



Melamine-derived carbon sponges for oil-water separation



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ABSTRACT

The elaboration and characterization of hydrophobic melamine-based sponges are presented. Sponges were obtained by single-step carbonization of commercial melamine foam having a 3D interconnected network. We show that optimized sponges can be elaborated from a simple pyrolysis treatment with rather low temperatures of 500–600 °C. These materials exhibited excellent absorption capacities (they absorbed 90 to 200 times their own weight), a very high porosity of 99.5%, a low density around 7 mg/cm³ and water contact angles ranging from 120° to 140° close to superhydrophobicity. The relationship between hydrophobicity and physicochemical evolution on heat treatment (carbonization process, diffusion of additives, porosity evolution) was studied in detail. The as-prepared carbon sponges are compressible up to 80% with a Young's modulus ranging from 0.58 kPa to 0.80 kPa, and keep part of their elastic properties after a hundred compression-decompression cycles. The carbonized sponges were characterized by thermogravimetric analysis (TGA), infra-red spectroscopy (FTIR), Raman spectroscopy, elemental analysis (EA), X-ray photoelectron spectroscopy (XPS) and scanning electronic microscopy (SEM). These characteristics make these materials promising absorbents for water depollution: oil-spill clean-ups or removal of oils and organic solvents from water, especially for the recovering of the pollutant by simple squeezing of the absorbent.

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1. Introduction

With the expansion of oil production and transportation, risk of oil spills and other accidental pollution is more and more present. Several techniques exist to solve the problem of pollution including the use of chemical dispersants, and physical techniques such as combustion, pumping and creaming. Among all these methods, the use of sorbent materials to remove oil from water is considered to be one of the most efficient.

Furthermore, common sorbents are low cost and made of various raw materials including (porous) inorganic materials (zeolites, activated carbons, clays), natural organic fibers (straw, wool, cotton) [1–8] and synthetic organic polymers (polypropylene, alkyl

acrylate copolymers) [9–11]. However, these materials have some limitations such as low absorption capacity, poor recyclability, poor selectivity and are not environmental friendly.

New advanced absorbent materials have been developed to remedy these drawbacks, including polymer foams [12–14], graphene and/or carbon nanotubes sponges [15–20], graphite foams [21], carbon foams [22,23], ultralight carbon aerogels or hydrogels [24–27], carbon materials grafted or deposited on polymer sponges [28–30], hydrophobic polymer coatings on polyurethane sponges [31–35], etc, with superhydrophobic properties.

Recently, absorbents based on commercial melamine sponges start to be investigated [36–45]. This melamine raw material is interesting due to its characteristics: low cost, low density, high porosity, good elasticity, flame retardancy property and environmental friendliness. Nevertheless, pristine melamine is hydrophilic and chemical modifications are needed for oil-water separation applications. Recently, several authors reported the interest of applying a pyrolysis treatment to melamine sponges under inert

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atmosphere in order to obtain a (super)hydrophobic absorbent. This included pyrolysis treatments at temperatures above 700 °C [37] or pyrolysis pre-processing with coating additives [43,44] or pyrolysis post-processing with additives [40].

In this work, we present a simple, one-step, cost effective and scalable pyrolysis method to elaborate elastic hydrophobic carbon sponges from melamine foams with excellent absorption capacities. We tried to characterize and understand the effect of pyrolysis temperature on the sponge properties (structural, chemical, mechanical) to determine the best process of carbonization at low temperatures in order to obtain the best absorption capacity. Our results show that both from absorption and mechanical points of view a pyrolysis treatment limited to 500–600 °C and without the introduction of additives or further processing, is sufficient to obtain hydrophobic sponges suitable for water depollution or oil-spill clean-up applications. In fact, the superhydrophobic property is not mandatory to obtain a good absorbent for oil-spill depollution. The as-produced materials were tested for oil and solvent absorption. We studied the mechanical response of the sponges as well as their chemical evolution as a function of temperature.

2. Materials and experimental section

2.1. Materials

Melamine foams, melamine-formaldehyde (MF) sodium bisulfite copolymer (Fig. 1) were commercially available units manufactured by Wako according to BASF's patents (Basotect®) and used as raw material. The melamine structure corresponds to a s-triazine cycle where hydrogens on carbon are replaced by $-NH_2$ groups. The commercial foam is a melamine-formaldehyde-sodium bisulfite copolymer prepared from melamine mixed with formaldehyde and a blowing agent to create the porosity (such as hydrocarbons, chlorinated and/or fluorinated hydrocarbons, alcohols, esters, isocyanates, carbonates and bicarbonates with acids, etc). A hydro-methylation reaction occurs [46–48] where the hydrogens of $-NH_2$ groups are transformed in methylol groups ($-CH_2OH$), followed by a reticulation reaction between methylolmelamines, and results in an insoluble and infusible three-dimensional network (Fig. 1).

The solvents and oils used in the absorption experiments are: chloroform ($\geq 99\%$, Sigma-Aldrich), dimethylformamide ($\geq 99.8\%$, DMF – Riedel-de Haën), ethanol ($\geq 96\%$), *n*-hexane ($\geq 95\%$) and toluene ($\geq 99.5\%$, Acros Organics); an Algerian crude oil ($d = 0.76$) and a commercial sunflower oil ($d = 0.9$). All these chemicals were used as received.

2.2. Preparation of carbonized foams

The carbon sponges were obtained by placing the MF foam in a

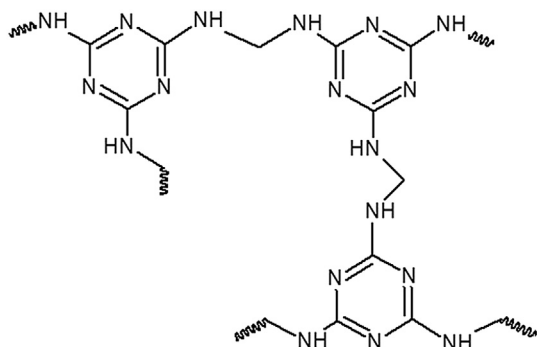


Fig. 1. Chemical architecture of the polymerized melamine sponge.

quartz tube inside an electric furnace heated to a defined temperature between 300 °C and 800 °C, for 1 h under nitrogen atmosphere, with a heating ramp of 10 °C/min. A flow of nitrogen was used during 20 min before the pyrolysis to ensure a neutral atmosphere. The volume shrinkage for carbonized sponges can reach 86% of the original foam volume (Fig. 2). Samples are referred to their heat treatment temperature values in °C.

2.3. Characterization techniques

Physical (wetting, compressibility) and chemical (thermogravimetric analysis – TGA, infra-red spectroscopy – FTIR, Raman spectroscopy, elemental analysis – EA, X-ray photoelectron spectroscopy – XPS) probes as well as imaging techniques (scanning electronic microscopy – SEM) were used to characterize the sponges properties. Thermogravimetric Analysis was performed under nitrogen atmosphere with a heating rate of 10 °C/min from 20 °C to 1000 °C. Fourier Transform Infrared spectra were collected in the 400–4000 cm^{-1} range to identify molecules and the chemical composition of samples. The Raman spectroscopy was used with blue wavelength excitation at 473 nm to determine the molecular composition and in particular the type of carbon component. The elemental composition was determined by Elemental Analysis using a combustion method at 950 °C. The XPS experiments were performed on an ESCALB220i-XL apparatus (Fisons Instruments) equipped with monochromated Al K α as X-ray source and hemispherical analyzer, to identify the nature of atoms and chemical bonds by the energy shift. The pass energy was set at 20.0 eV with the energy step of 0.1 eV. The micromorphologies were observed by Scanning Electron Microscopy with a Nova NanoSEM 450 (FEI). The sessile drop method was used to characterize the wetting properties of the as-processed samples. For such experiments a home-made device was used. The compressive mechanical tests were performed with two parallel flat-surfaces and a 100 N detection cell at various deformation speeds. More details on the characterization techniques are presented in the Supplementary information.

3. Results and discussion

3.1. Characterization of carbonized sponges

As shown in Fig. 2, pyrolysis leads to a strong evolution of the sponge volume. The apparent density decreased from 8.3 mg/cm^3

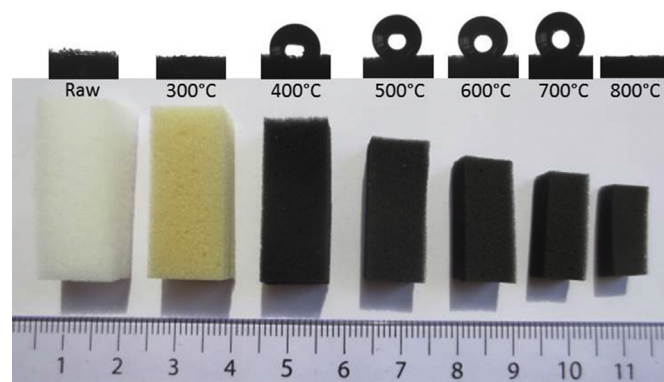


Fig. 2. Photograph of the raw foam (white) and carbonized foams (brown and black) between 300 °C and 800 °C (from left to right). On top, pictures of a water droplet deposited on top of the corresponding sponge in the contact angle experiments. For raw, 300 °C and 800 °C samples, water was immediately absorbed by the sponge. (A colour version of this figure can be viewed online.)

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