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Sucrose-based carbon foams with enhanced thermal conductivity

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ABSTRACT

Composite carbon foams based on sucrose char and graphite powder as matrix and filler, respectively, were prepared and characterised. The aim was to offer cellular monoliths with moderate thermal conductivity (3–10 $\mathrm{W\,m^{-1}\,K^{-1}}$) for hosting phase-change materials designed for seasonal thermal storage. These materials were successfully obtained in this work, not only having the requested thermal properties (with conductivity up to 7 $\mathrm{W\,m^{-1}\,K^{-1}}$) but being very strong as well (with modulus and compressive strength up to 150 and 5 MPa, respectively). Such excellent performances could be achieved by using the graphite filler having the lowest particle size, allowing the best dispersion inside the carbon matrix. We showed that graphite filler amount had an impact on foam rise and on pore structure, hence the need of limiting its addition in the initial formulation, but not on pyrolysis behaviour or carbon foam yield. This paper thus presents one more successful application of a plant-derived resource, sucrose, for producing high value-added materials.

1. Introduction

Carbon foams are a new generation of materials with a huge potential of applications as they can be prepared either in glassy or graphite form with tailored thermal and electrical properties (Gallego and Klett, 2003). For example, they may be used as thermal protection materials, heat sinks and radiators, host structures for phase-change materials, ablative materials and lightweight fire resistant cores for sandwich composites (Gallego and Klett, 2003; Ford, 1964; Lafdi et al., 2008; Yu et al., 2006). They are also efficient as electromagnetic interference shielding materials, as electrodes in batteries, and as catalyst supports (Amini et al., 2011; Moglie et al., 2012; Inagaki et al., 2015).

Several preparation processes of carbon foams were reported so far, among them blowing of carbon precursors followed by carbonisation, template methods, compression of exfoliated graphite and assembly of graphene nanosheets, etc. (Inagaki et al., 2015). Common precursors are synthetic organic polymers of high carbon yield, such as phenol–formaldehyde, furfural resin, polyimide and polyarylacetylene (Inagaki et al., 2004; Lei et al., 2010; Lorjai et al., 2009; Zhang et al., 2010). After pyrolysis, foams prepared from these materials are made of glassy carbon, i.e., are not or very hardly graphitisable, and are considered as thermal insulators. Coal, coal tar pitch and petroleum pitch are alternatives to synthetic organic polymer precursors, and the production technologies for producing carbon foams with controlled properties are well known (Chen et al., 2006; Wang et al., 2008). Their resultant carbon foams are graphitic, and therefore present quite high values of thermal conductivity.

Carbon foams can be used as hosts for phase-change materials (PCMs) in thermal storage application. PCMs are generally divided in two groups, organic and inorganic. At temperatures below 100 °C, organic PCMs have several advantages, such as ability to melt congruently, self-nucleation and non-corrosive behaviour. Graphite foams work well as a thermal enhancers and hosts of organic PCMs, particularly at low temperature due to their high thermal conductivity, high porosity, low thermal expansion coefficient, and chemical inertness (Inagaki et al., 2015). However, most graphite foams of high thermal conductivity are also very expensive and are too conductive, which is a serious problem for seasonal heat storage applications for which very long discharge times are required. In contrast, cheaper but glasslike carbon foams have too low thermal conductivity, typically much less than 1 $\mathrm{W\,m^{-1}\,K^{-1}}$ (Palomo del Barrio, 2012). For hosting phase-change materials for seasonal heat storage, carbon foams should simultaneously be cheap and have moderate thermal conductivities within the range 3–10 $\mathrm{W\,m^{-1}\,K^{-1}}$ (Palomo del Barrio, 2012). The present work aimed at producing carbonaceous porous matrices for hosting phase-change materials for seasonal heat storage, using a "green" precursor.

The preparation of carbon materials from renewable resources, and especially derived from crops, is a hot topic nowadays. The

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corresponding processes are indeed not only much greener, but well-chosen biomolecules used as precursors also present quite good carbon yields. Among them sucrose, which is a well-known and widely available agricultural product containing 42.1 wt.% of carbon, was reported to be an excellent source of carbon materials in a number of published works (Prabhakaran et al., 2007; Jana and Ganesan, 2009; Narasimman and Prabhakaran, 2012a,b, 2013; Jana et al., 2013). The present paper deals with the preparation of carbon foams from sucrose and the improvement of their thermal conductivity by addition of graphite in their formulation.

Prabhakaran et al. (2007) were the first to synthesise carbon foams from sucrose. The carbon foams (heat-treated within the temperature range 600–1400 °C) presented values of bulk density from 0.115 to 0.145 g cm^{-3}. These carbon foams comprised spherical cells of diameters 450–850 μm, and the cells were interconnected through circular or oval-shaped windows of sizes 80–300 μm. The compressive strength of carbon foams of density 0.145 g cm^{-3} obtained by pyrolysis at 1400 °C was 0.89 MPa.

Similarly, low-density carbon foams were synthesised from an aqueous acidic sucrose solution for trapping ^{137}Cs from primary system of sodium-cooled fast reactor (Jana and Ganesan, 2009). Carbon foams with bulk densities ranging from 0.053 to 0.085 g cm^{-3} were prepared by foaming molten sucrose (using aluminium nitrate as catalyst and blowing agent) and converting it into solid organic foams followed by dehydration and carbonisation (Narasimman and Prabhakaran, 2012a). Sucrose was also employed for preparing ultralow cost reticulated carbon foams using household cleaning pad wastes used as sacrificial templates (Jana et al., 2013).

All carbon foams produced according to the aforementioned processes based on sucrose as the main carbon source (Prabhakaran et al., 2007; Jana and Ganesan, 2009; Narasimman and Prabhakaran, 2012a,b, 2013; Jana et al., 2013) had low density, low thermal conductivity and poor mechanical strength. In contrast, carbon foams derived from coal and pitch presented a wider range of densities and superior mechanical properties. The low density of carbon foams based on sucrose is due to their lower carbon yield than that of coal and pitches. The present work reports the synthesis and the characterisation of bio-based carbon foams derived from sucrose, using graphite powder as filler, for the purpose of improving their thermal conductivity and mechanical strength. Carbon foams intermediate between glassy and graphitic foams were thus obtained, having the required range of thermal conductivity for seasonal heat storage applications.

2. Experimental

2.1. Carbon foams synthesis

Food-quality sucrose powder was purchased at the supermarket. An aqueous solution containing 20 g of sucrose and 1 g of $Ni(NO_3)_2$, $6H_2O$ in 10 mL of distilled water was first prepared in a Teflon beaker, in which 0–9 g of graphite powder was added and then the solution was homogenised by mechanical stirring, using a Teflon-lined blade mixer working at 500 rpm. The solution/suspension was placed in a ventilated oven at 120 °C over a period of 48 h for foaming and drying. The "green" foam thus obtained was cut into regular shapes for carbonisation and subsequent characterisation. The green foam samples were named GF–G_a b, where GF means green foam, G_a is the graphite grade and b the corresponding amount.

Carbonisation of the foam samples was carried out in a tubular oven under a flow of very pure nitrogen. The heating rate was 3 °C min^{-1} up to 900 °C, and the latter temperature was maintained for 2 h before the oven was let to cool under nitrogen flow. After pyrolysis, the samples were named CF–G_a b, where CF means carbon foam (pyrolysed at 900 °C).

All graphite fillers used in the present study were kindly supplied by Imerys Graphite & Carbon (formerly Timcal Ltd., Bodio, Switzerland), and are known on the market as TIMREX® SFG6, SFG15 and SFG44. These synthetic graphites are in the form of highly anisotropic flakes, and are mainly used as additive for improving the electrical conductivity in various technologies. The characteristic size D90 of SFG6, SFG15 and SFG44 particles are 6.5, 17.9 and 48.8 μm, respectively, where D90 means that 90% of the grains have a diameter lower than the aforementioned values.

2.2. Carbon foams characterisation

The bulk density, ρ_b (g cm^{-3}), was calculated from the weights of cuboid samples of known dimensions. The skeletal density, ρ_s (g cm^{-3}), was assumed to be the same as that of graphite (2.2 g cm^{-3}). This value was indeed confirmed by helium pycnometry (Accupyc 1340, Micromeritics, USA) and therefore suggests that the porosity is fully open, an important feature for the foreseen application, i.e., hosting phase-change materials in the pores of the carbon foam. From bulk and skeletal density, the porosity, Φ (dimensionless) of the materials was calculated as:

$$\Phi = 1 - \frac{\rho_b}{\rho_s} \tag{1}$$

Surface morphology and cell structure of the foams were examined by scanning electron microscopy (SEM, Hitachi TM3000), using a detector of backscattered electrons for seeing deeper in the cells. Many previous works from our team indeed showed that, if secondary electrons have to be preferred for the topological contrast, the detector of backscattered electrons is far better for visualising the bottom of the cells and making one's idea of their interconnectivity (Zhao et al., 2010; Zúñiga Ruiz et al., 2015).

Thermal conductivity measurements were carried out at room temperature by the transient plane source method (Hot Disk TPS 2500, ThermoConcept, France). The method is based on a transiently heated plane sensor, used both as a heat source and as a dynamic temperature sensor. It consists of an electrically conducting pattern in the shape of a double spiral, which has been etched out of a thin nickel foil and sandwiched between two thin sheets of Kapton®. The plane sensor was fitted between two identical cuboid pieces of sample, each one with a plane surface facing the sensor. The thermal conductivity was then calculated with the Hot Disk 6.1 software.

The mechanical properties of carbon foams was also analysed, using an Instron 5944 universal testing machine (Instron, USA) equipped with a 2 kN sensor. The compression was carried out in quasi-static conditions at a constant load rate of 1 mm min^{-1}. Young's modulus and compressive strength were derived from the resultant stress – strain curves. Young's modulus was defined as the slope of the linear, initial, part of the curve presenting the steepest slope, whereas the compressive strength was defined as the highest height of the long serrated pseudo-plateau (see Celzard et al., 2010 for details).

3. Results and discussion

3.1. Carbon foams' structural properties

Before discussing the effects of experimental synthesis conditions on the resultant carbon foams characteristics, a few explanations about the foaming process should be given. It is well known that sucrose undergoes caramelisation upon heating. Caramelisation of sucrose involves the formation of glucose and fructose anhydrides and their further condensation to polymeric