

Development and Characterisation of Phenolic Foams with Phenol-Formaldehyde-Chestnut Tannins Resin

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ABSTRACT: With the depletion of fossil resources, tannin extracts can be a natural alternative to some synthetic products. Hydrolysable chestnut tannin extracts have been used to partially replace phenol in PF resins for phenolic rigid foams. Phenol-formaldehyde-chestnut tannin (PFT) phenolic foams were initially made from copolymerized PFT resins of different molar ratio. The PFT foams so prepared were tested for thermal conductivity, these being slightly worse than that of pure PF foams; and for mechanical and water absorption, these two properties being better than those of pure PF foams. Indeed, PF resins represent an important part of synthetic resins. They are used in different fields of application such as in phenolic foams or for the preparation of particleboard. So it is important to work on the possibility of going green with these resins.

KEYWORDS: Biopolymers and renewable polymers, cellulose and other wood products, foams, biomaterials

1 INTRODUCTION

During the last decades we have witnessed an important increase in oil prices. Consequently, considerable research has been carried out on the use of natural resources to replace petrochemicals. These developments have occurred in several diverse industrial sectors. Natural materials such as condensed polyflavonoid tannins have been used to develop new biobased materials such as, for example, biobased adhesive resins, insulation foams or floral foams [1–9]. Condensed polyflavonoid tannins are extracted from wood and/or bark after a simple hot water extraction. The tannins used up to now for the production of rigid foams are exclusively condensed polyflavonoid tannins.

However, another class of tannins exists, namely hydrolysable tannins, the main components of which are oligomers of pentagalloyl glucose. Some research work has already been done on the use of hydrolysable tannins (chestnut tannin extracts) in the development of phenol-formaldehyde (PF) adhesives for wood-based panels [10]. The PF adhesives are synthetic resins extensively used in the wood-based panel industry.

Thus, the substitution of phenol in some proportion with a renewable resource such as hydrolysable tannin in PF resins while maintaining the same performance would be of interest. In this article, the possibility of preparing phenol-hydrolysable-tannin formaldehyde copolymer resins and using them for the preparation of phenolic foams was studied. Chestnut wood tannin extract was the tannin chosen for this research as it is the most abundant hydrolysable tannin.

2 EXPERIMENTAL

2.1 Resins Synthesis

2.1.1 Phenol-Formaldehyde Control Resin, P/F Ratio of 1/1.7

A PF resin (ratio P/F of 1/1.7) was synthesized according to systems already reported by coreacting 212.5 g of 80% phenol, 84.5 g of sodium hydroxide as a 30% water solution and 249.5 g of formaldehyde as a 37% aqueous solution [11].

The mixture is then slowly brought to reflux at 94°C under continuous mechanical stirring. Once a temperature of 90°C is reached, the mixture is left for 2 hours. The resin is then cooled and the pH is adjusted to 7 with a 45% solution of phenol sulfonic acid in ethylene

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glycol. The mixture is then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

2.1.2 Phenol-Chestnut Tannins-Formaldehyde Resin, P:T 70:30 and P/F Ratio of 1/2.5

The procedure for the synthesis of PFT resin was adapted from a previous work [10]. Spray-dried chestnut (*Castanea sativa*) wood tannin extract from Silva Chimica (San Michele Mondovi, Italy) was used.

For the PFT resin at P:T 70:30 and P/F ratio of 1/2.5, 30% of synthetic phenol by mass was replaced with spray-dried chestnut tannin extracts; and 148.75 g of 80% phenol, 99.48 g of 96% paraformaldehyde powder and 57.4 g of a 30% sodium hydroxide water solution were used.

First phenol and tannins (55 g) were dissolved in a water/methanol mixture (62.7 g of water/9.6 g of methanol). Paraformaldehyde was then added. This mixture was heated at 40°C for 30 minutes under reflux and continuous mechanical stirring. The temperature was then increased to 94°C, and 57.4 g of 30% sodium hydroxide water solution were added in four equal parts of 14.35 g each at regular intervals of 15 minutes.

After the last addition of sodium hydroxide, which occurred 45 minutes after the first addition, the mixture was further heated for 15 minutes to reach a total reaction time of 1 hour.

The resin was then cooled to room temperature and the pH adjusted to 6 with a 65% formic acid water solution. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

2.1.3 Phenol-Formaldehyde with Chestnut Tannins Resin, P:T 70:30 and P/F Ratio of 1/1.7

For PFT resin, P:T 70:30 and P/F ratio of 1/1.7, 30% of synthetic phenol by mass was replaced with spray-dried chestnut tannin extracts; and 148.75 g of 80% Phenol, 67.29 g of 96% paraformaldehyde powder and 57.4 g of a 30% sodium hydroxide water solution were used.

First phenol and tannins (55 g) were dissolved in a water/methanol mixture (62.7 g of water/9.6 g of methanol). Paraformaldehyde was then added. This mixture was heated at 40°C for 30 minutes under reflux and continuous mechanical stirring. The temperature was then increased to 94°C, and 57.4 g of 30% sodium hydroxide water solution were added in four equal parts of 14.35 g each at regular intervals of 15 minutes.

After the last addition of sodium hydroxide, which occurred at 45 minutes after the first addition, the

mixture was further heated for 1 hour and 15 minutes to reach a total reaction time of 2 hours.

The resin was then cooled to room temperature and the pH adjusted to 7 with a 45% solution of phenol sulfonic acid in ethylene glycol. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

2.2 Resins Characterisations

2.2.1 Exothermal Behaviour

The aim of this test was to measure the reactivity of the resin as a function of time. The test consists of adding a defined amount of catalyst in a defined amount of resin. This mixture is then stirred while the temperature is recorded. The peak of the maximum of temperature reached and the time at which it occurs were recorded. This test was performed on the day of the synthesis of the resin and then repeated weekly.

For the PF resin, 10 g of resin was added to 0.3 g of a 65% solution of phenol sulfonic acid in ethylene glycol. For the PF resin coreacted with chestnut tannin, 5 g of resin was added to 5 g of a 45% solution of phenol sulfonic acid in ethylene glycol. A large amount of resin was prepared at the beginning of the test and then one sample of resin was tested weekly.

2.2.2 Viscosity

Viscosities were determined with a Brookfield viscometer at 25°C.

2.3 Development of Foams

All foams were prepared equally using the same procedure and under the same set of conditions. Their characteristics were then determined.

Some surfactants were first added to the PF or PFT resin, like Cremophor ELP, which is a nonionic solubilizer, and DC 193, which is a silicone polyether copolymer. The amounts of surfactants were determined to optimise the appearance of the foams (homogeneity, no big holes...). After this, a blowing agent was added to the mix and then an acid catalyst was finally added.

For foaming, pentane was used as blowing agent (blowing point was at 36°C). The reaction between the PFT resin and the acid catalyst was exothermic. Foam hardening occurs at the end of foaming. A different foaming approach was also tried: thus, foaming was carried out with 4,4' diphenylmethane diisocyanate (pMDI), without pentane, if flammable reactive solvents are not wanted in the process. In this approach foaming was caused by the CO₂ released by reaction of the pMDI with water.

In the preparation of tannin foams 65% *para*-toluene sulfonic acid in water is generally used. However, this was found to be unsuitable for the PFT foams. Thus, different catalysts had to be tried.

The reagents were first mixed together to ensure homogeneity of the mixture. The mixture was then poured in a plastic beaker of 250 mL, in which the walls were covered with aluminum foil in order to easily remove the foam.

Different foams were prepared by changing the catalyst (65% solution of phenol sulfonic acid in ethylene glycol, 65% solution of phenol sulfonic acid in water

and 65% solution of phenol sulfonic/sulfuric acids [50/50] in ethylene glycol).

The foams were dried at room temperature for 24 hours and cut off at their core. The samples were stored at 20°C and 60% relative humidity for 3 weeks.

Foams were prepared with both types of PFT resins. At first a foaming temperature of 80°C was tried. Afterwards a lower temperature of 60°C was tried. Several foam types were prepared (Table 1 and Figure 1) with different catalysts and with different foaming agents (chemical and physical).

Table 1 Procedures of foams.

Resin	PF. P/F ratio of 1/1.7	PFT. P:T 70:30 and P/F ratio of 1/2.5			PFT. P:T 70:30 and P/F ratio of 1/1.7					
		1	2	3	A	B	C	D	E	F
Foam	PF	1	2	3	A	B	C	D	E	F
	Mass (g)									
<i>Resin</i>	25	25	25	25	25	25	25	25	25	25
<i>Cremophor ELP</i>	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
<i>DC 193</i>	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45
<i>Pentane</i>	1.5	1.5	1.5	/	1.5	1.5	/	1.5	1.5	/
<i>Phenol sulfonic acid at 65% in ethylene glycol</i>	3.5	8.75	/	/	8.75	/	/	8.75	/	/
<i>Sulfuric/phenol sulfonic acids (50/50) at 65% in ethylene glycol</i>	/	/	8.75	/	/	8.75	/	/	8.75	/
<i>Phenol sulfonic acid at 65% in water</i>	/	/	/	8.75	/	/	8.75	/	/	8.75
<i>pMDI</i>	/	/	/	3	/	/	3	/	/	3
<i>Foaming temperature (°C)</i>	80	80	80	80	60	60	60	80	80	80
<i>Average density (kg/m³)</i>	0.0298	0.0463	0.0645	0.0746	0.1007	0.0944	0.1267	0.0925	0.0908	0.1169

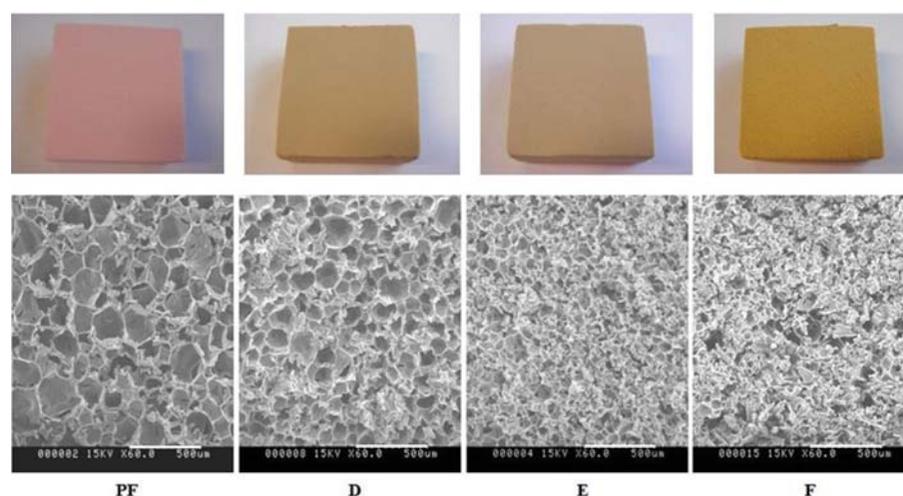


Figure 1

Table 2 Solid content and viscosities of resins.

Resin	PF, P/F ratio of 1/1.7	PFT, P:T 70:30 and P/F ratio of 1/2.5	PFT, P:T 70:30 and P/F ratio of 1/1.7
Solid content (%)	77	72.2	75.9
Viscosity at 25°C (mPa.s)	3700	3420	4755

2.4 Characterisation of Foams

Characterisation of the foams (appearance, density, mechanical resistance) is necessary to determine their applications.

Solid contents and viscosities of all resins used for making the foams are in the same range, around 75% and 3900 mPa.s (Table 2), in order that a meaningful comparison of the foams' characteristics be obtained.

2.4.1 Scanning Electron Microscopy (SEM)

The SEM observations were done with a Hitachi S-520 scanning electron microscope and with prior metallization of samples.

Foams were observed perpendicularly to their growth direction at x60 magnification. The samples tested had a density close to the average of the densities of the foam samples. The PF foam (P/F ratio of 1/1.7) and PFT (P:T 70:30 and P/F ratio of 1/1.7) foams prepared at 80°C were studied (Foams D, E and F).

2.4.2 Mechanical Resistance under Compression

The mechanical tests were performed in compression (NF EN 13166) by using an Instron 5944 universal testing machine equipped with a 2 kN head load cell. Compression was performed at a constant rate of 2.0 mm/min. The sample sizes were 1.5 × 3 × 3 cm³ and they were tested in the axial direction of the foam growth. The two samples that were tested had a density close to the average of the densities of the foam samples.

2.4.3 Thermal Conductivity

Thermal conductivity was measured using the transient planar source method (NF EN 13166) with a thermal conductivity analyzer Hot Disk TPS 2500, with a power of 10 mW for 40 seconds and equipped with a sensor 5501 with a radius of 6.403 mm. These tests were performed at room temperature and controlled humidity. The sensor was placed between two samples of size 1.5 × 3 × 3 cm. Conditions of the laboratory air were: 22°C +/- 1°C, 50% +/- 2% relative humidity.

Two samples that have been tested have a density close to the average of the densities of the foam samples. Two samples are needed to do one test, and it was repeated one time.

2.4.4 Water Absorption

The water absorption test involved keeping foam samples immersed in water for an entire week. Then, samples were removed from the water and drained for fifteen minutes on a 30° inclined grid (Iram1861).

The absorption related to the initial volume of the sample was determined using the formula: $\frac{\text{final mass} - \text{initial mass}}{\text{Initial volume}} \times 100$

. Masses are in grams and volumes in cm³. The samples that were tested had a density close to the average of the densities of the foam samples.

3 RESULTS AND DISCUSSION

3.1 Characterisations of Resins

3.1.1 Exothermic Behaviour

Concerning the exothermic behaviour for the PF resin at P/F molar ratio 1/1.7, the maximum temperature seems to decrease over time, but the starting temperature also seems to influence the final reactivity of the resin (Table 3).

For the PFT resin at P:T 70:30 weight ratio and P/F molar ratio of 1/2.5, elapsed time to peak temperature globally increases with resin ageing, and the difference between highest and starting temperature increases with time. However, the peak temperature increases with resin ageing while the opposite would have been logically expected. This phenomenon could be explained by the increase of the starting temperature, which implies an augmentation of peak temperature. An alternative explanation is that the PFT resin reactivity increases over time. This appears so because the starting temperature only increases 2°C between the first and the last test, while the peak temperature increases to 4.5°C. The PFT resin at P:T 70:30 and P/F molar ratio of 1/2.5 seems to remain reactive for a rather long time after it has been synthesized (Table 3).

Table 3 Exothermal behaviour of PF and PFT resins.

Resin	Days	Starting temperature (°C)	Maximal temperature (°C)	Difference between maximal and starting temperature (°C)	Elapsed time before the peak of temperature
PF, P/F ratio of 1/1.7	J	17.5	32.9	15.4	7 min 30 sec
	J + 7	19.2	29.2	10.0	7 min 30 sec
	J + 14	21.3	37.2	15.9	7 min 57 sec
	J + 28	21.7	37.4	15.7	7 min 50 sec
	J + 35	20.1	30.2	10.1	6 min 42 sec
PFT, P:T 70:30 and P/F ratio of 1/2.5	J	18.5	27.5	9.0	3 min 30 sec
	J + 7	19.3	29.5	10.2	2 min 30 sec
	J + 14	20.7	31.0	10.3	2 min 50 sec
	J + 28	20.4	32.0	11.6	3 min 03 sec
PFT, P:T 70:30 and P/F ratio of 1/1.7	J	19.2	29.1	9.9	1 min 56 sec
	J + 7	19.3	29.5	10.2	2 min 30 sec
	J + 14	20.7	32.2	11.5	4 min 15 sec
	J + 28	20.5	32.6	12.1	4 min 00 sec

Table 4 Viscosities of PF resin (P/F ratio of 1/1.7) and PFT resin (P:T 70:30 and P/F of 1/2.5).

Resin	Storage	At room temperature		At 35°C	
	Days	Viscosity (cP)	% of increase	Viscosity (cP)	% of increase
PF, P/F ratio of 1/1.7	J	12607	/	13370	/
	J + 14	21125	67.57	69500	419.82
	J + 21	27050	114.57	Unmeasurable, too thick	/
	J + 28	29941	137.50	Unmeasurable, too thick	/
	J + 35	32579	158.42	Unmeasurable, too thick	/
PFT, P:T 70:30 and P/F ratio of 1/2.5	J	5191	/	5284	/
	J + 14	6530	25.80	Unmeasurable, gelled	/
	J + 21	10885	109.70	Unmeasurable, gelled	/
	J + 28	16041	209.04	Unmeasurable, gelled	/
	J + 35	21718	318.40	Unmeasurable, gelled	/

For the PFT at P:T 70:30 and P/F molar ratio of 1/1.7, the elapsed time to the peak of temperature increases with the ageing of the resin (Table 3). However, the maximum temperature also increases with the ageing of the resin; and the difference between maximal and starting temperature also increases with the time.

By comparing the PFT resins of different P/F molar ratio, we note that the maximum temperatures reached are substantially the same. However, for the P/F 1/2.5 resin, the times required to achieve the maximum temperature are longer and increase more rapidly with the ageing of the resin. Thus, the PFT resin with P/F ratio of 1/1.7 is the best one as regards this property.

3.1.2 Viscosity

The viscosity of the PFT resins and PF resin were compared after storing the resins at room temperature (around 20°C) and 35°C. The viscosities increase as a function of storage time. This test was conducted on a PF resin of molar ratio 1/1.7 and PFT resin P:T 70:30 and P/F molar ratio 1/2.5 (Table 4).

The viscosity of the PFT resin P:T 70:30 and P/F ratio of 1/2.5, only shows a small increase of 26% after 14 days of ageing. However, we can see that in the long term the PFT resins are not very heat resistant. This could be explained by the reactivity of these

resins, which are quite important, and because of the coreactions between PF resin groups and chestnut tannins oligomers which are favored by the temperature. Thus, the lengths of the chains are increasing, so therefore the viscosity is also increasing.

With the PFT resin, P:T 70:30 and P/F ratio of 1/1.7, after a week the resin sample almost gelled.

However, by reducing the initial viscosity to 3000 or 3500 cP, the resin remains reactive and usable for a longer time and the viscosity does not increase much over time. Thus, the foams have been prepared with a resin which was aged for one month. The starting viscosity is thus a crucial parameter for the storage and the use of such resins over time.

3.2 Characterisations of Foams

3.2.1 Macroscopic Observation

Foams cured at 80°C and prepared with pMDI were slightly denser. Foams with pentane as blowing agent when mixed acids are used as catalyst are denser than those catalyzed with only phenol sulfonic acid.

Foams with a PFT resin and phenol sulfonic acid as catalyst were beige coloured compared to those obtained with the control PF resin, which were pink. Foams made with PFT resin and with the mix of acids are slightly clearer and their pores are finer than for foams made with PFT resin and with only phenol sulfonic acid. The PFT foams obtained with pMDI are orange coloured.

Foams cured at 60°C have almost the same appearance as those obtained at 80°C. Foams prepared with pMDI are also slightly denser. On the other hand, with pentane foaming, the one with the acids mixture is of lower density than the one with only phenol sulfonic acid, whatever the foaming temperature used.

3.2.2 Scanning Electron Microscopy

The PF only foams present the greatest porosity. Coreacting chestnut tannins with the PF resin yields foams of finer porosity (Figure 1).

Foams with the mix of acids (phenol sulfonic and sulfuric acids [50/50] at 65% in ethylene glycol) as catalyst present a finer porosity than the one with just phenol sulfonic acid. They are also more resistant to cutting than the one with pMDI foaming and with phenol sulfonic acid at 65% in water as catalyst (Figure 1).

Foams with phenol sulfonic acid at 65% in ethylene glycol as catalyst, have a bigger porosity than those catalysed with either the mix of acids or with pMDI. These last two have similar porosity (Figure 1).

3.2.3 Mechanical Resistance

The PF foams with and without chestnut tannins have typical behaviour of cellular solids with open porosity. Their deformation under compression takes place in three phases: a linear elastic phase, a plateau stress phase and finally a densification phase (Table 5 and Figures 2 to 4).

As regards the PFT resin P:T 70:30 and P/F ratio of 1/2.5 (Table 5 and Figure 2):

- Mechanical resistances of foams are directly related to their densities.
- The foams prepared with pMDI are the densest and the strongest.
- The experimental foam made with the mix of acids is the one that is closest to PF control resin foam, P/F ratio of 1/1.7, while it is denser than the latter.
- Foams made with phenol sulfonic acid at 65% in ethylene glycol, the density of which is closer to the one of PF control resin foam, are slightly weaker.

Looking at the first part of the compression curve, PFT foams deform less than PF foams. The foaming temperature influences the characteristics of the PFT foams, P:T 70:30 and P/F ratio of 1/1.7 (Table 5 and Figures 3 and 4). Thus, for the compressive strength at 20% strain, for foams made with pMDI and the mix of acids, the strongest is the one prepared at 60°C. On the contrary, the temperature did not have a big influence on the formulation with phenol sulfonic acid at 65% in ethylene glycol. Foams made with pMDI which are denser are also the most mechanically resistant. This time foams resistances are not directly related to their densities. Indeed, foam B has a compressive strength at 20% strain higher than foam A, whereas the density of foam A is higher.

Foams made with 65% phenol sulfonic acid in ethylene glycol are those closest to the PF foam, while they are much denser than the latter.

When we are looking at the first part of the curve, phenolic foams with tannins deform less under compression than the pure PF foam. This phenomenon is more pronounced for a foaming temperature of 80°C.

By comparing the foams produced with the two types of PFT resins catalysed with the mix of acids, at the same foaming temperature (80°C), almost the same mechanical properties are obtained. However, it can be said that the resin with a P/F molar ratio of 1/2.5 provides slightly more resistant foam.

Of the foams catalysed with the 65% phenol sulfonic acid in ethylene glycol, those made with 1/1.7 P/F molar ratio are the most resistant.

Table 5 Mechanical test results of foams.

Resin	Formulation	Compressive strength at 20% strain (MPa)	Young's modulus (MPa)	Densification (%)	σ_{pic} (MPa)	$\sigma_{plateau}$ (MPa)
PF, P/F ratio of 1/1.7	PF	0.1694	2.89	86.65	/	0.1779
	1	0.0771	1.72	74.64	/	0.0786
PFT, P:T 70:30 and P/F ratio of 1/2.5	2	0.1659	4.48	71.51	/	0.1970
	3	0.3128	8.63	76.22	/	0.3206
	A	0.1611	1.93	85.08	0.1636	0.1621
	B	0.2343	9.09	86.63	0.2421	0.2200
PFT, P:T 70:30 and P/F ratio of 1/1.7	C	0.3541	19.07	75.90	0.3956	0.3632
	D	0.1747	5.50	85.77	/	0.1844
	E	0.1617	5.31	83.30	/	0.1690
	F	0.2862	22.02	77.53	0.3441	0.3013

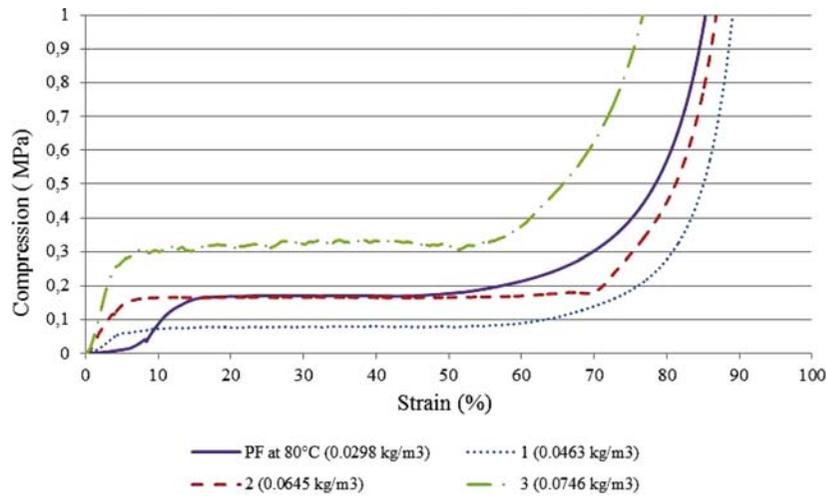


Figure 2

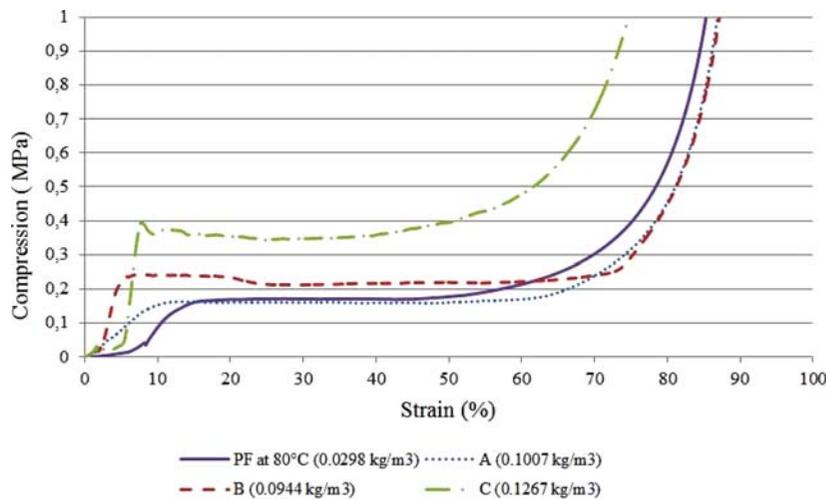


Figure 3

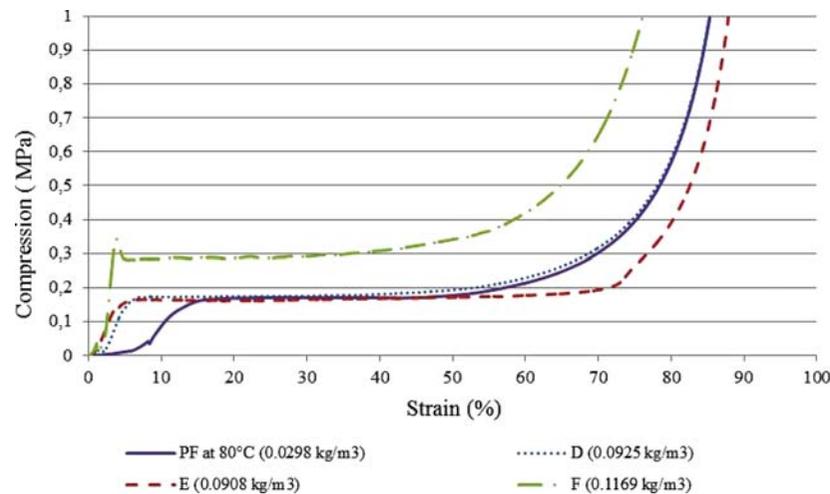


Figure 4

Foams prepared with pMDI have similar mechanical properties, although foams made with a P/F molar ratio of 1/2.5 are slightly stronger. The compression stress-strain curve of this foam has a peak before the plateau, which is not the case for the 1/1.7 P/F molar ratio foam.

3.2.4 Thermal Conductivity

As a reference, thermal conductivity of the control PF foam, P/F molar ratio 1/1.7, was measured. The value was 0.04350 W/(m.K), for a density of 0.0298 kg/m³.

When foaming at 80°C (Table 6), the more insulating PFT resin is the one with pMDI of finer porosity than the pure PF foam. The PFT foams are less insulating than pure PF foams. Foam 2, which has a density comparable to that of the PF foam, presents a thermal conductivity that is almost twice as high. The foam (with the mix of acids) having a fine porosity is the one which also has a higher thermal conductivity. If fine porosity is wanted, then pMDI addition gives a better level of insulation.

The PFT foams prepared at 60°C (Table 6) are slightly more insulating than those prepared at 80°C, but slightly denser. The most insulating foams are those made with pMDI.

The PFT foams are markedly less insulating than pure PF foams, which is most probably due to the higher proportion of polymeric carbohydrates present in hydrolysable tannins. In all these cases the thermal conductivity of these foams does not appear to be directly related to their densities.

By comparing foams produced with the two types of PFT resins at the same foaming temperature (80°C), foams made with phenol sulfonic acid at 65% in

Table 6 Thermal conductivity results of foams.

Resin	Formulation	Thermal conductivity (W/(m.K))	
PF, P/F ratio of 1/1.7	PF	0.04350	
	1	0.08397	
	PFT, P:T 70:30 and P/F ratio of 1/2.5	2	0.10435
		3	0.07373
		A	0.07908
	PFT, P:T 70:30 and P/F ratio of 1/1.7	B	0.07607
C		0.06052	
D		D	0.08677
		E	0.07671
		F	0.07327

ethylene glycol and with pMDI have almost the same thermal properties.

For foams catalysed with the mix of acids, the foam at P/F molar ratio of 1/1.7 is the most insulating one.

As regards the influence of the catalyst type with pentane foams, the most insulating foams are those exclusively prepared with 65% phenol sulfonic acid in ethylene glycol for the PFT resin at P:T 70:30 and P/F molar ratio of 1/2.5. Conversely, for the PFT resin at P:T 70:30 and P/F ratio of 1/1.7 the most insulating foam is the one prepared with the mix of acids.

The PFT foams with pMDI are the most insulating ones when compared to those foamed by pentane. However, they are denser and they have a finer

Table 7 Water absorption results of foams.

Resin	Formulation	Percentage of absorbed water relative to the volume (%)
PF, P/F ratio of 1/1.7	PF	35.40
PFT, P:T 70:30 and P/F ratio of 1/2.5	1	23.79
	2	25.35
	3	30.34
	A	26.97
	B	25.13
PFT, P:T 70:30 and P/F ratio of 1/1.7	C	27.17
	D	27.56
	E	22.23
	F	34.22

porosity than other foams with tannins. They seem to present a fine closed-cell porosity.

3.2.5 Water Absorption

The PFT foams appear to be more water resistant than pure PF foams prepared with the PF control resin, P/F ratio of 1/1.7 (Table 7).

For the PFT resin, P:T 70:30 and P/F ratio of 1/2.5, the most water resistant foam is the one with pentane as blowing agent and 65% phenol sulfonic acid in ethylene glycol as catalyst.

For the PFT resin, P:T 70:30 and P/F ratio of 1/1.7, the most water-resistant foams are the one with pentane as blowing agent and the mix of acids as catalyst, whatever the foaming temperature used. In general the foams with pentane as blowing agent are more water resistant than the one with pMDI (for this type of foaming it is better to use a foaming temperature of 60°C for best water resistance). Concerning foams made with the mix of acids, the one which is slightly more water resistant is the one foamed at 80°C. The water absorptions of foams prepared with phenol sulfonic acid at 65% in ethylene glycol are similar.

Therefore, there is no general connection between the water absorption and the foaming temperature. Moreover, there appears to be an evident link between density and water absorption of such PFT foams; the less dense they are, the more water resistant they are.

4 CONCLUSIONS

The preparation of PFT resins with P/F molar ratio of 1/1.7 is possible. This is the same molar ratio as

commercial PF resins. Thus, the substitution of chestnut tannins for part of the phenol in such resins is possible. This approach is an alternative route to make value-added foams different from the condensed tannin/furanic foams already presented [3–7] by using a different raw material.

The study of the effect of the catalysts used shows that the use of sulfuric acid and phenol sulfonic acid yields less friable foams. The catalyst generally used for the preparation of tannin foams is *para*-toluene sulfonic acid at 65% in water, but this was found to be unsuitable for PFT foams. Moreover, foams obtained with the mix of sulfuric acid/phenol sulfonic acid are highly homogeneous and have very fine porosity. A further point of interest is that it is possible to replace pentane blowing agent with pMDI using the development of CO₂ of its reaction with water for foaming. As pentane is inflammable, explosive and has a low boiling point (36°C), one needs to take precautions to use and store it in a factory; the pMDI route is also a viable alternative.

Furthermore, the use of chestnut tannins in PF foams improves foam. Thus, PFT resin seems to remain reactive for rather a longer time than PF resins after its synthesis.

Concerning mechanical resistance, PFT foams deform less under compression and are more resistant than the pure PF control foam. In addition to that, PFT foams based on hydrolysable tannins appear to be more water resistant than PF foams.

Conversely, PFT foams have a thermal conductivity between 0.061 and 0.104 W/(m.K), which is higher than PF foam; this can be explained by the fact that they are also much denser.

The PFT foams which seem to be the most interesting are those which are more insulating and more mechanically resistant to water, which are those foamed at 60°C with a PFT resin at a P/F ratio of 1/1.7. These are also the ones of highest density.

This study shows that it is totally possible to replace an amount of petrochemicals by a natural resource such as chestnut tannins in the formulation of phenolic resins and phenolic foams.

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REFERENCES

1. A. Sauget, X. Zhou, A. Pizzi, Tannin-resorcinol-formaldehyde resin and flax fiber biocomposites. *J. Renew. Mater.* **2**, 1–9 (2014).
2. X. Zhou, A. Pizzi, A. Sauget, A. Nicollin, X. Li, A. Celzard, H. Pasch, K. Rode. Lightweight tannin foam/composites sandwich panels and the coldset tannin adhesive to assemble them. *Ind. Crops Prod.* **43**, 255–260 (2013).
3. G. Tondi, A. Pizzi, R. Olives, Natural tannin-based rigid foams as insulation for doors and wall panels, *Maderas: Ciencia y Tecnología*, **10**, 219–227 (2008).
4. G. Tondi, W. Zhaos, A. Pizzi, G. Du, V. Fierro, A. Celzard, Tannin-based rigid foams: A survey of chemical and physical properties, *Bioresour. Technol.* **100**, 5162–5169 (2009a).
5. G. Tondi, C.W. Oo, A. Pizzi, A. Trosa, M.F. Thevenon. Metal adsorption of tannin based rigid foams. *Ind. Crops Prod.* **29**, 336–340 (2009).
6. C. Lacoste, M.C. Basso, A. Pizzi, M.P. Laborie, A. Celzard, Pine tannin-based rigid foams: Mechanical and thermal properties. *Ind. Crops Prod.* **43**, 245–250 (2013).
7. M.C. Basso, S. Giovando, A. Pizzi, M.C. Lagel, A. Celzard. Alkaline tannin rigid foams. *J. Renew. Mater.* (2014) In press 2014.
8. L. Pilato, Phenolic Resins: A Century of Progress, Springer-Verlag Berlin Heidelberg (2010).
9. L. Hu, H. Pan, Y. Zhou, M. Zhang, Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review. *BioResources* **6**, 3515–3525 (2011).
10. S. Spina, X. Zhou, C. Segovia, A. Pizzi, M. Romagnoli, S. Giovando, H. Pasch, K. Rode, L. Delmotte. Phenolic resin adhesives based on Chestnut (*Castanea sativa*) hydrolysable tannins. *J. Adhes. Sci. Technol.* **27**, 2103–2111 (2013).
11. C. Zhao, A. Pizzi, A. Kühn, S. Garnier, Fast advancement and hardening acceleration of low condensation alkaline phenol-formaldehyde resins by esters and copolymerized urea. II. Esters during resin reaction and effect of guanidine salts. *J. Appl. Polym. Sci.* **77**, 249–259 (2000).