

## **Towards a feasible and scalable production of bio-xerogels**

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### **ABSTRACT**

#### Hypothesis

The synthesis process of carbon xerogels is limited, mainly due to two drawbacks that prevent their introduction onto the market: i) the long time required for producing the material and ii) the reagents used for the synthesis, which are costly and harmful to the environment. Microwave radiation is expected to produce a reduction in time of more than 90%., while the use of tannin instead of resorcinol will probably result in a cost-effective carbonaceous material.

#### Experiments

Resorcinol-tannin-formaldehyde xerogels containing different amounts of tannin, either with or without a surfactant (sodium dodecyl sulfate), were synthesized by means of two different heating methods: conventional and microwave heating. The effects of the surfactant, the heating method and the addition of tannin upon the porous structure and the chemical composition of the final materials were evaluated.

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## Findings

It was found that the addition of surfactant is essential for obtaining highly porous xerogels when using tannins. The heating method also plays an important role, as conventionally synthesized samples display a greater volume of large pores. However, tannins are less sensitive to microwave radiation and their use results in tannin-formaldehyde xerogels that have a porous structure and chemical composition similar to those of resorcinol-formaldehyde xerogels.

**Keywords:** xerogels, tannins, microwave radiation, surfactant, porous properties

## **1 Introduction**

Carbon xerogels are porous materials that are obtained by drying and carbonizing an organic gel [1]. The organic gel is usually synthesized by the polymerization of hydroxylated benzenes and aldehydes in the presence of a solvent [2]. These materials have attracted interest due to the fact that their porous structure and chemical composition can be controlled by the right choice of synthesis conditions [3-5], to produce a wide range of tailor-made and purpose designed materials, whose characteristics meet the needs of specific applications. Hence, it can be said that carbon xerogels are high value-added materials that have a strong commercial potential. However, the synthesis process is handicapped by two major drawbacks that prevent their introduction onto the commercial market: i) the conventional synthesis process, which involves heating the precursor solution in an electric furnace, requires several days to produce organic xerogels [2]; and ii) the most common reagents used for the synthesis, resorcinol and formaldehyde, are costly and harmful to the environment [6].

In 2011, Calvo et al. (2011) addressed the first drawback by applying microwave radiation to all three stages of the synthesis process: sol-gel reaction, curing and drying. By this heating method, a reduction in time of more than 90% was achieved (from several days to 5-6 hours), while the materials obtained displayed similar chemical and porous properties to those conventionally synthesized [7, 8]. Organic xerogels synthesized by microwave heating are generally prepared from resorcinol and formaldehyde and, as mentioned above, these reactants are harmful to the environment. However, some authors have reported that by means of conventional synthesis it is possible to obtain carbon gels by using phenol [9], cresol [10, 11], tannins [6, 12] or

cellulose [13] as hydroxylated benzenes and furfural [14] or hexamethylenetetramine [15] as aldehydes.

Of all the possible reagents mentioned above, tannins are considered to be the most viable option at industrial scale as they are “eco-friendly”, cheap and non-toxic [16]. Condensed (flavonoid) tannins are phenolic compounds derived from wood. Because they contain reactive hydroxyl groups, they are similar to resorcinol in the way they react towards aldehydes and are transformed from sols to gels [17]. These advantageous chemical characteristics explain why in recent years the number of studies on the use of tannins for the synthesis of different carbonaceous materials has increased [16-20]. The first study to deal with the use of tannins for the synthesis of carbon gels was focused on the synthesis of aerogels and cryogels [19, 20], since xerogels gave rise to highly dense materials with a poorly developed porous structure. Amaral-Labat et al. (2013) were the first to synthesize highly porous tannin-based xerogels by adding Pluronic F-127 as surfactant [17]. Nevertheless, a period of ten days was needed to obtain these conventionally synthesized xerogels. Furthermore, in order to dissolve the Pluronic, it was necessary to use an organic solvent, which increased the cost of the final product.

The aim of the present work is to address the two main drawbacks that have so far prevented the fabrication of a cost-competitive carbonaceous material at industrial scale and its commercialization, by means of the microwave-assisted synthesis of tannin-formaldehyde xerogels. An attempt has been made to synthesize organic xerogels by conventional and microwave heating using tannin instead of resorcinol. Moreover, an anionic surfactant, which does not require the addition of an organic solvent, was employed to produce highly porous materials. All of the synthesized xerogels were

characterized from the point of view of their chemical and porous structure so as to determine the effect of using tannin instead of resorcinol and to ascertain possible differences in properties due to the synthesis method employed.

## **2 Materials and methods**

### *2.1 Raw materials*

Commercial wattle tannin extracted from *Acacia Mearnsii (De Wild)* barks was used for the present study. This raw material was kindly supplied by SilvaChimica (San Michele Mondovi, Italy) under the name Fintan OP. The industrial extraction process of tannins has been explained in detail elsewhere [16]. Briefly, fresh bark was leached in a sodium bisulphite aqueous solution at 70°C. The resulting solutions were concentrated and then spray-dried to yield a light-brown powder containing 80-82 wt. % of phenolic flavonoid materials, 4-6 wt. % of water, 1 wt. % of amino acids, the remaining components being monomeric and oligomeric carbohydrates in the form of broken pieces of hemicellulose. As from now, the light-brown powder thus obtained will be referred to simply as tannin (T).

Other chemicals used included resorcinol (Sigma Aldrich, 99%), formaldehyde (Roth, 37 wt. % in water, stabilized by 10-15 wt. % methanol), sodium dodecyl sulfate (Sigma Aldrich) and sodium hydroxide (Carlo Erba).

### *2.2 Preparation of organic xerogels*

Organic gels were synthesized by the polycondensation of resorcinol (R), tannin (T) and formaldehyde (F) using deionized water as solvent, sodium hydroxide as catalyst and sodium dodecyl sulfate (S) as surfactant. The method employed for preparing the

precursor solutions was the same in all cases. Resorcinol was first dissolved in deionized water in unsealed glass beakers under magnetic stirring. Once the resorcinol had dissolved, tannin was added, still under stirring at room temperature, until complete dissolution. Formaldehyde was then introduced into the solution. Finally, sodium dodecyl sulfate was added and the resulting mixture was stirred until a homogeneous brown solution was obtained.

All the gels were synthesized from 20 ml of precursor solution. The final pH value was adjusted to 5.5 by adding sodium hydroxide. In all cases, the resorcinol-tannin/formaldehyde weight ratio and the percentage of solids were fixed at 1.2 and 25 wt. %, respectively. Ten different precursor solutions using different amounts of tannin, ranging from 0 to 100 wt. % to replace resorcinol either partly or completely, were prepared. Anionic surfactant was added to five of these solutions, in amounts that would ensure that their concentration was 5 wt. %, whereas the other five solutions were kept surfactant-free. Each solution was split into two batches and subjected to two different heating methods: conventional (C) or microwave (MW) heating. The resultant organic xerogels obtained after drying (see details below) were labelled 'RTF' followed by the percentage of tannin used to replace the resorcinol, i.e., 0, 25, 50, 75 and 100 wt. %. An 'S' was appended to the name of those samples containing surfactant. Finally, 'C' or 'MW' was added to indicate the type of heating applied. For example, the sample RTF-75-S-MW refers to a microwave-assisted synthesized xerogel prepared with 75 wt. % of tannin (the other 25 wt. % being resorcinol) and 5 wt. % of surfactant.

### *2.2.1 Conventional synthesis*

The precursor solutions were poured into sealed glass tubes which were then placed in a ventilated oven at 85 °C for 72 h to undergo gelation and curing. Afterwards, the tubes were opened and introduced again into the oven at 85 °C for 48 h for the purpose of completely drying the organic gels by evaporation of the solvent. This temperature was selected according to the procedure proposed by Job et al. for the conventional synthesis of RF xerogels [2].

### *2.2.2 Microwave-assisted synthesis*

In the case of microwave-assisted synthesis, the precursor solutions were poured into unsealed glass beakers (transparent to microwaves) which were placed in a multimode microwave oven (in-lab design and construction) at 85 °C for 3 h to undergo gelation and curing. After the formation of the polymeric structure, any excess water was eliminated by continuing to heat the gel in the microwave oven until constant mass was reached. This drying step lasted from 1 to 2 h. These heating conditions were selected from previous studies on the synthesis of RF xerogels by microwave heating [3].

## *2.3 Sample characterization*

### *2.3.1 Porous properties*

The specific pore volume and the average pore size were measured by means of mercury porosimetry (Autopore IV, Micromeritics) and by applying Washburn's equation to the corresponding data. Measurements were performed between 0.0035 and 414 MPa. Bulk and skeletal densities were determined by helium (Accupyc II 1340, Micromeritics) and envelope (Geopyc 1360 Envelope Density Analyzer, Micromeritics) pycnometry, respectively. The overall porosity was determined from the bulk and skeletal densities.

### *2.3.2 Chemical composition*

The chemical composition of the samples was determined by elemental analysis (C, H, O, N, S), using an Elemental Vario Cube (from Elementar) microanalyzer.

### *2.3.3 FT-IR spectroscopy*

The chemical structure of the RTF xerogels was investigated by using an Infrared Affinity-1 spectrometer (Shimadzu, Japan) over a range of 4000–400  $\text{cm}^{-1}$  and by applying an average of 20 scans at a maximum resolution of 4  $\text{cm}^{-1}$ . For this purpose, pellets were prepared by pressing 1 mg of sample ground together with 100 mg of dry potassium bromide.

### *2.3.4 Sample morphology*

Scanning Electron Microscope observation (FEI Quanta 600 FEG) was employed to evaluate the morphology of the materials.

## **3 Results and discussion**

### *3.1 Replacement of resorcinol by tannin*

Figure 1 shows the main porous properties of the resorcinol-tannin-formaldehyde xerogels prepared by the different heating methods. As explained above, the set of samples labelled RTF-MW were synthesized by means of microwave heating, while those labelled RTF-C were conventionally synthesized.



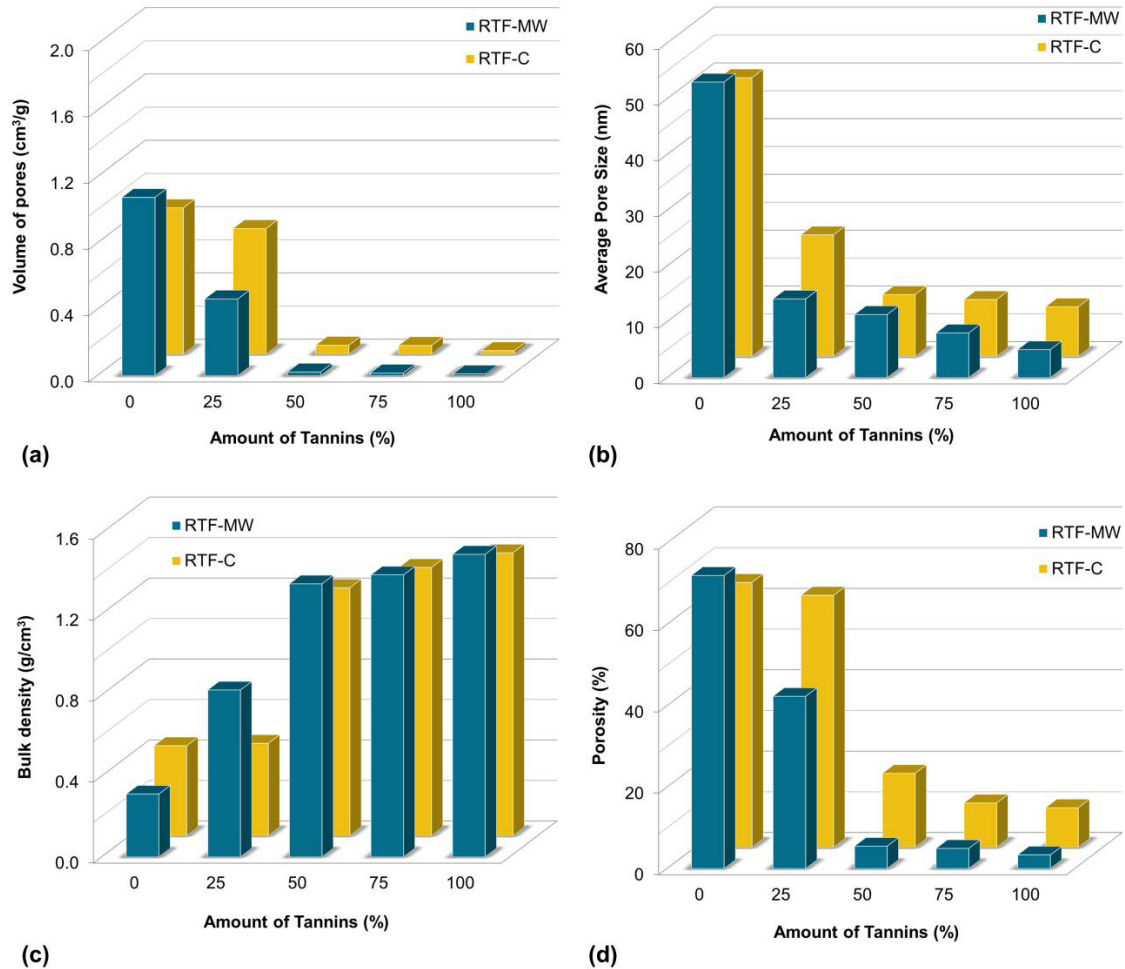


Figure 1. Porous properties of xerogels prepared using different heating methods in the absence of surfactant.

The two sets of samples showed no significant differences in properties despite the fact that the RTF-MW samples were synthesized in unsealed beakers, which should have caused them to undergo greater shrinkage due to the evaporation of the solvent throughout the synthesis process, resulting in strong capillary forces at the liquid-vapour interface [3]. However, the time required for gelation in microwave-assisted synthesis is much shorter and, although a certain degree of shrinkage did occur, the gelation time was not long enough for the polymeric structure to totally shrink [8], leading to

materials with porous properties similar to those of conventionally synthesized samples (Figure 1).

Pore volume, average pore size, porosity and density depend largely on the amount of tannin added to the precursor solutions, as illustrated in Figure 1. Regardless of the heating method, the addition of tannin resulted in a poorer development of the porous structure (i.e. porosity decreased from 65% to 10% and from 77% to 3% in the group of RTF-C and RTF-MW samples, respectively), as shown in Figure 1d.

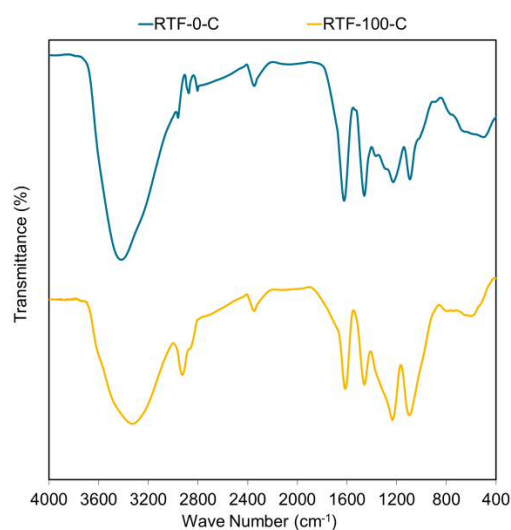
The replacement of resorcinol by tannin not only led to a change in the porous properties of the RTF xerogels but also affected their chemical composition, as can be seen in Table 1. The elemental analysis data of conventionally synthesized samples depends on the amount of reactants used to prepare the precursor solutions. The data in Table 1 indicate that the replacement of resorcinol by tannin caused an increase in the content of hydrogen, oxygen and nitrogen, whereas the percentage of carbon decreased. The RTF-MW set of samples (not shown in the Table 1) followed the same trend.

*Table 1. Elemental analysis of RTF-C xerogels.*

Sample	Elemental Analysis (wt. %, dry basis)				
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
RTF-0%-C	63.4	4.8	31.8	0.0	0.0
RTF-25%-C	61.7	4.9	33.4	0.0	0.0
RTF-50%-C	60.2	5.4	34.3	0.1	0.0
RTF-75%-C	56.4	5.6	37.9	0.1	0.0
RTF-100%-C	54.3	5.4	40.1	0.2	0.0

The increase in nitrogen content was probably due to impurities in the tannin as a result of the manufacturing process. The differences in the rest of elements can be attributed to the RT/F mass ratio chosen to prepare the precursor solutions, as the molecular weight

of resorcinol and tannin is very different (110.1 g/mol for resorcinol and between 800 and 1200 g/mol for tannin). Thus, for the same volume of precursor solution, there are fewer tannin molecules in sample RTF-100-C than resorcinol molecules in sample RTF-0-C. For this reason, sample RTF-100-C contains a smaller amount of carbon, even though a tannin molecule has a greater number of carbon atoms than a resorcinol molecule. On the other hand, the large size and the lack of flexibility of tannin molecules cause steric hindrance and therefore, the addition of formaldehyde is less effective than when resorcinol is used. Consequently, even though there are fewer tannin molecules in sample RTF-100-C, more OH groups remain unreacted, leading to an increase in the percentage of oxygen and hydrogen (see Table 1 and Table 3). These results are also corroborated by the infrared spectroscopy spectra presented in Figure 2.



*Figure 2. FT-IR spectra of samples RTF-0-C and RTF-100-C.*

The absorption bands assigned to C-O-C stretching (1000-1200  $\text{cm}^{-1}$ [12]) and C-O-H bonds attributed to aromatic rings (1200-1300  $\text{cm}^{-1}$  [12]) are more intense in sample RTF-100-C than for RTF-0-C, which indicates more oxygen and hydrogen content in

the tannin based sample. On the other hand, sample RTF-100-C shows slightly less intense peaks in the absorption region of 1600 and 1400  $\text{cm}^{-1}$  attributed to the characteristic mode of aromatic rings and C-H bonds, respectively [2], probably due to the lower amount of aromatic rings. The more intense bands around 2900-2800  $\text{cm}^{-1}$ , which can be attributed to C-H bonds [2], indicates that chains between tannin molecules are larger. Finally, large peaks at 3500  $\text{cm}^{-1}$ , characteristic of O-H bonds vibration, can be observed. Accordingly, tannin based sample probably have less amount of aromatic rings which are linked by larger chains. As a result, larger voids between clusters are formed. However, the structure is not able to withstand the surface tension created during drying and the structure collapses, resulting in a non-porous material. Nevertheless, a comparison of the RTF-100-C and RTF-0-C samples reveals that both resorcinol and tannin react with formaldehyde, leading to the same types of bond. This demonstrates the great potential that tannins offer as a substitute for resorcinol, even in a case such as this, where the complete replacement of resorcinol by tannin leads to poorly porous polymeric structures (Figure 1).

### *3.2 Addition of surfactant*

Figure 3 shows the main porous properties of resorcinol-tannin-formaldehyde-surfactant xerogels prepared using the two different heating methods. Irrespective of the heating method, the effect of the surfactant is clear from a comparison of Figure 1 and Figure 3. As expected, the dissolved surfactant formed micelles, leaving negative charges in contact with the reaction medium, which exerted repulsive forces on the resorcinol and tannin anions [1]. As a result, during the sol-gel reaction, the structure formed more slowly and farther away from the surfactant anions, leading to a greater volume of pores of larger size than when no surfactant was used (see Figure 1a and 3a and Figure 1b and

3b, respectively). Thus, it seems that the addition of sodium dodecyl sulfate is a key factor for the synthesis of highly porous materials.

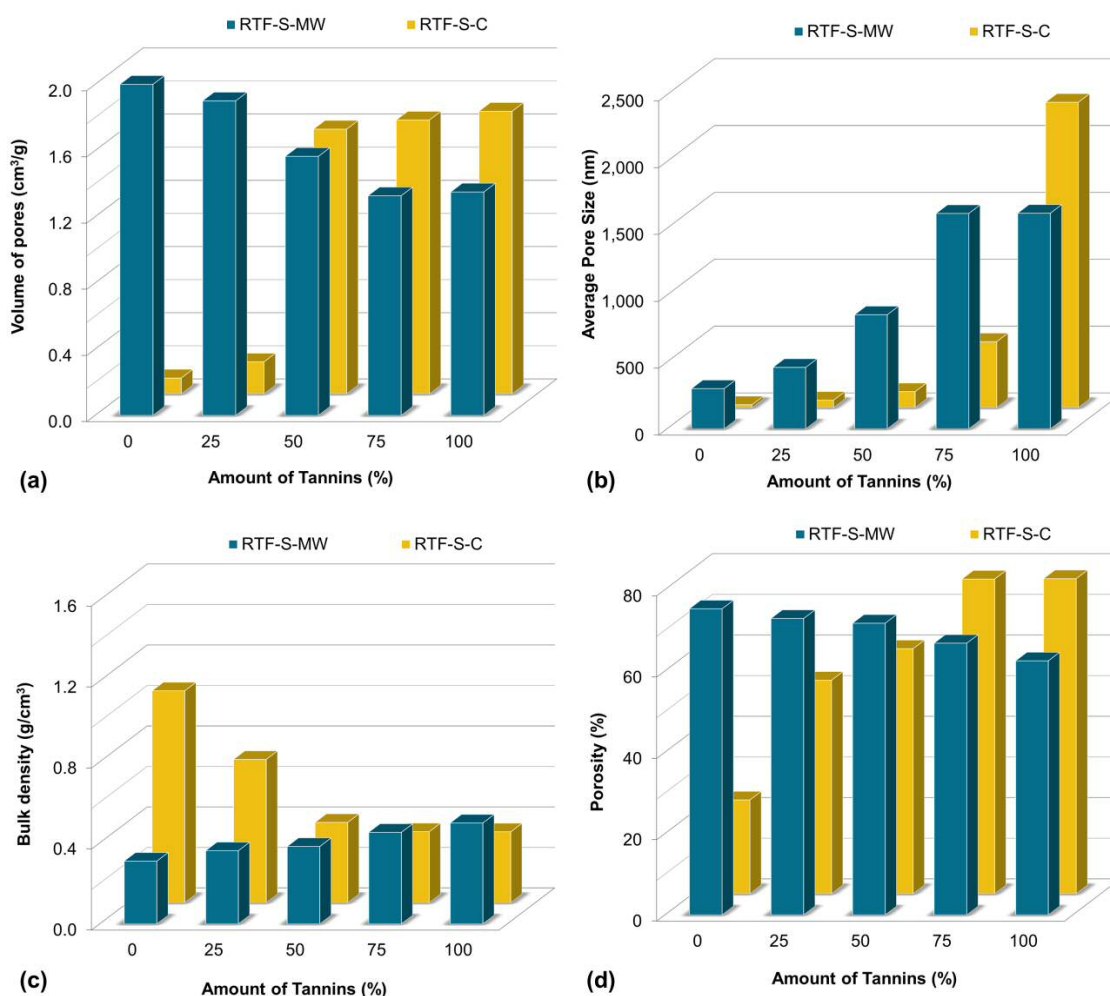


Figure 3. Porous properties of xerogels prepared using different heating methods in the presence of surfactant (5 wt. % of sodium dodecyl sulfate).

If the heating methods are compared, only the pore size follows the same trend in both the RTF-S-C and RTF-S-MW sets of samples (Figure 3b). It can be seen that the size of the pores increased as an increasingly higher amount of tannin replaced the resorcinol.

This trend may be related to the size of the tannin molecules, which is larger than that of

the resorcinol molecules, resulting in larger clusters and therefore, larger voids between clusters, as shown in Figure 4.

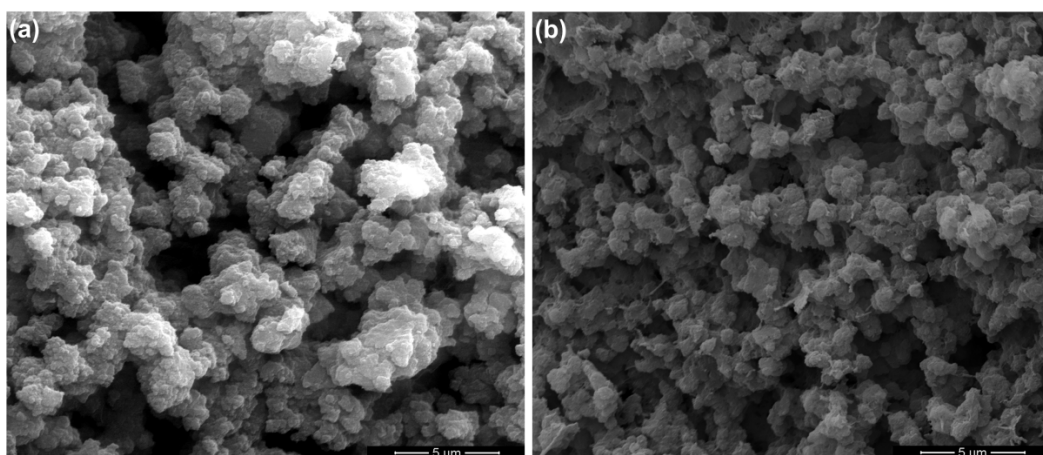


Figure 4.

Figure 4. SEM images of samples RTF-100-S-MW (a) and RTF-0-S-MW (b).

On the other hand, the specific pore volume, density and overall porosity exhibit opposite trends depending on the heating method (Figure 3). This is probably due to the fact that microwave radiation increases the reaction rate and hence the gelation point is reached faster. Thus, a smaller number of large clusters were formed during the polymerization reaction, as shown in Figure 5. The size of the clusters determines the size of the pores, which are larger in sample RTF-75-S-MW than in sample RTF-75-S-C (Figure 3b). It should also be noted that, generally, samples with small clusters exhibit greater densities. However, sample RTF-75-S-C has a low density value (Figure 3c). In this case, drying by conventional heating led to a slight shrinkage and, as the materials were highly branched (Figure 5a), the structure was able to withstand the surface tension created by the water content. Consequently, the structure did not collapse, resulting in a material with a larger volume of pores and greater porosity (Figure 3a and 3d).

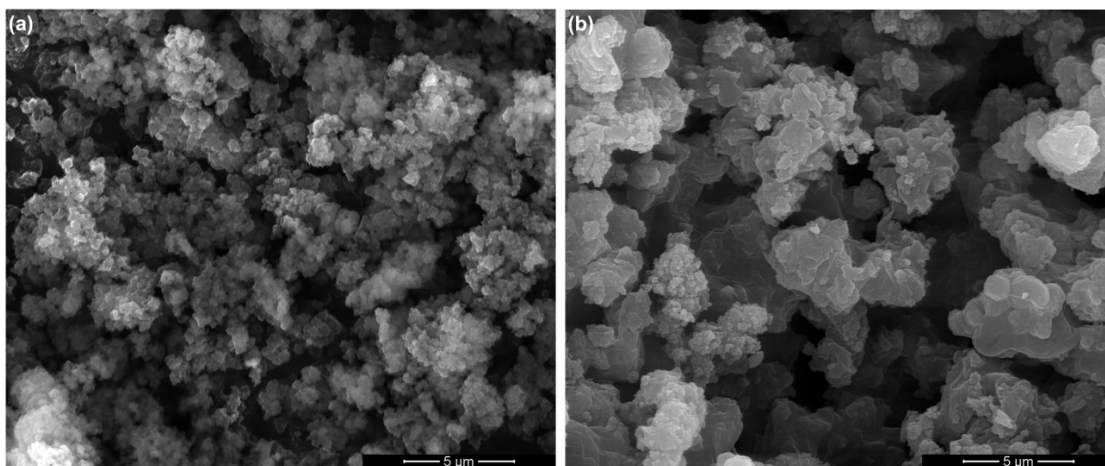


Figure 5. SEM images of samples RTF-75-S-C (a) and RTF-75-S-MW (b).

However, the differences between the RTF-S-MW samples are much smaller than those in the RTF-S-C series. In fact, the porosity decreased from 85% to 20% in the RTF-S-C samples series, whereas the decrease in porosity in the samples synthesized by microwave heating was only from 70 to 65%. Similarly, the density variations ranged from 0.3 to 1.0 g/cm<sup>3</sup> and only from 0.2 to 0.4 g/cm<sup>3</sup> for the RTF-S-C and RTF-S-MW series, respectively. Thus, the final porous properties of the xerogels obtained by adding tannin were less affected by MW heating than by conventional heating. This is because microwave causes the rotation of the permanent and induced dipoles of polar molecules, generating energy which is subsequently dissipated as heat [7]. Hence, the larger amount of OH groups in the tannin molecules favours the absorption of microwave energy and increases the temperature of the reaction medium. In light of this, tannin appears to be an excellent option as a reagent for the microwave-assisted synthesis of carbon xerogels.

The results of the present work are also in good agreement with those reported by Amaral et al. (2013). These authors conventionally synthesized TF xerogels at different

pH values using Pluronic F-127 as surfactant. The porous properties of a sample synthesized from a precursor solution with a pH value of 5 are shown in Table 2.

*Table 2. Porous properties of RTF xerogels synthesized via different routes.*

Sample	Density (g/cm <sup>3</sup> )	Porosity (%)	Volume of pores (cm <sup>3</sup> /g)	Average pore size (nm)
RTF-100-S-MW	0.47	62	1.4	1613
RTF-100-S-C	0.31	77	1.7	2285
[17]	0.31	78	2.2	14000

It can be deduced from the data in Table 2, that the RTF xerogels synthesized by adding sodium dodecyl sulfate as surfactant exhibit similar properties to those obtained using Pluronic F-127, although their average pore size is substantially lower. The xerogels synthesized by microwave heating underwent a slight shrinkage during drying, resulting in a slightly smaller pore size and a denser material (Figure 3b and 3c). Nevertheless, microwave heating seems to be a very promising technology as xerogels with a well-developed porous structure are obtained by employing a natural reactant and an easy, fast and scalable synthesis process [7].

As for the chemical composition of the samples with and without surfactant, the elemental analysis data provided in Table 3 show that the trends were similar in both cases. The 4 wt. % sulphur content and the slightly higher percentage of hydrogen and oxygen could have been due to the composition of the surfactant. The fact that the elemental analysis of the samples with and without surfactant showed the same trends suggests that no interaction occurred between the surfactant and the polymeric structure. These findings are confirmed by the infrared spectroscopy spectra in Figure 6.



Table 3. Elemental analysis of RTF-X-S-C xerogels.

Sample	Elemental Analysis (wt. %, dry basis)				
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
RTF-0-S-C	58.5	5.8	31.2	0.0	4.4
RTF-25-S-C	58.6	6.3	31.1	0.1	3.9
RTF-50-S-C	56.6	6.5	32.5	0.1	4.2
RTF-75-S-C	55.1	6.6	34.1	0.1	4.1
RTF-100-S-C	53.7	6.6	35.8	0.2	3.7

Sample RTF-100-S-C exhibits the same absorption bands as sample RTF-100-C and the surfactant. No additional bonds were formed, indicating that no reaction occurred between the polymeric structure and the surfactant. This will facilitate the removal of the surfactant during carbonization and ensure that the porous structure remains similar to that of the organic samples, although some possible shrinkage may occur due to the carbonization process itself.

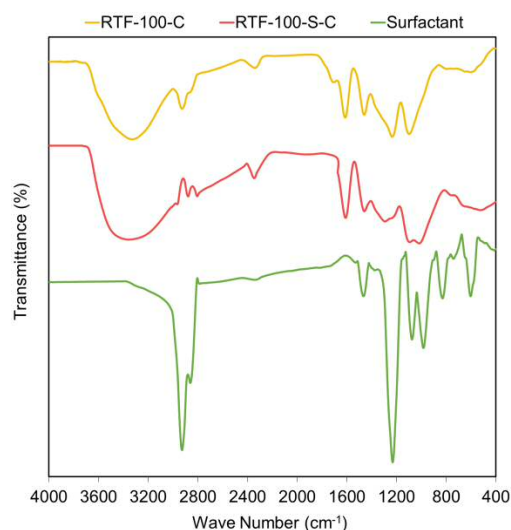


Figure 6. FT-IR spectra of samples RTF-100-C, RTF-100-S-C and anionic surfactant (sodium dodecyl sulfate).

## **Conclusions**

Organic xerogels by conventional and microwave heating using tannin instead of resorcinol has been synthesized. Heating by microwave radiation during the three stages of the synthesis process (sol-gel reaction, curing and drying), a reduction in time of 95% was achieved, as expected by the results presented in previous work [8]. It has been demonstrated that microwave-assisted synthesis of tannin-formaldehyde xerogels is a viable process which gives rise to materials with similar properties to those obtained by conventional heating [17]. However, to obtain tannin-formaldehyde xerogels with a well-developed porous structure it is necessary to use surfactants. The addition of 5 wt. % of sodium dodecyl sulfate yielded xerogels with 77% and 62 % of porosity under conventional and microwave heating, respectively. Although microwave heating produces slightly less porosity, this method is preferable as it is viable at industrial scale, allowing carbon xerogels to be produced at a lower cost.

Accordingly, in the present work, the two main drawbacks that have so far prevented the production of carbon xerogels at industrial scale and its commercialization have been successfully addressed. However, there are still many efforts to be done in this field as the final porous properties of the gels depends largely on the synthesis conditions, as explain in previous work [3]. Hence, it would be interesting to optimize the process including all the variables (pH, ration of reagents, dilution, etc) and their interrelation [3], in order to control the porous properties of tannin-formaldehyde carbon xerogels. The final step would be the substitution of formaldehyde by other monomer more environmental friendly, in order to obtain a real bio-xerogel material with tailored porosity.

## **Acknowledgements**

Financial support from the Ministerio de Economía y Competitividad of Spain MINECO (under Projects MAT2011-23733, IPT-2012-0689-420000 and CTQ2013-49433-EXP) is greatly acknowledged. NRR is also grateful to MINECO for her predoctoral research grant. The French authors also gratefully acknowledge the financial support of the CPER 2007-2013 “Structuration du Pôle de Compétitivité Fibres Grand’Est” (Competitiveness Fibre Cluster), through local (Conseil Général des Vosges), regional (Région Lorraine), national (DRRT and FNADT) and European (FEDER) funds.

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## **FIGURE CAPTIONS**

Figure 1. Porous properties of xerogels prepared using different heating methods.

Figure 2. FT-IR spectra of samples RTF-0-C and RTF-100-C.

Figure 3. Porous properties of xerogels prepared using different heating methods (for the RTF-S-MW and RTF-S-C samples).

Figure 4. SEM images of samples RTF-100-S-MW (a) and RTF-0-S-MW (b).

Figure 5. SEM images of samples RTF-75-S-C (a) and RTF-75-S-MW (b).

Figure 6. FT-IR spectra of samples RTF-100-C, RTF-100-S-C and anionic surfactant (dodecyl sulfate).

## **TABLE CAPTIONS**

Table 1. Elemental analysis of RTF-C xerogels.

Table 2. Porous properties of RTF xerogels synthesized via different routes.

Table 3. Elemental analysis of RTF-X-S-C xerogels.