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Preparation and structural characterisation of model cellular vitreous carbon foams

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ABSTRACT

The aim the present work was to produce carbon foams with as different as possible porous structures but with similar composition and carbon texture for studying precisely the influence of different structural parameters such as density, cell size or interconnectivity on the physical properties of these foams. Over 60 different cellular carbon foams were obtained by pyrolysis of phenolic-furanic rigid foams, whose structure was tailored through some changes in the formulations. The structures of all of these materials were thoroughly characterised through scanning electron microscopy (SEM) and X-Ray microtomography. Both methods proved to give very consistent results, justifying the use of the simpler one, i.e., SEM. Very broad ranges of bulk densities ($0.015 \leq d \leq 0.333\ g\ cm^{-3}$) and of average cell diameters ($100 \leq D \leq 5000\ \mu m$) were obtained. Despite these very different morphologies, elemental analysis, helium pycnometry and Raman spectroscopy studies showed that the carbon constituting the foams can be considered as identical. The results presented here should be used as a basis for the most thorough and extensive studies of physical properties of vitreous carbon foams.

1. Introduction

Because of their porous nature, rigid foams often offer a good compromise between lightness and performances, hence their growing use in the transportation sector. But beyond lightness, foams can be optimised, depending on the foreseen application, in order to obtain good thermal or acoustic insulators, or shock absorbers for example [1]. Other fields are currently of increasing interest, such as high-temperature insulation, electromagnetic shielding, catalysis or energy conversion [2]. The development of these cutting-edge applications is due to significant progresses in the preparation and characterisation methods of these materials on the one hand, and to the emergence of new functional materials such as ceramics and carbon foams on the other hand.

The present work follows these trends as it deals with the preparation of cellular vitreous carbon foams of controlled structure, thus allowing studying and modelling their physical properties with an unprecedented accuracy. So far, most foams are indeed such that the cell size increases when the bulk density decreases [1], and therefore it has never been possible to definitely attribute some changes of physical properties either to cell size, total porosity or any other parameter. In a former work, decorrelation of cell size and bulk density was approached but was not completely successful [3]. However, the latter pioneering paper opened the route to many new formulations. Most carbon foams presented here were thus derived from thermoset phenolic-furanic polymeric foams. Although similar materials had been produced in the lab since 2009 [4], an extensive formulation and optimisation work allowed for the first time to obtain the amazingly broad range of vitreous carbon foams presented here. As we deal here with model materials having controlled structures, a route is open to the in-depth investigation of the effect of each structure parameter on various physical properties, either validating existing models or suggesting more refined versions, or even evidencing new phenomena. Doing so, the optimisation of these materials should be possible, depending on the intended field of application.

This type of studies has already been partially attempted in the past, but failed at getting materials of constant composition for which all parameters could be really controlled. Indeed, it has not been possible until now to obtain broad ranges of structures while maintaining everything else constant when using polymeric, ceramic or metal foams. For example, in the polymeric foams investigated by Maheo et al. [5], the material constituting the cell

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walls was heterogeneous due to a surfactant gradient. In alumina foams, some changes in the microstructure of the struts were observed when the cell size was varied [6]. Regarding metallic foams, their preparation processes limit the diversity of structures, which remains low compared to that of polymeric foams. And finally, the carbon foams existing so far were also difficult to use for this purpose because their manufacturing processes also limited their variability. In this work, organic phenolic-furanic foams of various types were used as precursors which were advantageously converted into cellular carbons made of the same vitreous carbon but with different porous structures.

A precise methodology was adopted here for all cellular foam samples in order to limit the impact of the other experimental parameters and thus to achieve greater repeatability. All these materials were then thoroughly investigated by scanning electron microscopy and X-Ray micro tomography (porous structure), elemental analysis (chemical composition), helium pycnometry (skeletal density) and Raman spectrometry (carbon nanotexture). Based on the data reported here, further works dealing with the influence of precise parameters of the porous structure on the physical properties of carbon foams will be possible.

2. Materials and methods

2.1. Preparation of model cellular carbon foams

2.1.1. Formulations and syntheses

Cellular vitreous carbon foams were produced from phenolic-furanic resins, condensed tannins co-reacted with furfuryl alcohol in the present case, according to the very general route already detailed in Ref. [7]. Herein, some refinements and changes in the formulations allowed obtaining the broadest range ever for this kind of materials (see Table 1). The formulations PEG, TRITON PLURO, PMDI and TW were all based on what has been referred to as the “standard” formulation [7], which was called STD when prepared with the specific methodology presented here. These formulations were derived from works reported elsewhere [3,8,9] by addition of various surfactants and plasticisers.

The formulation SF corresponds to tannin-based foam without formaldehyde such as the one presented in Ref. [10]. The formulation PPPT corresponds to STD modified by changing the blowing agent from diethyl ether to pentane, adding pMDI as copolymer, Triton X-100 as surfactant and PEG3400 as plasticiser.

T1, T2, T3P, T3DE, T4 and RT were produced by bringing much more significant changes as before to the STD formulation, e.g. mimosa tannin (Fintan OP$^{®}$ kindly supplied by SilvaChimica, St. Michele Mondovi, Italy) was replaced by quebracho tannin (Fintan Q$^{®}$ from the same company) as the main phenolic component. Formaldehyde was replaced by small amounts of glutaraldehyde in T2, T3 and T4 formulations. When diethyl ether was replaced by pentane, more difficult to incorporate into the resin, surfactants were required. Finally, the formulation RT was handled in a different way, by letting it boil for 1 h in an oven at 45 °C until hardening, thereby leading to a very different pore structure (see below).

A special attention was paid to the repeatability of the precursor organic foams, known to be affected for instance by the type and the size of the mould, the room temperature, etc., and hence a specific experimental protocol was developed. Thus, the ingredients of the present foaming formulations were carefully mixed in a 2-L polypropylene box. The latter was next covered with a PVC film and with a non-woven mat of flax fibres wrapped into an aluminium foil (see Fig. 1), and immediately placed in an oven pre-heated at a slightly lower temperature than the boiling point of the blowing agent. Such closed system thermally insulated the mould and retained the heat generated by the reaction, thereby reducing the temperature gradient between the top and the bottom of the foam, and also limited the shrinkage of the materials after foaming. In some cases, however, depending on the formulations, the materials were introduced just after foaming into the oven pre-heated at a higher temperature for accelerating the curing and thus stabilising the foams before they can shrink. Many samples were then cut off the as-obtained big foam blocks for structural and physical characterisation.

14 types of self-blowing formulations giving foams with different structures were thus produced (see Table 1). The range of available porous structures was further considerably broadened by varying as much as possible the amount of blowing agent. The

Table 1
Formulations of the different types of foams.

Type of formulation	Tannin [g]	Furfuryl alcohol [g]	Cross-linking agent [g]	Water [g]	Blowing agent [g]	Plasticiser [g]	Surfactant [g]	PMDI [g]	Catalyst [g]	Foaming temperature [°C]
STD	30	10.5	7.4	6	1.5–6	–	–	–	11	34
PEG	30	10.5	7.4	6	1–6	8 (400)	–	–	11	34
TRITON	30	10.5	7.4	6	1.5–6	8 (400)	1.2 (T)	–	11	34
PLURO	30	10.5	7.4	6	1–6	8 (400)	1.3 (P7400)	–	11	34
PMDI	30	10.5	7.4	6	1.5–6	–	–	–		34
T1	30 (Q)	14		9	1–7.5	–	1	–	8 (PSA)	34
T2	30 (Q)	14	4.5 (G)	8	5.5 (P)	–	1	–	9 (PTE)	34
T3P	30 (Q)	14	4.5 (G)	9	4.5 (P)	–	1	1.3	8.5 (PSA)	40[a]
T3DE	30 (Q)	14	4.5 (G)	9	4.5	–	1	1.3	8.5 (PSA)	40[a]
T4	30 (Q)	28.5	1.1 (G)	–	1.6 (P)	3.8 (EG)	0.6 (P6200) 6.3 (SLES)	–	8.2	100[a]
TW	30	10.5	7.4	6	5 (P)	12 (400)	1.2 (TW)	–	11	100[a]
PPPT	30	10.5	7.4	6	4.5 (P)	8 (3400)	1.2 (T)	3.6	11	34
SF	30	21	–	6	3	–	–	–	11	34
RT	30 (Q)	14	–	10	3 (P)	–	0.6 (P6800) 3 (SLES)	–	6 (PTE)	45

Tannin: Mimosa (Fintan OP$^{®}$) or Q = Quebracho (Fintan Q$^{®}$).
Crosslinking agent: Formaldehyde (37%) or G = Glutaraldehyde.
Blowing agent: Diethyl ether or P = Pentane.
Plasticiser: 400, 3400 = Polyethylene glycol with molecular weight 400 or 3400; EG = Ethylene glycol.
Surfactant: Cremophor ELP$^{®}$ or SLES = Sodium Lauryl Ether Sulphate; P6200, P6800, P7400 = PLURONIC$^{®}$; TW = TWEEN 80$^{®}$; T = TRITON X-100$^{®}$.
Catalyst: paratoluenesulphonic acid at 65% in water or PTE = paratoluenesulphonic acid at 65% in ethylene glycol; PSA = phenolsulphonic acid at 65% in water.

[a] Foaming around 20 °C but the foam was quickly put in an oven at the mentioned temperature for hardening and avoiding any shrinkage.