Carbon foams from polyacrylonitrile-borneol films prepared using coaxial electrohydrodynamic atomization

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ABSTRACT
A new approach is described for preparing carbon foam (CF) through coaxial electrohydrodynamic atomization (EHDA). Using polyacrylonitrile (PAN) and borneol as a carbonaceous precursor and a blowing agent, respectively, hybrid PAN-borneol films were prepared and transferred to a honeycomb PAN membrane through blowing, drying, and pre-oxidation with the CF prepared by carbonization of the PAN film. Scanning electron microscopy observations showed that the CF has a homogeneous structure, having pores with an average diameter of 2.34 ± 0.73 μm. The surface of the CF, which had a thickness of 10 μm, was smooth and compact. The coaxial EHDA process can be exploited for preparing CF with tailored structures.

1. Introduction
Carbon foam (CF) has attracted increasing attention due to its interconnected three-dimensional (3D) microstructure and unique properties, such as low density, adjustable thermal and electrical conductivity, high temperature tolerance, and high mechanical strength [1,2]. Ford [3] first proposed a process to generate CF from thermosetting organic polymers in 1964, and since then, CF has developed along three directions. First, different carbonaceous precursors, such as coal, coal tar pitch, petroleum pitch, furfural alcohol, polyacrylonitrile (PAN), resorcinol–formaldehyde, phenol–formaldehyde resins and aromatic compounds, have been investigated for CF production [4–8]. Second, various processes and techniques, such as typical blowing, pressure-releasing and self-bubbling techniques, have been developed to generate CF [9–13]. Third, the functionalization of CF and its potential applications have been continuously broadened; these include traditional applications (e.g., heat exchangers, microwave absorbers, aerospace application, thermal protection, and electrode materials) and the use of biological carbons (e.g., biofilms, catalyst supports, filters, and foam reinforced composites) [14–17].

The CF produced using the traditional method often has pores with diameters that range from 200 μm to 600 μm. For biological applications, the desired pore size should be smaller than 50 μm, matching the size of a cell. Li et al. reported CFs prepared from mesophase pitch through the supercritical process, with pore sizes ranging from 10 μm to 50 μm [18–20]. However, the development of modern advanced technologies – particularly nanotechnology – has paved the way for the creation of new methods for CF production, with smaller pore sizes and adjustable properties.

Electrohydrodynamic atomization (EHDA), including electrospinning, electrospraying and ink-printing, generate products at the micro and nano scales by directly exploiting electrical forces [21–25]. One of the powerful capabilities of the EHDA process is that it can copy structures from the macro scale to products at the micro and nano scales. Through
interactions between electrons and fluid liquid for example, electrospinning and electrospraying can easily duplicate the structure of macro jet devices (e.g., concentric and side-by-side spinnerets/spraying heads) to generate products with special microstructures, such as core–sheath nanofibers, core–shell microparticles, and side-by-side nanofibers/particles [26–30].

Based on the above mentioned literature, we investigate the manipulation of microstructures for CF production using coaxial EHDA films that are utilized as templates. PAN is extensively used in electrospinning because it is good precursor for the preparation of CNFs [31–33]. Pre-positioning the borneol in a confined micro-region prior to removal facilitates the generation of pores in the PAN films on a micro scale.

2. Experimental

2.1. Materials

PAN powders ($M_w = 50,000$) were purchased from Jinshan Petrochemistry Co., Ltd. (Shanghai, China). Borneol (purity over 95%) was purchased from Shanghai Winherb Medical S & T Development Co., Ltd. (Shanghai, China). Methylene blue, N,N-dimethylacetamide (DMAc), and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were of analytical grade and were used without further purification.

2.2. Preparation

The core solution was prepared by dissolving 20 g borneol and 0.01 g methylene blue in 100 mL acetone. The sheath solution consisted of 3 g PAN in 100 mL DMAc. Through pre-experiments, the core and sheath flow rates were selected as 0.2 and 2 mL/h respectively. Two syringe pumps (KDS100 and KDS200, Cole-Parmer, IL, USA) and a high-voltage power supply (ZGF 60 kV/2 mA, Shanghai Sute Corp., Shanghai, China) were used for carrying out the EHDA. Following optimization, the applied voltage was fixed at 15 kV. The aluminum foil wrapped collector was placed 15 cm away from the nozzle of the spraying head. The EHDA process was conducted under ambient conditions at 22 ± 4 °C and relative humidity of 61 ± 5%. The EHDA was recorded using a digital video recorder (Canon PowerShot A490, Tokyo, Japan). A homemade concentric spraying head was used to conduct the coaxial EHDA.

To investigate the capability of EHDA in manipulating microstructures, the EHDA process was divided into two steps: (1) continuous spraying for 5 h under core and sheath flow rates of 0.2 and 2 mL/h respectively; and (2) continuous spraying for 0.5 h under a sheath flow rate of 2 mL/h. The collected films were dried overnight at a temperature of 150 °C in an Electric Blast Drying Oven (DHG-9140A, Shanghai Jing Hong Laboratory Instrument Co., Ltd., Shanghai, China).

2.3. Characterization

The morphology of the PAN-borneol films was assessed using a Quanta FEG450 scanning electron microscope (SEM) (FEI Corporation, Netherlands). The cross-section of the films was prepared through manual breaking. Prior to the examination, the samples were Pt sputter-coated to render them electrically conductive.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) analysis was performed on a Spectrum 100 FT-IR spectrometer (Perkin-Elmer, USA) over a range from 500 cm $^{-1}$ to 4000 cm $^{-1}$ at a resolution of 2 cm $^{-1}$. Thermogravimetric analysis (TGA) was carried out on a Pyris 1 thermogravimetric analyzer (Perkin-Elmer, USA).

The cross-section of the CF was directly observed using SEM. The average pore size in the CF was determined by measuring pore diameters through SEM images at more than 100 different sites using Image J software (National Institutes of Health, MD, USA).

3. Results and discussion

3.1. Strategy for preparing CF from PAN

The diagrammatic sketch of the coaxial EHDA strategic process, which is used to prepare the CF from PAN, is shown in Fig. 1. The strategy included three steps: (1) conducting a coaxial EHDA process to encapsulate borneol and generate a “wet” PAN-borneol film; (2) drying the “wet” film and removing borneol through heating and blowing to produce a honeycomb PAN membrane; and (3) transferring the PAN film into CF through pre-oxidation, carbonization, and graphitization as well as pre-determining the parameters for carbonization through TGA measurements.

3.2. Process of the coaxial EHDA

A diagram of the modified coaxial EHDA process is shown in Fig. 2a. A homemade concentric spraying head (Fig. 2b) was employed. This manipulated two different fluids to flow in a concentric way, with two syringe pumps (Fig. 2c) used to drive them independently. An alligator clip was used to connect the inner stainless steel capillary of the spraying head to the high voltage power supply (Fig. 2d). Under selected fabrication parameters, a typical fluid jet trajectory was created (Fig. 2e and f). The fluid jet consisted of a straight thinning jet emitted from a compound Taylor cone, followed by an atomization region wherein the fluids are broken up continuously into fine droplets in the electric field. The compound Taylor cone
(photos taken horizontally) exhibited a clear core/shell structure with the blue solutions consisting of methylene blue and borneol in the core part (Fig. 2e). Taken at a 45° angle, the photos verified the fast and violent atomization of the droplets (Fig. 2f).

The critical voltage applied to a fluid in initiating the Taylor cone formation and the straight thinning jet \(V_c\) has a close relationship with the diameter of the concentric spraying head [34], and is given by:

\[ V_c \sim \sqrt{\frac{d^2}{\varepsilon R}}. \]

where \(V_c\) is the critical voltage for a jet emanating from the meniscus tip, \(d\) is the electrode separation, \(\varepsilon\) is the permittivity, \(\gamma\) is the surface tension, and \(R\) is the principal curvature of the liquid meniscus. A small diameter spinneret orifice gives the value of \(R\); hence, only a small \(V_c\) is needed to initiate the EHDA process. The self-made spraying head used in this study had outside and inner diameters of 1.2 and 0.3 mm, respectively (Fig. 1c), thereby facilitating the initiation of coaxial EHDA. In addition, the inner capillary protruded slightly from the surface of the outer capillary, which ensured that the sheath PAN solutions fully surrounded the core borneol solutions.

### 3.3. PAN-borneol films

The EHDA initially generated near-monodisperse droplets whose sizes varied from hundreds of micrometers to tens of nanometers [35,36]. Subsequently, the droplets shrank rapidly due to the rapid evaporation of solvents resulting from the Coulomb explosion (Fig. 2e and f). Generally, the large surface area of the microdroplets allows the fast removal of solvents and the generation of semi-solid or solid products. Often, the solvent in the droplets does not evaporate totally, forming thin films and leaving microparticles on the collector. Thus, the efficiency of solvent removal from droplets is a key factor in determining the format of the final products. Exhausting all the solvent is crucial in preparing electrosprayed particles. Different methods have been employed to remove solvents from droplets, such as using a cross flow of nitrogen/air or liquid bath to extract sufficient solvent and coagulate the particles [35,36]. Here, the EHDA was conducted to prepare semi-solid membranes, i.e., keep the solvents in the sheath fluids from complete evaporation in order to form a continuous film with the solid borneol microparticles buried in them.

Fig. 2 – Implementation of the coaxial EHDA process: (a) the diagram of the process; (b) digital picture of the homemade concentric spraying head; (c) digital picture showing the arrangement of the apparatus; (d) connection of the power supply and the spraying head, and the angle \(\theta\) in taking photos of the atomization process; (e) and (f) typical atomization processes (taken horizontally at a 45° angle) under core and sheath flow rates of 0.2 and 2.0 mL/h, respectively, voltage of 15 kV, and collected distance of 15 cm (taken under 12× magnification).
an area of 30 cm² by estimate (Fig. 3c and d). However, a few borneol microparticles were still present at the cross-section of the PAN films, as shown by the white circle in Fig. 3d. These borneol microparticles did not sublimate and escape from the PAN films during the blowing and drying process. ATR-FTIR (Fig. 3e) also demonstrated the presence of borneol in the PAN films, verified by the 2950 and 1061 cm⁻¹ wavenumbers in the solid film resulting from –OH vibrations. However, a comparison of the spectra of pure PAN and the prepared solid film in Fig. 3e showed that some of the borneols were oxidized into camphor (i.e., an ingredient that sublimates easily). This was demonstrated by the fact that the intensity at 1734 cm⁻¹ for C=O was stronger than 2245 cm⁻¹ for C=N in the solid film, whereas that at 1732 cm⁻¹ was weaker than 2243 cm⁻¹ in the PAN spectra.

Two TGA tests were carried out to determine the carbonization parameters of the PAN films. The TGA test on process A was conducted by directly heating the PAN films, after blowing and drying, from 50 °C to 900 °C at a rate of 10 °C under nitrogen atmosphere. The TGA test on process B was conducted by pre-oxidation of the PAN films in a muffle furnace (SX-5-12, Zhuzhou Huada scientific Co. Ltd., Hunan, China) under 265 °C for 1 h.

For process A, the weight loss of the first stage at 200 °C to 250 °C is (6.88–6.14)/6.88 × 100% = 10.8% resulting from the sublimation and decomposition of residual borneol and oxidized camphor in PAN films after blowing and drying. The weight loss of the second stage at 300 °C to 900 °C is (6.14–2.63)/6.14 × 100% = 58.2%, resulting from carbonization of the PAN. For process B, borneol and camphor were not discerned from the TGA curve. The weight loss at 50 °C to 900 °C is (6.51–2.94)/6.51 × 100% = 54.8%, resulting from the pre-oxidized atmosphere driving out all the borneol and camphor. Thus, the pre-oxidation of honeycomb PAN films provides a higher char yield.

3.4. CF

The morphologies of CF are shown in Fig. 4. Specifically, the whole visual effect of the special structure of the prepared CF, which has a smooth solid surface and a homogeneous structure of inner pores, is shown in Fig. 4a. The pores indicated by “A” in Fig. 4a were resulted from the bigger aggregated borneol particles (white particles shown in Fig. 3b). The images shown in Fig. 4b and c are the bottom and top regions of the CF, respectively. The bottom was slightly compact than the central part because of gravity and the “wet” property of the films during the EHDA process, whereas the top surface had a compact structure with a thickness of 10 µm because of the sprayed sheath PAN solutions during the EHDA processes. Further image enlargement of the CF showed obvious smooth ligaments and junctions without discerned microcracks in their framework (Fig. 4d). However, a number of tiny pores were discerned on the top surface (Fig. 4e) resulting from the diffusion of borneol in the collected “wet” membrane. Fig. 4f gives the diameter distributions of CF pores, which had an average diameter of 2.34 ± 0.73 µm, reflecting a highly uniform structure.

Certainly, the pore size of the CF can be manipulated by adjusting the ratio and flow rate of sheath and core fluids, the concentration of carbonaceous precursors and blowing agents in the core/sheath solutions, and the parameters of the EHDA process such as applied high voltages, needle diameter, and collected distance. The functional components (particularly some metal and their oxidations) can be incorporated into the CF through both the sheath liquid and core solution.

4. Summary

The coaxial EHDA process is a useful tool for generating new types of CFs. By pre-positioning borneol blowing agents in
microscale PAN films using EHDA and by transferring by blowing/drying, honeycomb PAN membranes are generated and used as templates for further production of CF. TGA results verified that pre-oxidation of the PAN films favored higher char yields, and SEM observations showed that the CF had a homogeneous structure with the average diameter pores at $2.34 \pm 0.73 \mu m$. The surface of the CF was smooth and compact with a thickness of $10 \mu m$. This study pioneered a new, easy, and effective methodology in fabricating CF with tailored microstructures.

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Fig. 4 – Characterization of the CF: (a)–(e) SEM images of different sites and under varied magnifications; and (f) Distribution of CF pore diameter.