Modelling the physical properties of glasslike carbon foams

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Modelling the physical properties of glasslike carbon foams

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Abstract. In this work, model alveolar materials – carbon cellular and/or carbon reticulated foams – were produced in order to study and to model their physical properties. It was shown that very different morphologies could be obtained whereas the constituting vitreous carbon from which they were made remained exactly the same. Doing so, the physical properties of these foams were expected to depend neither on the composition nor on the carbonaceous texture but only on the porous structure, which could be tuned for the first time for having a constant pore size in a range of porosities, or a range of pore sizes at fixed porosity. The physical properties were then investigated through mechanical, acoustic, thermal and electromagnetic measurements. The results demonstrate the roles played by bulk density and cell size on all physical properties. Whereas some of the latter strongly depend on porosity and/or pore size, others are independent of pore size. It is expected that these results apply to many other kinds of rigid foams used in a broad range of different applications. The present results therefore open the route to their optimisation.

1. Introduction

The research presented here lies in between physics of heterogeneous media, materials chemistry and engineering science. The goal was to prepare model cellular materials, with the main objective of solving a number of open questions in physics and allowing either to validate existing models, to propose more refined versions, or to observe new phenomena. If this type of studies has already been partially attempted in the past (see [1]), it has never been possible so far to produce model alveolar materials whose structural parameters can be independently and significantly varied at constant composition. The originality of the present studies is then based on the use of vitreous carbon for developing rigid foams with perfectly controlled morphologies and composition, enabling both rigorous physical studies and their optimization for specific performances in terms of mechanical, thermal, acoustic, and electromagnetic properties. Ultimately, it should be possible to optimize these rigid foams depending on the planned applications.

Herein, the leading idea was therefore to produce model cellular materials from phenolic-furanic resins based on different formulations and preparation routes, allowing a strict control of the porous

structure. Since such materials presented different chemical compositions possibly influencing the resultant physical properties to investigate, all were next pyrolysed at 900°C for producing carbon monoliths having the same final composition and the same carbonaceous texture. As a result, a broad range of porous materials could be obtained for the first time, based on which the influence of porous structure on mechanical, acoustic, thermal and electromagnetic properties could be investigated with an unprecedented accuracy.

2. Materials preparation and characterization

2.1. Materials preparation

Most carbon foams prepared here were obtained after pyrolysis of rigid cellular foams derived from phenolic-furanic (thermoset) resins. If this type of foam is not completely new [2–6], many new formulations were produced herein, and for the first time, the development of a variety of structures formerly impossible to achieve by other processes was carried out. Over 60 cellular foams made of vitreous carbon with different structures were produced through the pyrolysis at 900°C of foamed phenolic polymers.

It is known for long [6] that the density and the cell size of such foams can be varied through the amount of foaming agent. In the present study, significant changes in the structure were also obtained by the addition of various plasticizers, surfactants and copolymers. Hence, 14 types of formulations giving different structures (called STD, PMDI, T1, ...) were developed, and the amount and the nature of the foaming agent were varied to expand the range of available structures. The properties were then studied on the basis of these 14 families of formulations. Indeed, it was found to be more rigorous, and easier (in terms of repeatability) to model the behaviour of each set of materials and then compare the sets with each other. The details about the formulations and their impact on the final porous structure have been abundantly discussed elsewhere [7], and therefore will not be recalled here.

Reticulated carbon foams were also produced by templating of commercial reticulated polyurethane foams and using the same pyrolysis process as for cellular foams. Such materials not only allowed obtaining other types of structures but provided an appropriate basis of comparison with cellular foams. Indeed reticulated foams represent the only type of vitreous carbon foams currently on the market.

2.2. Materials characterization

2.2.1. Porous structures. The carbon foams were first characterized in terms of apparent density measurements, and cell size. The average cell size was determined for all foams from the quantitative analysis of images obtained with a scanning electron microscope (SEM) and an X-ray microtomograph.

2.2.2. Nature of the carbon. Given the chemical nature of the precursors, phenolic-furanic resins, the resultant carbon after pyrolysis was always glasslike, as expected. A number of carbon foams prepared from the most different formulations were then studied by elemental analysis (chemical composition), helium pycnometry (skeletal density) and Raman spectroscopy. The relative density was calculated from the values of bulk and skeletal density.

2.2.3. Physical properties. As for mechanical properties, a comparative study based on quasi-static compression tests carried out with or without plates glued to the samples' faces was performed on a large number of samples. The tests were done with an Instron 5944 universal testing machine equipped with a 2 kN head. The permeability and the sound absorption of 10 mm-thick samples were measured with a lab-made air permeameter and a two-microphone impedance tube (between 800 and 6300Hz), respectively. The thermal conductivities of the foams were determined at room temperature using the hot disk method, using a Hot Disk TPS 2500 S apparatus. Finally, the electromagnetic

properties were measured over a broad frequency range from static regime to near infrared using a complete set of RLC meters and network analysers, waveguides and THz spectrometers.

3. Results and discussion

3.1. Carbon foams' general features

Figure 1 shows only a few examples of carbon foams obtained in this work. Two are cellular foams, i.e., comprised of more or less spherical cells connected with each other through more or less open circular windows, whereas the two other ones are reticulated foams, i.e., are only based on struts; in other words, reticulated foams don't have pore walls. The important feature to remember is that, thanks to so many formulations, foams with different pore sizes could be obtained at constant bulk density, i.e., constant porosity, whereas the opposite also applied based on foams having a fixed pore size but different porosities.

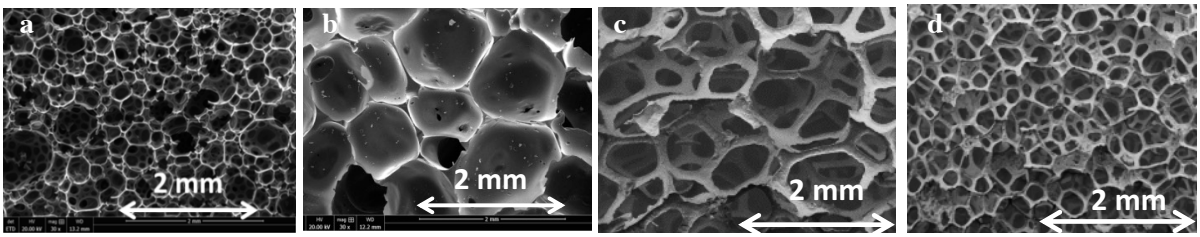

Figure 1. Examples of SEM pictures of carbon foams prepared from different formulations and methods: (a-b) cellular foams; (c-d) reticulated foams.

Such essential feature is presented in figure 2. For each type of formulation, a regression between density and cell size could be obtained. The ranges of bulk densities ($0.015 \leq d \leq 0.333$ g cm^{-3}) and average cells sizes ($100 \leq D \leq 5000$ μm) obtained here were the broadest ever investigated within the same piece of work.

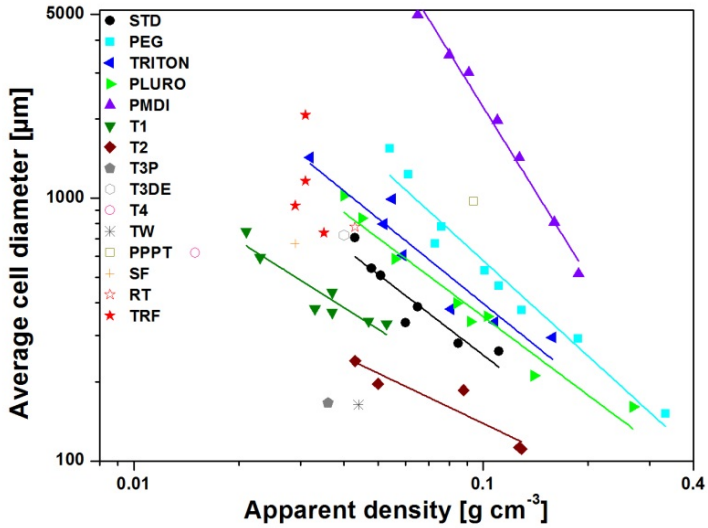

Figure 2. Average cell sizes determined from SEM pictures (and confirmed by micro-computed tomography) as a function of bulk density, for the different foams tested.

It was also shown from elemental analysis that the carbon content of these foams was high and quite comparable, 91.5 ± 2.5%. The skeletal densities measured with helium pycnometry were all approximately equal to 1.98 g cm^{-3}. The Raman spectra of the 3 foams having the most different

formulations were very similar again and had, after fits and deconvolutions of the bands, exactly the same D1/G intensity ratio. For the characterizations carried out in this work, we considered that these carbons had nearly identical chemical composition, and that the differences of properties measured thereafter were thus only due to the differences of porous structures.

3.2. Physical properties

3.2.1. Mechanical properties. The compression tests showed that gluing plates to the samples' surfaces did not change the value of the measured maximal compressive stress, but allowed determining much more accurately the compressive modulus. Indeed, without plates, the applied stress was localized on the only struts in contact with the plateau of compression and led to a progressive rupture of the structure, contrarily to the global rupture occurring with plates. The compressive modulus increased with the apparent density for all foams but with different trends (see figure 3). Without plates, the modulus was much lower and could be described with the same law, namely that of Gibson and Ashby (G&A) for open-cell foams [8], for all the foams studied.

However with plates, and whereas a similar relation was also relevant for reticulated foams, the relation of G&A for closed-cell foams was used for cellular foams. The latter relationship took the fraction ϕ of solid only contained in the struts into account, which was then determined for different groups of foams in figure 3. It is the first time that the modulus of cellular open-cell foams was shown to exhibit similar behaviour to that of closed-cell foams.

As for the maximal compressive stress, it increased with density for all the foams according to the law of G&A for open-cell foams. However, it was found that cellular foams having relatively thick cell walls exhibited higher maximal stress than reticulated foams of the same density. Moreover, unlike the prediction of the theory of Weibull [9], no effect related to the cell size could be observed for these foams.

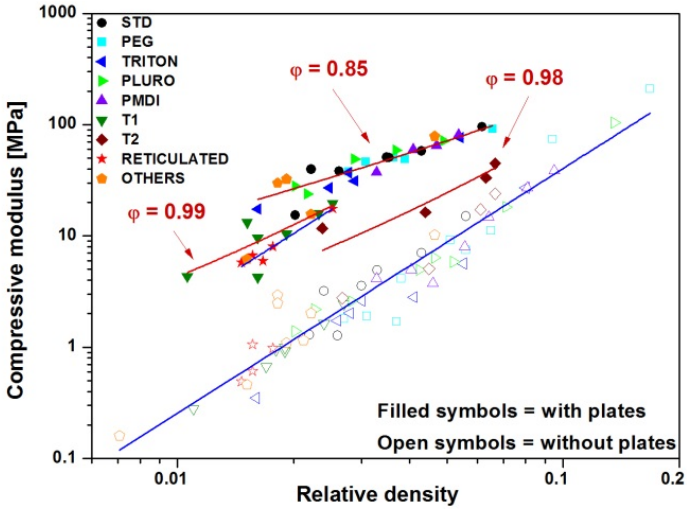

Figure 3. Compressive modulus as a function of relative density of the foams tested with and without plates. Different equations coming from G&A [8] were fitted. φ represents the fraction of solid (see text).

3.2.2. Acoustic properties. The determination of the permeability allowed showing that the latter property was not directly linked to the porosity but increased with the average cell size for all the foams studied. For the reticulated foams, the permeability was the highest and, using the data of figure 1, it could be concluded that the permeability directly increased with the cell size. The sound absorption of these foams was low (see figure 4) and, based again on the data of figure 1, decreased with the increase of cell size. As for the cellular ones, the permeability was relatively low and

depended on the equivalent windows diameter (also called hydraulic diameter, not given here but which can be calculated according to [10]). For these cellular foams, the sound absorption was higher and largely increased with the hydraulic diameter. An optimum of permeability was found in the range $1 \times 10^{-9} – 3 \times 10^{-9}$ m^2, leading to the highest values of sound absorption coefficient.

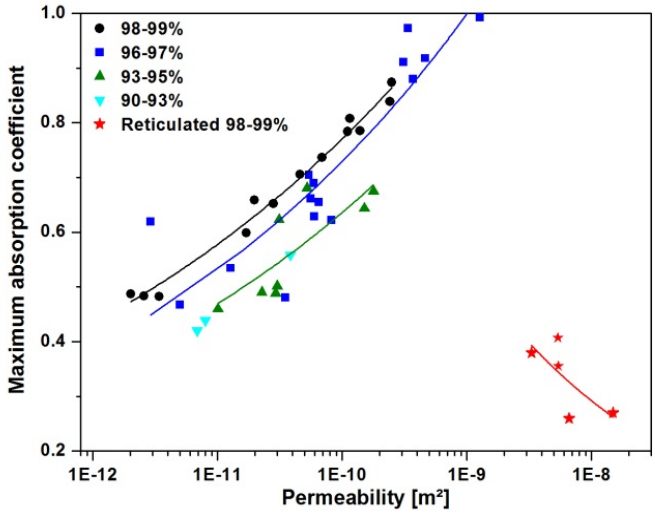

Figure 4. Maximum sound absorption coefficients as a function of permeability for different classes of porosity (expressed as vol. % in the legend, see text).

3.2.3. Thermal properties. The thermal conductivities of 68 carbon foams were measured at room temperature and found to range from 0.041 to 0.18 W m^{-1} K^{-1}, for respective bulk densities within the range 0.029 – 0.264 g cm^{-3} (see figure 5). The model of Glicksman [11], based on a simple geometry of the porous medium, fitted these results pretty well. The fraction of solid contained only in the struts, ϕ, was found to be 0.86 for the cellular foams by neglecting the effects of radiation (i.e., very close to ϕ = 0.85 determined in mechanical studies, so in excellent agreement). However, the measured conductivities of several foams, especially the lightest ones, were higher than the values determined by this model because the effects of the radiations were no more negligible, even at room temperature, for foams of low densities and / or large cell sizes.

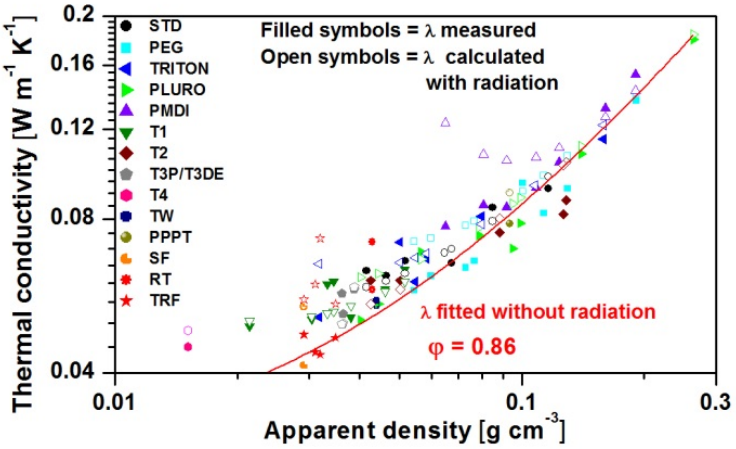

Figure 5. Fit and calculation of the model of Glicksman [11] for the thermal conductivities, λ, measured at room temperature by the Hot Disk method, for the different foams tested.

The model of Glicksman was then used by taking into account the radiation contribution (without the contribution of the cell walls to the extinction coefficient) for calculating the thermal conductivities from the values of density and cell size. The values obtained from this second model are in good agreement with the experimental values of the high-density foams but not with those having low densities and large cell sizes. This result proves that the contribution of the cell walls needs to be measured and should be taken into account for a more accurate description of the experimental data.

3.2.4. Electromagnetic properties. Only a few results are reported here. It was found that the bulk density is the dominant parameter until the end of the microwave range. Similarly to what occurs in a percolating system, the real part of the permittivity and the electrical conductivity increased with bulk density according to power laws whose exponents decreased with frequency (figure 6). The conductivity in the static regime continuously increased with temperature according to Mott's law for disordered conductors (see [12]), whose coefficients changed from a typical value of 2D material to that of 3D material when the thickness of the cell wall increased. This is the first time that such behaviour was observed in rigid foams.

No change of electromagnetic properties was found by varying other structural parameters such as cell size or interconnectivity. At low frequencies, the carbon foams behaved similarly to metals with high impedances, tangential losses and reflection, and became conductors with losses at a frequency which depended on the density (in the microwave range). Reflection decreased and absorption increased with the decrease of density or the increase of frequency. When the frequency increased further, the carbon foams switched from a more capacitive to a more resistive behaviour, the impedance and tangential losses decreased slowly, and the absorption then became the main mechanism.

The cellular foams finally tended to behave as black bodies at high frequencies (above the terahertz range).

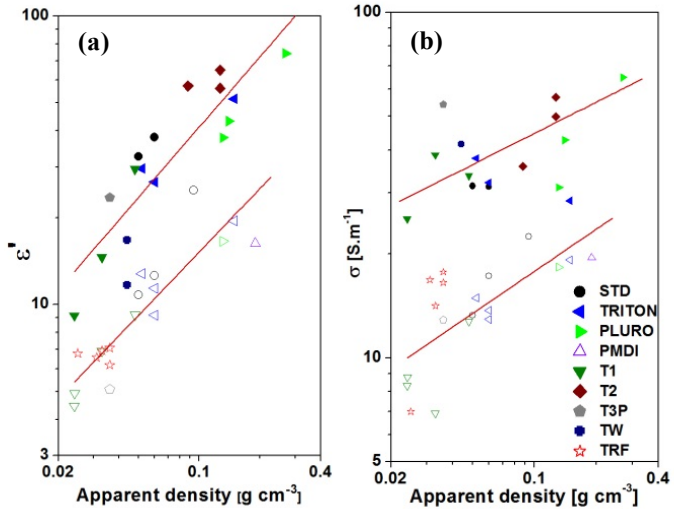

Figure 6. Dielectric constant (a) and electrical conductivity (b) at 8.64 GHz (filled symbols) and at 26 GHz (open symbols), as a function of apparent density, for the different foams tested.

4. Conclusions

In this work, model alveolar materials – carbon cellular and/or reticulated foams – were produced in order to study and to model their physical properties. Cellular carbon foams were obtained by pyrolysis of rigid phenolic-furanic foams presenting many different structures. Reticulated foams were also prepared from polymeric commercial foams through a template method. It was shown that very

different morphologies could be obtained whereas the constituting vitreous carbon from which they were made was the same. The physical properties of these foams were investigated through mechanical, acoustic, thermal and electromagnetic measurements. The following could be concluded.

Concerning mechanical properties: (1) the compressive strength increases with the thickness of cell walls; (2) the famous Gibson and Ashby (G&A) law for open cell foams applies to reticulated foams and to cellular foams measured without plates glued to their faces; (3) the G&A law for closed cell foams (in which the fraction of solid only contained in the struts was determined and taken into account) applies to cellular foams measured with plates glued to their faces; (4) brittle foams with perforated cell walls have modulus as high as that of closed cell foams; (5) no influence of cell size on modulus and compressive strength is noticed.

Concerning acoustic properties: (1) at fixed cell size, the permeability of reticulated foams is about 100 times higher than that of cellular foams; (2) the permeability of reticulated foams increases according to a power law of cell size with an exponent 2 times higher than that of cellular foams; (3) the cell size controls the average sound absorption coefficient of all foams and an optimum of permeability is clearly observed at which the sound absorption coefficient is the highest.

Concerning thermal properties: (1) Glickman's model best fits the results of conductivity vs bulk density, using a fraction of solid only contained in the struts which was found to be identical to that determined by mechanical tests; (2) but the model is not accurate enough for foams having low density and/or high cell size if the radiation contribution is not taken into account.

Concerning electromagnetic properties: (1) the real part of the permittivity and the electrical conductivity are controlled by bulk density up to the THz range; (2) the foams are reflective at low frequency and turn to absorptive at high frequency; (3) no influence of cell size is noticed; (4) cellular foams nearly behave as black bodies in the THz – infrared range.

These conclusions were not all supported by the data presented in this paper, which is definitely much too short for its content, but are robust and expected to apply to many other kinds of rigid foams. The results demonstrate that bulk density and cell size are the main parameters controlling all physical properties, and are therefore the keys of their optimisation for any given application.

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