, was 2,5-dihydroxy benzoic acid (LaserBio Labs (France). Calibration was done with red phosphorous (LaserBio Labs (France)). To enhance ion formation, a concentrated solution of sodium chloride (NaCl) (Carlo Erba Reactifs (SDS) (France)) was added to the matrix (10 mg/mL in distilled water). The sample and the matrix solutions were mixed as three parts of the matrix solution, three parts of the sample solution, and one part NaCl solution; 0.5 to 1 µL of the resulting mixture was placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer. Each peak value in the resulting positive mode spectra shown in Figs. 1 and 2a,b and Tables 1 and 2 must be decreased by 23 Da, this being the molecular weight of the Na^+ included as NaCl in the matrix and attached to the oligomers, to obtain the molecular weight of the chemical species of the peak.

The MALDI-TOF spectra were recorded on an AXIMA Performance instrument (Shimadzu Scientific Instruments; Manchester, UK). The irradiation source was a pulsed nitrogen laser with 3-ns intervals at a wavelength of 337 nm. The measurements were carried out using the following conditions: polarity: positive; flight path: linear; mass: high (20-kV accelerating voltage); and 100 to 150 pulses per spectrum. The delayed extraction technique was used to apply delay times of 200 to 800 ns.

Foam Preparation

The foams were prepared as follows: tannin in powder form was gradually added to a mixture of furfuryl alcohol, formaldehyde, and water and was mixed by hand. Mechanical homogenization could also be used. This was followed by the addition of the blowing agent, in this case diethyl ether (Sigma-Aldrich (Merck) (France)), and continuing manual mixing until homogenization of the whole mixture. The acid catalyst was then added and the mixture was stirred continuously for 10 s.

In the case of sample D, the oil-grafted tannin exp. 2 was homogenized in glycerol at 80 °C. The resulting product was cooled before adding it to the mixture of furfuryl alcohol and formaldehyde and finally adding the non-grafted tannin extract.

Foam Characterization

Friability properties

The friability was assessed manually (Ortrand *et al.* 2001) in accordance with the following protocol. Each sample was rubbed five times, without additional pressure nor stress, against the paper surface, along a 3.5 cm distance. Kimtech Science paper was used (Precision Wipes Tissue Wipers, Kimberly-Clark Professional, Nanterre, France). For each formulation, the hydrophobized foam and the standard one were rubbed simultaneously on the paper to afford comparison of the results to the control experiment.

Apparent density, relative density, and porosity

The total porosity, $\emptyset$ (dimensionless), was calculated according to Eq. (1), in which ρ_{ap} (g.cm^{-3}) and ρ_s (g.cm^{-3}) are the apparent density and the skeletal density of the foams, respectively:

$$\emptyset = 1 - \frac{\rho_{ap}}{\rho_s} \tag{1}$$

Here, ρ_{ap} is simply the weight/volume ratio of parallelepiped samples of accurately known dimensions; ρ_s, the density of the solid from which the considered material was made, was estimated, after grinding the sample, by helium pycnometry using an Accupyc II 1340 (Micromeritics, USA) apparatus. For that purpose, all samples were crushed in an agate mortar and evacuated at 60 °C under vacuum to avoid errors arising from humidity.

Contact angle measurement and surface free energy

Wettability is characterized by measuring the contact angle formed between a liquid drop and a solid surface. This measurement is considered to be a relatively simple, useful, and sensitive tool for assessing the surface energy of solids.

Contact angle measurements were performed with a liquid-solid contact angle analyzer (DSA100, KRÜSS®, Hamburg, Germany) using the sessile drop method. Twomicroliter droplets of liquid were placed on the sample with an automatic drop deposition system. The contact angle was calculated by the computer software from the droplet image. Measurements were performed at an ambient temperature of 20 °C and 50% relative humidity and they were repeated at least 10 times on fresh surfaces. The obtained data were averaged, and standard deviations were calculated.

Contact angles were measured using three liquids: Milli-Q® deionised water (Millipore (Guyancourt, France)), ethylene glycol, and diiodomethane (Sigma-Aldrich (Merck) (France)).

In the literature, the general equation describing the interaction of the surface tension of a liquid and a solid is called the Young equation (Young 1805),

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta \tag{2}$$

where γ_s (mN/m) is the surface free energy (SFE) of the solid, γ_{sl} (mN/m) is the SFE corresponding to the solid-liquid interface, γ_l (mN/m) is the SFE of the measuring liquid, and θ (°) is the contact angle between the solid and the measuring liquid. In the absence of precise information of surface roughness, Eq. 2 was used without any correction for the effect of roughness.

There are several methods to analyze the SFE. In this study, the Owens, Wendt, Rabel, and Kaelble (OWRK) method was used to estimate the SFE of the foam from the contact angles with various liquids. In doing so, the SFE is divided into a polar part and a disperse part,

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{3}$$

$$\gamma_l = \gamma_l^d + \gamma_l^p \tag{4}$$

where γ_s^d (mN/m) and γ_l^d (mN/m) are the disperse surface energy component of the solid and liquid, respectively, and γ_s^p (mN/m) and γ_l^p (mN/m) are the polar surface energy component of the solid and liquid, respectively.

Moreover, the interfacial solid-liquid free energy (γ_{sl}, mN/m) can be calculated as the geometric mean of the contributions of the liquid and solid:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\sqrt{\gamma_s^d \cdot \gamma_l^d} + \sqrt{\gamma_s^p \cdot \gamma_l^p}\right) \tag{5}$$

Using this approach, Owens, Wendt, Rabel, and Kaelble developed a linear equation (Owens and Wendt 1969; Kaelble 1970), in which the slope and the intercept are given by the square root of the polar and disperse components of the SFE, respectively:

$$\frac{\gamma_l\,(1+\cos\theta)}{2\sqrt{\gamma_s^d}} = \sqrt{\gamma_s^p}\sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \tag{6}$$

Thus, measurement of contact angles with various test liquids (Table 2), with known surface tension and relative components, enables the determination of SFE as a sum of polar and disperse parts.

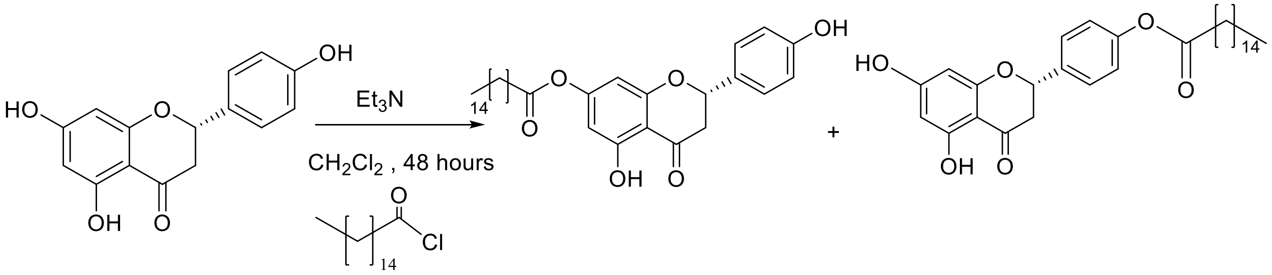
Water vapor sorption

Water vapor adsorption-desorption isotherms were acquired with volumetric equipment (3-flex by Micromeritics Instrument Corporation (USA)) able to combine pressure and volume increments and measure the water adsorbed at equilibrium. Before analysis, the samples were outgassed under secondary vacuum at room temperature for at least 72 h. Adsorption isotherms were acquired by dosing water vapor between 1% and 90% relative humidity (RH) at 20 °C and measuring the water adsorbed at equilibrium for each P/P_0 value. Once 90% RH was reached, desorption started, and the volumes adsorbed at equilibrium for each point were measured to build the desorption branch of the isotherm. At least 60 points, pairs of relative pressure-volume adsorbed in cm^3 STP/g, were recorded for each adsorption-desorption isotherm. The equilibrium times were quite long; usually, the entire adsorption-desorption process lasted for 10 days.

RESULTS AND DISCUSSION

Synthesis of Oil-grafted Tannins

Recently, on the basis of acquired expertise on chemical modification of natural compounds to obtain amphiphilic or lipophilic antioxidants for diverse applications such as surfactants or gelators (Obounou-Akong *et al.* 2013a,b), fatty acids or amines have been grafted onto flavonoids including catechin, naringenin, and mesquitol (Scheme 1) (Sahmim, unpublished results 2015).



Scheme 1. Grafting of fatty chain on flavonoids used as models

Thus, the same approach, *i.e.*, introducing the lipophilic part by the same way of esterification of some phenol groups of the tannins with fatty acid derivatives to lead to oil-grafted tannins, was chosen. The natural tannin extract underwent acylation using the fatty acid chloride derivatives; *i.e.*, decanoyl chloride and hexadecanoyl chloride.

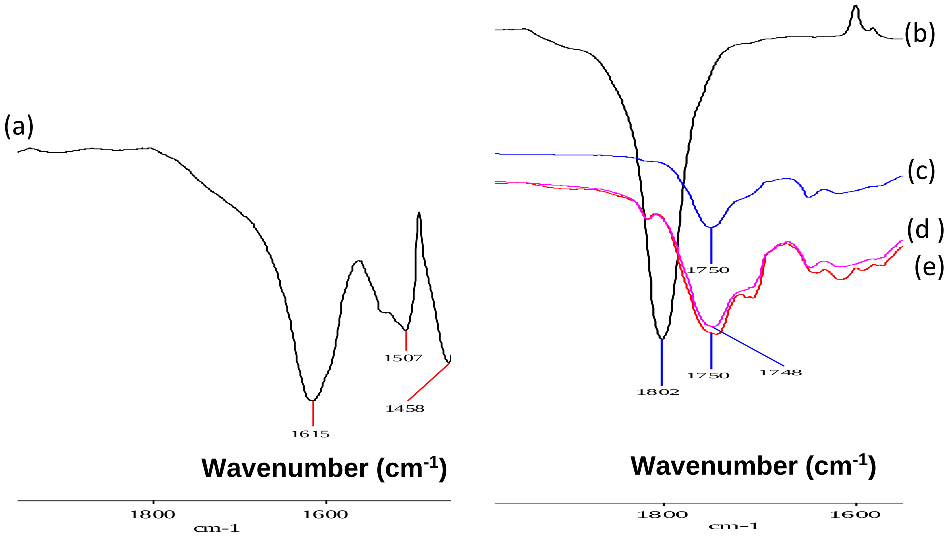
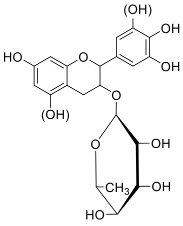
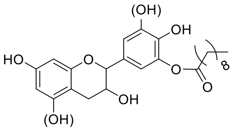
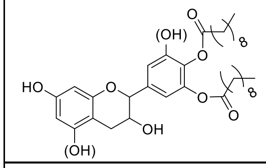
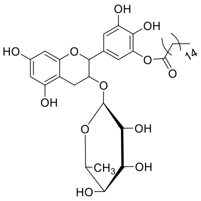


Fig. 1. Infrared spectra of natural mimosa tannin and oil-grafted tannins: (a): natural mimosa tannin; (b): fatty acid chloride; (c-e): oil-grafted tannins

The reaction conditions were adapted from a previous patent (Nkiliza 1998) and used a combination of DMAP and triethylamine as organic bases in chloroform as a solvent. The starting tannin is not fully soluble in chloroform, but the resulting suspension proved to be sufficiently reactive. After the sample was stirred for 12 h at room temperature, the grafted tannin was precipitated. The natural mimosa tannin and each oil-grafted tannin batch were then characterized first by infrared spectroscopy (IR) (Fig. 1).

Table 1. Characterization of Mimosa Tannin and Oil-Grafted Tannins by MALDI-TOF MS

Molecules	MW Experimental	MW Calculated	Remarks
Fisetinidin	272 = 271 Da + H^+	274 Da	Free flavonoid units
Gallocatechin + Na^+	332 = 309 Da + Na^+	306 Da	
Robinetinidin and/or catechin:  + Na^+	463 = 440 Da + Na^+	436 Da	Glycosylated flavonoid units
Robinetinidin and/or catechin + C10 chain: 	638 = 615 Da + Na^+	622 Da	Free flavonoid monoester
Robinetinidin and/or catechin + 2 X C10 chains : 	796 = 773 Da + Na^+	777 Da	Free flavonoid diester
Gallocatechin + C16 chain:  + Na^+	748 = 725 + Na^+	722 Da	Glycosylated flavonoid monoester

A comparison between the spectra shows the disappearance of the C=O band of acid chloride at 1815 cm^{-1} and the appearance of a novel band at 1750 cm^{-1} corresponding to the carbonyl band of an ester. These initial observations are in favor of the formation of an ester on the tannin and therefore of the grafting of one or more fatty chains. The previously mentioned patent (Nkiliza 1998) and the results obtained with the esterification of flavonoid-monomer (Sahmim, unpublished results 2015) contribute to a conclusion that esterification has been realized at a phenolic position rather than at an aliphatic position. The IR band is high enough to correspond to the carbonyl band of a phenolic ester rather than an aliphatic ester. Even if there is no direct scientific evidence, there is a strong presumption of this fact.

To confirm the structures prepared, the natural mimosa tannin extract and each oil-grafted tannin batch were also characterized by MALDI-TOF MS analysis (Figs. 2 through 4).

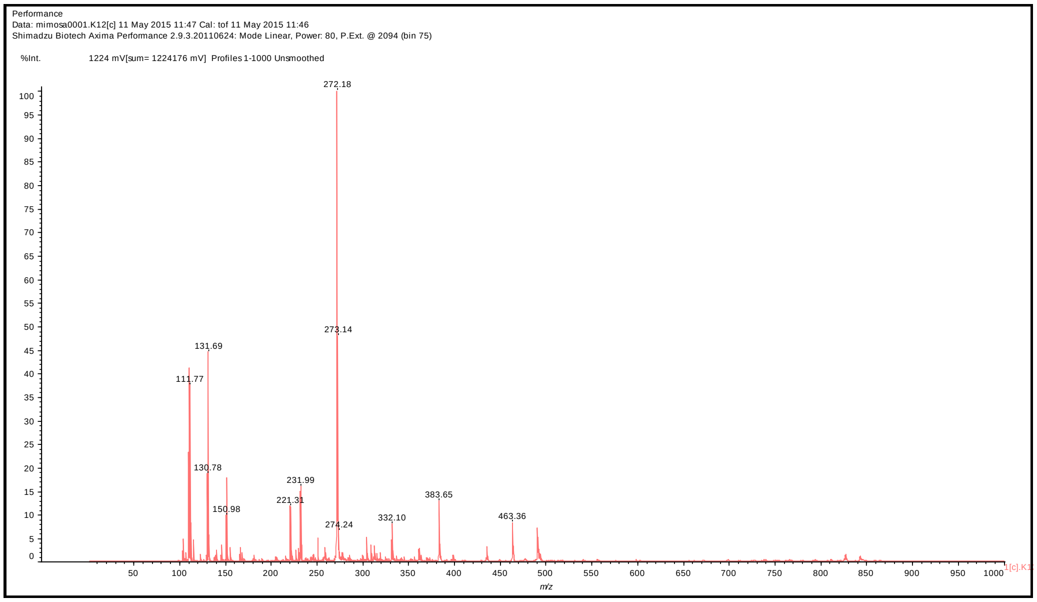


Fig. 2. MALDI-TOF mass spectrum of natural mimosa tannin

In mimosa (*Acacia mearnsii*, formerly *mollissima*, de Wildt) bark tannin extract, the flavan-3-ol repeating units (Fig. 2) are mostly 4,6-linked and sometimes 4,8-linked. Such flavonoid units are repeated 2 to 10 times to produce tannin with a number-average degree of polymerization of 4 to 5 (Pizzi 1983, 1994; Pizzi and Stephanou 1993).

From a chemical point of view, the position and the quantification of modified phenols is thus very tricky to determine. As a consequence, we focused in this study on the low-molecular mass regions of the MALDI-TOF spectra to identify grafted flavonoid monomers. However, it is expected that the linkage will take place in a similar fashion as the oligomeric structures level.

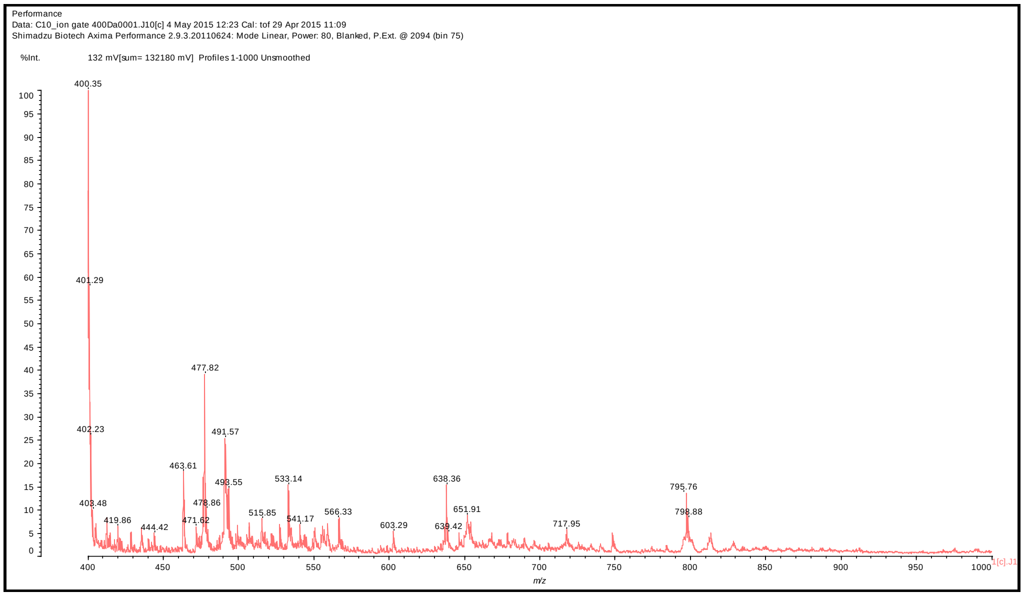


Fig. 3. MALDI-TOF mass spectrum of C10 oil-grafted tannin

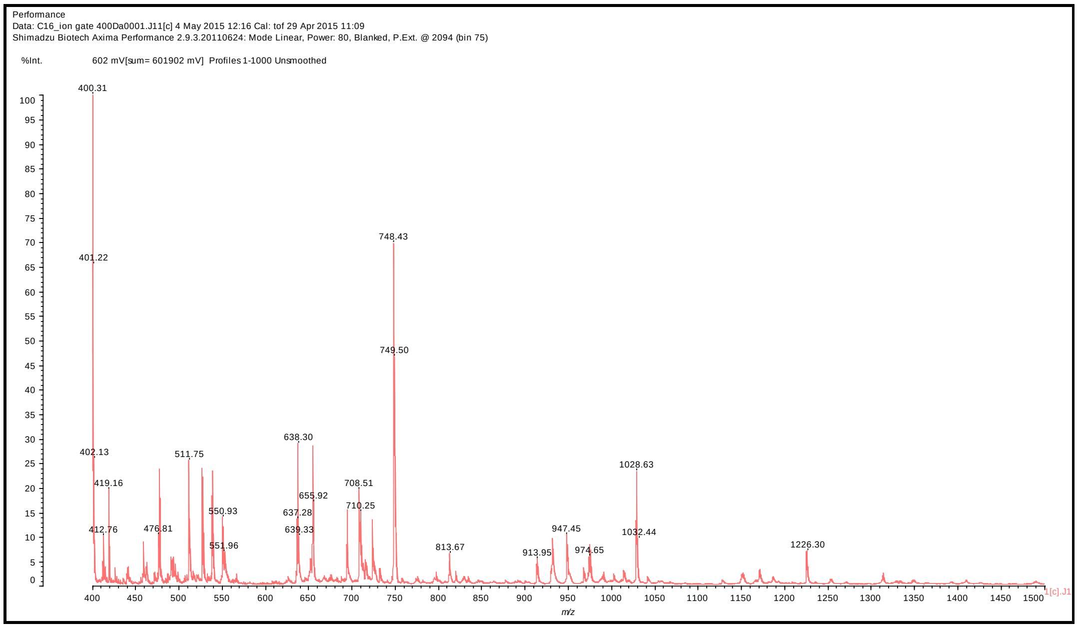


Fig. 4. MALDI-TOF mass spectrum of C16 oil-grafted tannin

The flavonoid constituent units of the tannin appear either under their native form or under a glycosylated form (rhamnose residue) at their C3 position.

These types of structures with a carbohydrate residue linked to the C3 site of flavonoids are well known (Davis and Brodbelt 2004; Kachlicki *et al.* 2008; Stevenson *et al*. 2010; Balaban Ucar *et al.* 2013; Drovou *et al.* 2015). While the MALDI analysis cannot indicate where the carbohydrate residue is exactly linked, it is most probable that this carbohydrate residue is linked to the C3 site (Balaban Ucar *et al*. 2013; Drovou *et al.* 2015).

Interestingly, the C16 chain gave rise only to monoesters (Fig. 4), whereas the shorter C10 chain allowed, according to the MALDI-TOF spectra (Fig. 3), diesterification of polyphenol molecules.

Foam Preparation

Table 2 shows the formulations used to check the effectiveness of the addition of oil-grafted tannins to standard rigid foam formulations. Formulations in which the level of substitution of the tannin by an oil-grafted tannin in the standard formulation (STD) were respectively 50% (A), 16% (B), and 8% (C and D) were tested.

Formulation A did not yield a foam, but rather a somewhat hard solid. This indicates that the oil-grafted tannin presents a totally different and much decreased reactivity than untreated tannin.

As a result, the rate of foaming and rate of hardening are uncoordinated, yielding the hard solid observed (Fig. 5).

Table 2. Composition of Tannin-Furanic Foams Tested With or Without Oil-Grafted Tannins

Formulation	STD	A	B	C	D
Mimosa tannin extract (g)	6	3	5	5.5	5.5
Oil-grafted mimosa tannin *exp.1* (g)	-	3	-	-	-
Oil-grafted mimosa tannin *exp. 2* (g)	-	-	1	0.5	0.5
Formaldehyde (g)	1.5	1.5	1.5	1.5	1.5
Furfuryl alcohol (g)	2	2	2	2	2
Water (g)	1.2	1.2	1.2	1.2	-
Diethyl ether (g)	0.6	0.6	0.6	0.6	0.6
pTSA* (g)	2.2	2.2	2.2	2.2	2.2
Glycerol (g)	-	-	-	-	2

*para-toluenesulfonic acid (65% ethyleneglycol)

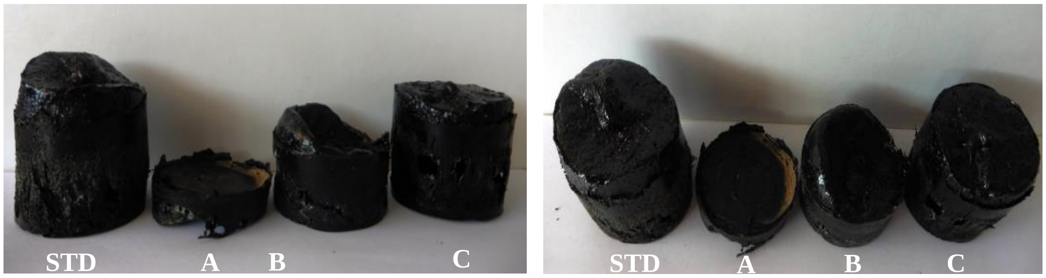


Fig. 5. Synthesized standard tannin foam (STD) and oil-grafted tannin foams (A-C)

This indicates that introducing very high proportions of heavily oil-grafted tannins alters the kinetics of foaming and cross-linking of the system. Thus, when higher proportions of oil-grafted tannins are desired in the foam, either the formulation needs to change to reach a balance between foaming and cross-linking or the level of grafting of the tannin needs to be decreased.

Formulation D yielded a good tannin-furfuryl alcohol-glycerol emulsion, which was compatible with both the blowing agent and the catalyst. However, the foaming and reaction were too rapid and exothermic. The resulting material was similar in appearance to formulation A (Fig. 5). However, formulation D constitutes a good starting formulation for further advancing and improving these materials by including, for example, an additive able to dissipate the heat generated and slow down foaming, or by modifying the proportion of furfuryl alcohol, or by modifying the load of catalyst and of furfuryl alcohol. Differently from A, where foaming takes a long time to start, in the case of D, it is rapid and abrupt (induction = 5 s). For all cases, the foams can be made more homogeneous by incorporating tensioactives to stabilize foaming.

The results and characteristics of the foams obtained are shown in Table 3. To test the friability of the finished foams, the STD and C foams were rubbed with a paper sheet five times each to check how much surface powder was lost and hence evaluate surface friability. From Fig. 6, it can be seen that the surface powder lost is much less in foam C than in the STD foam.

Table 3. Results and Some Characteristics of the Foams Prepared

Observations/ Properties	STD	A	B	C
Induction* time (s)	30	180	55	45
Hardening	Immediate	Immediate	Immediate	Immediate
Observations		Almost no foam expansion		
Density (g/cm^3)	0.12	-	-	0.17
Resistance at 80 °C		Appears to melt, particularly the foam skin		

*Period between the end of mixing (after catalyst addition) and the start of foam expansion

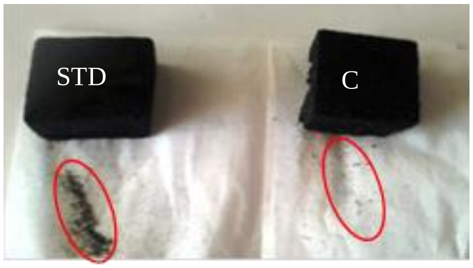


Fig. 6. Friability of standard foam (STD) and foam C

The water adsorption of the STD and C foams can be evaluated visually with ease, as seen in Fig. 7, by observing the situation of the water drop a few minutes after its deposition on the foam surface. Foam C is less hydrophilic, practically hydrophobic, than the STD foam, as the water drops slide on the surface of foam C without being adsorbed. Conversely, the water droplets are readily absorbed by the surface of the STD foam after a few minutes.

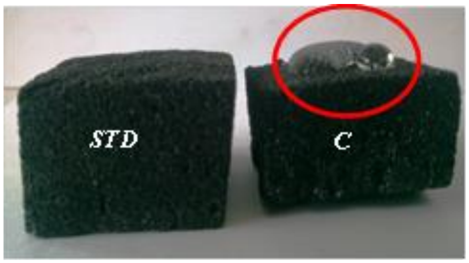


Fig. 7. Images of water drop placed on standard foam (STD) and grafted-tannin foam (C)

Foam Characterization

Two different foams were analyzed: standard foam (STD) and the foam corresponding to formulation C. The foams were characterized for porosity, wettability, surface energy, and water adsorption. Surface characterization of the solid provides better understanding of their behavior in different processes, such as water-cleaning and coating. Surface wettability and surface energy are most critical properties to be taken into consideration during formulation and development of a hydrophobic foam.

Figure 8 shows an image of the contact angle of a water drop placed on the two different surfaces: (a) standard foam (STD) and (b) grafted-tannin foam. In both cases, it was found that the contact angle was higher than 90 °C. However, the foam obtained from grafted-tannin has a much larger contact angle (lower wetting behavior) than the standard one.

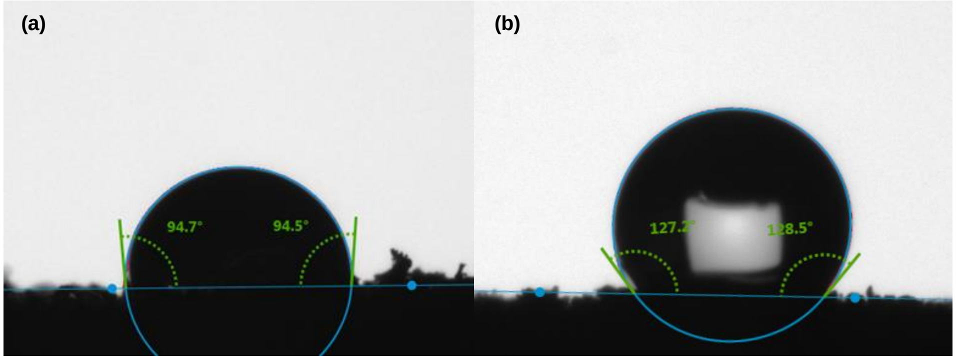


Fig. 8. Images of water drop placed on (a) standard foam, STD and (b) grafted-tannin foam, C

In Table 4, the averaged contact angles for all types of studied surfaces with the calculated surface energies are presented.

Table 4. Contact Angles and the Calculated Values of Total Γ_s, Dispersive Γ_s^d and Polar Γ_s^p Surface Energies

Sample	**Mean contact angle (°)**			**Surface energies (mN/m)**		
	Water	Ethylene glycol	Diiodomethane	γ_s	γ_s^d	γ_s^p
STD	94.06 (5.62)	57.86 (6.37)	66.28 (3.77)	28.92 (4.57)	25.35 (2.69)	3.57 (1.88)
C	128.09 (4.69)	93.65 (3.86)	84.22 (2.66)	15.86 (3.08)	15.84 (2.89)	0.02 (0.19)

Standard deviation in parentheses

The total energies of the two samples in the present study have two contributions, polar and dispersive (Table 5).

Table 5. Surface Energy with Polar and Disperse Surface Energy Components of Liquids Used for Wettability Test

Liquid	**γ_l (mN/m)**	**γ_l^p (mN/m)**	**γ_l^d (mN/m)**
Water	72.8	51	21.8
Ethylene glycol	47.7	21.3	26.43
Diiodomethane	50.8	-	50.8

Both components of surface energy were dramatically altered with the grafted tannin. The grafted tannin produces an important decrease in polar and dispersive contribution in the surface energy of foam C, from 3.57 to 0.02 mN/m and from 25.35 to 15.84 mN/m, respectively. The reduction of hydroxyl groups in foam C decreases the interaction of surface with polar liquids, and the surface became comparatively less wetting, which is reflected in the contact angle values.

Figure 9 shows the adsorption and desorption isotherms of water on the unmodified-tannin foam and the grafted-tannin foam. The amount of water adsorbed on the samples at the same relative pressure decreased with the grafted tannin.

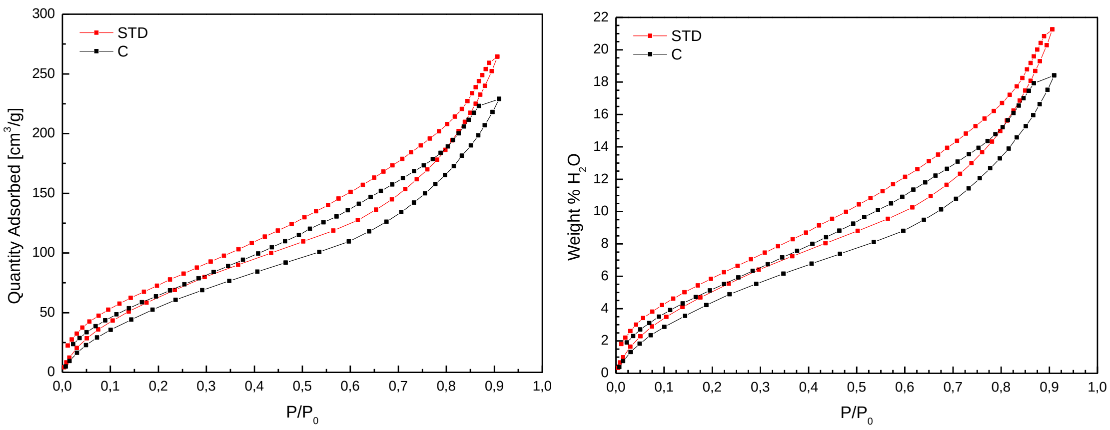


Fig. 9. Water adsorption isotherms at 20 °C

CONCLUSIONS

1. From the results obtained, it is clear that incorporating some oil-grafted tannins leads to tannin-furanic foams that are less friable. In their role of exterior-type plasticizers, oil-grafted tannins can markedly decrease the friability of tannin-furanic foams. Furthermore, these grafted tannins, contrary to classical exterior-type plasticizers, do not cause foam shrinkage. This is because the hardening of the foam is very rapid (Table 3) and not shifted in time in relation to foam expansion.
2. Furthermore, incorporation of oil-grafted tannins leads to tannin-furanic foams, which are less hydrophilic, practically hydrophobic. The wetting behavior of the foam was assessed from both static contact angles using the sessile drop method and water adsorption. Increased macroscopic hydrophobicity of the foam is evidenced by both techniques for the modified tannin foam. This is a very interesting effect that can be clearly seen with the addition of only small amounts, such as 8% of grafted tannins, to a standard foam formulation. The addition of higher proportions may well lead to even more hydrophobic foams, but reformulation appears necessary because of the loss of reactivity of the grafted tannin, or, alternatively, a lower level of grafting could be used to further investigate such an effect.

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