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A Celzard and J F Marêché

Multifunctional porous solids derived from tannins

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Abstract. Tannins are extremely valuable, non toxic, wood extractives combining reactivity towards aldehydes, low cost, natural origin and easy handling. When polymerized in the presence of suitable chemicals including blowing agent, ultra lightweight rigid tannin-based foams are obtained. If pyrolyzed under inert gas, reticulated carbon foams having the same pore structure and the same density are obtained. The most remarkable features of tannin-based foams are the following: mechanical resistance similar to, or higher than, that of commercial phenolic foams, tuneable pore size and permeability, infusibility, very low thermal conductivity, cheapness, ecological character, high resistance to flame and to chemicals. Carbon foams have even better properties and are also electrically conducting. Consequently, various applications are suggested for organic foams: cores of sandwich composite panels, sound and shock absorbers and thermal insulators, whereas carbon foams can be used as porous electrodes, filters for molten metals and corrosive chemicals, catalyst supports and adsorbents.

1. Introduction

Condensed tannins belong to the family of flavonoids. Characterized by aromatic rings bearing hydroxyl groups, they present reactivity rather similar to that of resorcinol or phenol, two synthetic molecules with which resins are actually prepared and commercialized. The flavonoid tannins used in the present study were extracted from mimosa barks, and are “green”, cheap but commercial raw materials that can replace resorcinol and phenol in a number of applications.

The aim of the present work was studying ultra lightweight rigid foams derived from tannins. Such materials could be used as such or after pyrolysis at 900°C under inert atmosphere. The former are organic materials which could replace the commercial synthetic phenolic foams, whereas the latter are reticulated vitreous carbon (RVC) foams with potential applications in the field of energy and environment. Preparation, main characteristics and physical properties are described in this paper.

2. Preparation of organic and RVC tannin-based rigid foams

Tannins were supplied by the company SilvaChimica (Italy) in the form of a light brown powder. When mixed with water, formaldehyde and an acidic catalyst, cross-linking occurs within a few minutes during which heat is released, leading to a hard black resin. Addition of furfuryl alcohol, another chemical of natural origin, both enhances the amount of heat produced and improves the

mechanical resistance of the resultant resin. Such phenomenon is used to produce the foaming of the resin, through boiling of a liquid previously incorporated to the formulation: the blowing agent.

The amount of boiling agent, here diethyl ether, controls the final density of the foam, ranging from 0.04 to 0.16 g cm⁻³. The formulation, see Table 1, is optimized in such a way that hardening and foaming occur simultaneously, so neither cracks nor pore collapse are observed. Foam preparation requires less than 2 minutes, is very easy, and any shape is possible, depending on that of the mould in which the liquid precursor has been poured. Finally, these are materials natural at the 95% level that are obtained, from which RVC foams can be prepared as follows.

Heating organic tannin-based foams in nitrogen at 4°C min⁻¹ up to 900°C leads to uncracked, flawless, highly porous carbonaceous materials. Given the composition of the initial resin, non-graphitizable, glasslike, carbon is produced. During heating, typically half of the mass as well as half of the volume of the material are lost. Because shrinkage is exactly compensated by weight loss, the bulk density of RVC foams is strictly equal to that of their tannin-based precursors.

Table 1. Typical formulation of organic tannin-based foams.

Compound	Amount	Role
Tannin	30	Base of the resin
Furfuryl alcohol	6 - 15	Strengthenener
Diethyl ether	1.5 - 5	Blowing agent
Water	6	Solvent
Formaldehyde (37% water solution)	7.4	Cross-linking agent
Para-toluene-4-sulphonic acid (65% water solution)	11	Catalyst

3. Main features and physical properties of tannin-based rigid foams

3.1. Characteristics of tannin-based foams

Bulk and skeletal densities, pore structure and cost have been determined as follows.

3.1.1. Density and porosity. Bulk density, being defined as the weight of one volume unit of material, was measured by careful weighing of parallelepiped samples of perfectly known dimensions. Bulk density is, as expected from simple calculations [1] and as shown in Figure 1, inversely proportional to the amount of blowing agent. Skeletal density is defined as the density of the solid from which the foam is made, and was measured by helium pycnometry. That of organic foam was found to be 1.59, whereas that of derived carbon materials was 1.98 g cm⁻³ [2,3]. From the two kinds of density values, total porosity could be calculated and is presented in Figure 2.

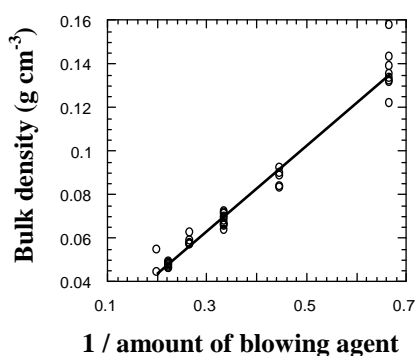


Figure 1. Bulk density of organic foams versus the inverse of the amount of blowing agent.

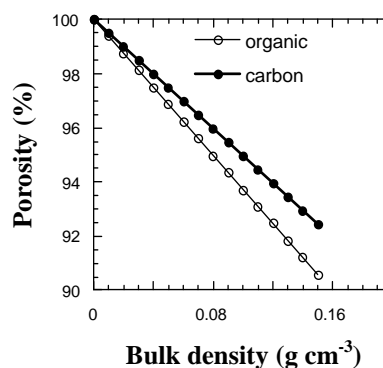


Figure 2. Porosity of organic and carbon foams as a function of their bulk density.

3.1.2. *Pore size.* Pores of carbon foams were thoroughly observed by Scanning Electron Microscopy (SEM). Secondary electrons best revealed cell diameters and pore walls, whereas backscattered electrons best allowed visualizing struts and windows connecting the cells. Figure 3 shows that the linear cell density (expressed in number of pores per inch: ppi) depends on the density, and Figure 4 presents the correlation between diameter and bulk density. Simple theoretical considerations justify that cell size is inversely proportional to bulk density [1].

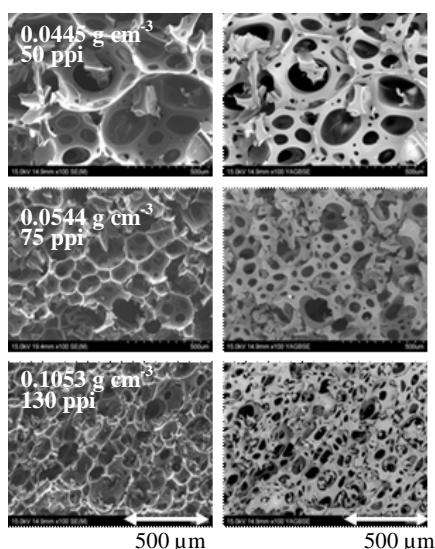


Figure 3. SEM pictures of carbon foams of various bulk densities. Left: secondary electrons; Right: backscattered electrons.

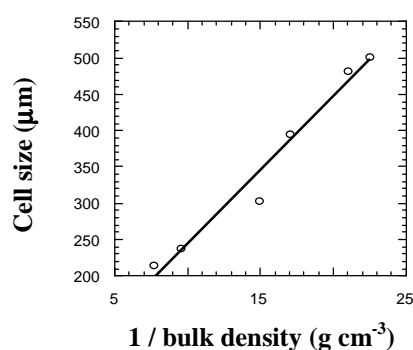


Figure 4. Pore size of carbon foams versus the inverse of their bulk density.

3.1.3. *Anisotropy.* Because the foams were grown vertically, anisotropy occurred. The cells are slightly elongated along the vertical direction, here referred to as the z-axis. The cells remain roughly circular in the orthogonal plane, here referred to as the xy-plane, see Figure 5. Anisotropy increases with bulk density and explains the slight differences observed between properties measured along z- or xy-directions (see next subsection).

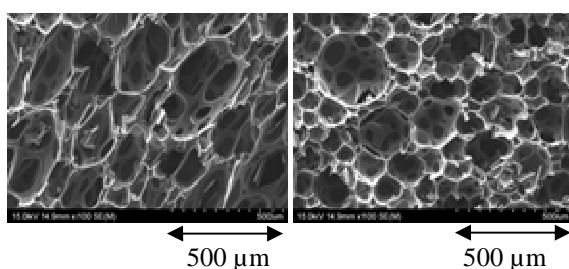


Figure 5. SEM views of the same carbon foam (density 0.067 g cm^{-3}) along two orthogonal directions. Left: z-axis; right: xy-plane.

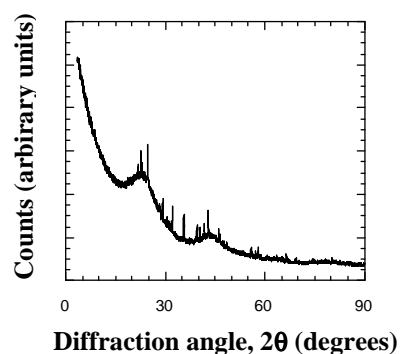


Figure 6. XRD pattern of carbon foam.

3.1.4. *Microscopic structure.* Organic foams were made of tannins and furfuryl alcohol cross-linked with formaldehyde, leading to an insoluble and infusible polymer network based on aromatic rings and oxygen-containing heterocycles. Such phenol-like precursors are known to lead to glasslike carbon

after pyrolysis. Figure 6 indeed shows that RVC foams are based on disordered carbon, as evidenced by the X-ray diffraction pattern. Small peaks correspond to impurities naturally present in tannins.

3.1.5. Cost. Tannins are typically six and thirty times cheaper than phenol and resorcinol, respectively. The other chemical used here: furfuryl alcohol, diethyl ether and formaldehyde, have a moderate cost. Thus, foams cheaper than 3€ per kg have been prepared. Given the cost of nitrogen gas and electric power, carbon foams having a cost lower than 10 € per kg are obtained, making them the cheapest RVC foams of the market.

3.2. Physical properties of tannin-based foams

Resistance to fire, permeability, surface area, mechanical properties, electrical and thermal properties have been investigated.

3.2.1. *Resistance to fire.* As expected from phenol-like resins, tannin-based organic foams present outstanding resistance to fire, irrespective to their bulk density. It not only requires heat densities as high as 50 kW m^{-2} for igniting the samples, but the peak heat released is never higher than 12 kW m^{-2} , i.e. two order of magnitudes lower than that of epoxy for example, see Figure 7. Besides, the gas yield of the materials undergoing combustion is extremely low. These findings mean that, if the imposed heat is removed, the materials self extinguish. Resistance to fire of carbon foams, though not measured in similar conditions, is even higher, given that materials submitted to a 3000°C oxyacetylenic flame in air also self extinguish, see Figure 8.

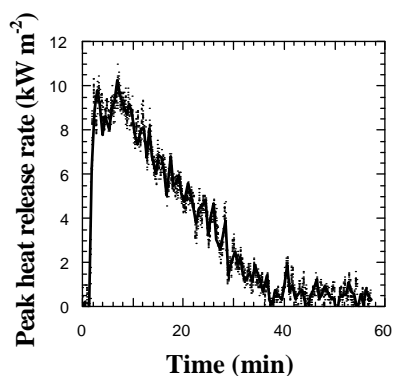


Figure 7. Peak heat release rate of organic foams submitted to a fire of power 50 kW m^{-2} .



Figure 8. Carbon foam submitted to a 3000°C oxyacetylenic flame in air. Neither flame nor smokes are emitted.

3.2.2. *Permeability and surface area.* Permeability of organic and carbon foams has been determined by flowing water at a know flow rate across samples of known thickness and cross-section under a given pressure. The results are presented in Figure 9, showing that permeability follows a power law of density with an exponent -2 . Such dependence has been justified theoretically [4]. From the results given in Figure 9, the surface area could be calculated, see Figure 10. The same kind of curve, presenting a maximum at a bulk density close to 0.07 g cm^{-3} , was fully recovered when the surface area was estimated from the pore structure, considering spherical pores in close packing [4]. The agreement is good between the two sets of data, and also with the values measured by both krypton adsorption [3] and by X-ray microtomography [5], close to $1 \text{ m}^2 \text{ g}^{-1}$ for a bulk density of 0.07 g cm^{-3} .

3.2.3. *Electrical and thermal conductivities.* Only carbon foams present measurable electrical conductivity, presented in Figure 11. Generalised effective medium theory [6] predicts that the electrical conductivity increases with bulk density through a power law whose exponent depends on the morphology of the cells. Values of 1.5 and higher are expected for spherical and elongated cells,

respectively. As seen in Figure 11, finding exponents slightly above 1.5 suggests slightly elongated cells, as expected. Whether the foams are organic or carbonaceous, the thermal conductivity is very low, although that of carbon is a little higher than that of the precursor resin. However, even after pyrolysis, the materials present extremely interesting insulating properties, given that the thermal conductivity of RVC foams of density 0.067 g cm^{-3} is 0.035 and $0.044 \text{ W m}^{-1} \text{ K}^{-1}$ along xy- and z-directions, respectively. These values are less than two times the conductivity of air at room temperature ($0.024 \text{ W m}^{-1} \text{ K}^{-1}$), and are of the order of magnitude of expanded polystyrene.

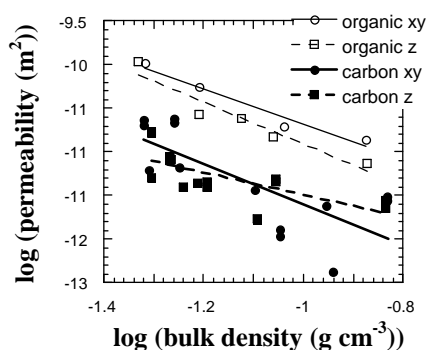


Figure 9. Permeability of organic and carbon foams, plotted in double-log scale so the power law dependence with an exponent close to -2 is evidenced.

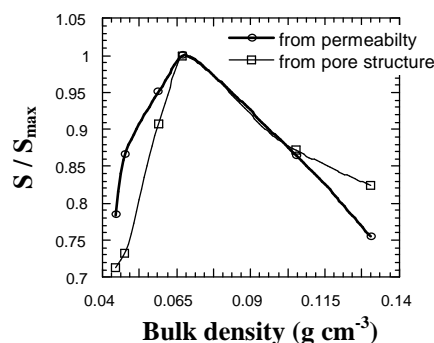


Figure 10. Normalised surface area of carbon foams, calculated by two methods.

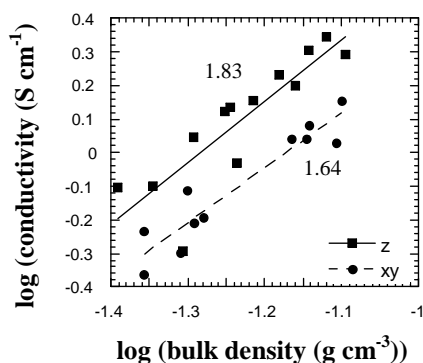


Figure 11. Electrical conductivity of carbon foams as a function of their bulk density, plotted in double-logarithmic scale. The slope of the straight lines fitted to the experimental points is given on the plot.

3.2.4. Mechanical properties. Compression of tannin-based foams leads to the typical behaviour of rigid cellular materials submitted to compression, see Figure 12: a linear elastic region, whose slope is the elastic modulus, followed by a long, serrated, plateau, corresponding to the collapse of successive cell layers, and finally a strong curvature upwards corresponding to the densification of the material once all the pores have been crushed. Elastic modulus and compressive strength both increase with bulk density and, due to the aforementioned anisotropy, present higher values along the z-axis. From these curves, the mechanical energy that can be absorbed by foams' irreversible crushing may be determined as the product of the compressive strength times the densification strain. As an example, the RVC foam of bulk density 0.13 g cm^{-3} can absorb 720 kJ m^{-3} . In other words, one m^3 of this foam may absorb the kinetic energy of a one ton car running at 140 km h^{-1} . Figure 13 shows that compressive strength again follows a power law of bulk density, with an exponent slightly higher than 1.5. According to Ashby et al. [7], exponents of 1.5 and 2 correspond to open cell and closed cell foams, respectively. Finding an intermediate value suggests that, as expected from SEM pictures, most of the cells but not all are open and fully connected with each other.

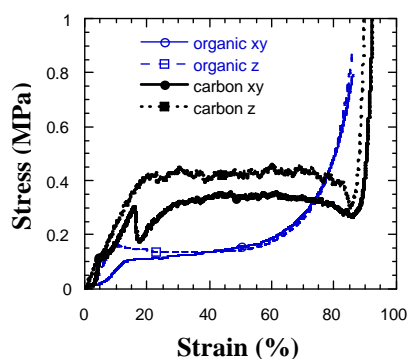


Figure 12. Strain – stress characteristics of organic and carbon foams having the same bulk density of 0.11 g cm^{-3} .

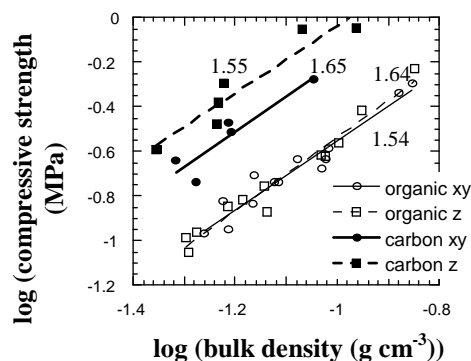


Figure 13. Power law dependence of compressive strength versus bulk density. The slopes are given on the plot.

4. Conclusion

Condensed tannins extracted from mimosa barks are extremely valuable chemicals. Being both low-cost and reliable raw materials, a rare feature for a natural product, tannins allow the preparation of “green” rigid foams having a number of interesting properties and characteristics. Organic foams are extremely efficient thermal insulators and present outstanding fire resistance. These features make them highly suitable for core materials in sandwich panels for marine and aircraft applications. Protection against shocks and sound absorption, presently in test, are also promising applications. It is important to recall that these materials are much cheaper than their phenolic counterparts, derived from the petrochemical industry, and presenting very similar mechanical properties.

After pyrolysis, glasslike (RVC) foams were obtained, having the same, tough narrower, pore structure. Their permeability and very high thermal and chemical resistance make them suitable as filters for hot corrosive fluids or molten metals. Their electrical conductivity allows using them as porous electrodes, and their wide, connected, pore volume, also suggests using these materials as catalyst supports. For that purpose, the inner surface of the cells may be covered by meso or microporous activated carbon through a preliminary step of impregnation with furfuryl alcohol, followed by pyrolysis and activation with steam. Doing so, a supported activated carbon is obtained [8], presenting a narrow surface porosity that is fully and quickly accessible. High adsorption and catalysis kinetics are thus expected. Finally, applications as scaffolds and heat insulation at high temperature are of interest and will be investigated soon.

Acknowledgments

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