Available online at www.sciencedirect.com

Journal of Applied Research and Technology

Journal of Applied Research and Technology 14 (2016) 54–61

www.jart.ccadet.unam.mx

Original

Microstructure of polyacrylonitrile-based activated carbon fibers prepared from solvent-free coagulation process

Norhaniza Yusof[a,b,*], Dipak Rana[c], Ahmad Fauzi Ismail[a,b], Takeshi Matsuura[c]

[a] *Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia*

[b] *Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia*

[c] *Department of Chemical and Biological Engineering, Industrial Membrane Research Institute, University of Ottawa, 161 Louis Pasteur Street, Ontario K1N 6N5, Canada*

Received 20 August 2015; accepted 4 February 2016

Available online 28 February 2016

Abstract

Polyacrylonitrile precursor fibers prepared using a solvent-free coagulation process were stabilized, carbonized, and physically activated by carbon dioxide into activated carbon fibers (ACFs). The activation temperature varied from 600 to 900 °C while the activation time was 1 h. Atomic force microscopy was used to observe the surface morphology, as well as the surface roughness of the ACFs. Higher pyrolysis temperature formed rougher surfaces, and increased the pore sizes. Meanwhile, Fourier transform infrared spectroscopy revealed more conversion of oxygen containing functional groups to carbonaceous materials as the activation temperature increased. Moreover, the microstructure properties were thoroughly characterized by the X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) studies. XRD analysis showed that the activation of the ACFs shrank the ordered structure, reducing the D-spacing from 0.358 to 0.347 nm for the fibers prepared at activation temperatures of 600 to 900 °C. Meanwhile, XPS analysis concluded that that the oxygen containing functional groups were still retained even at high activation temperatures while the nitrogen containing functional groups were reduced during the high temperature activation in the CO_2 atmosphere.

Keywords: Activated carbon fibers; Solvent-free coagulation process; Physical activation; Microstructure

1. Introduction

Activated carbon fibers (ACFs) can be prepared from various precursors namely polyacrylonitrile (PAN), coal, rayon, phenolic resins and pitches (Tsai, 1994). Different precursors will give different properties of ACFs and the pore texture of the ACFs significantly depends on the nature of the precursors (Chiang, Lee, & Lee, 2007). Among ACFs based on many different precursors, PAN based ACFs have attracted much attention of many researchers due to its high adsorption performance when compared to other counterparts. However, the organic solvents such as dimethylformamide (DMF) and dimethylacetamide (DMAc), which were often employed in the conventional coagulation bath in the fabrication of PAN fibers, could cause cancer after a long period of exposure due to its carcinogenic effects (Ismail, Rahman, Mustafa, & Matsuura, 2008; Yusof & Ismail, 2012a; Yusof, Ismail, Rana, & Matsuura, 2012). Therefore, in an attempt to reduce the hazardous effects, we investigated the properties of PAN/acrylamide (AM) fiber using a solvent-free coagulation bath in hollow fiber spinning of the polymer dope. It is known that the micro-structure of the ACFs finally obtained depends not only on the nature of the precursor but also on the conditions of activation that follows the precursor hollow fiber spinning, such as the activation temperature and the activation time (Sedghi, Farsani, & Shokuhfar, 2008). Nevertheless, there have been no detailed studies until now to know how the activation procedure affects the surface structure of PAN-based ACFs, particularly when the precursor PAN hollow fibers are spun in the solvent-free coagulation bath. It should be noted that the presence of pores on the rayon-based ACFs surface was recently confirmed using AFM (Wang et al., 2011; Zhao, He,

* Corresponding author.
E-mail address: norhaniza@petroleum.utm.my (N. Yusof).
Peer Review under the responsibility of Universidad Nacional Autónoma de México.

http://dx.doi.org/10.1016/j.jart.2016.02.001

Jiang, Li, & Li, 2007). It seems therefore very interesting to apply the AFM and other characterization methods to investigate the effect of activation conditions on the surface structures of the newly developed ACFs.

Therefore, the objectives of this study are to investigate the manipulation of the activation temperature toward the enhancement of micro porous structure of PAN/AM-based activated carbon fibers prepared using a solvent-free coagulation bath. In pursuit of this goal, the fibers were extensively characterized by means of atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectroscopy, wide angle X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). With the aid of these analysis methods, it is expected that this will be helpful for us to understand the relationship between the morphological behavior and chemical structure of PAN-ACFs prepared by different activation conditions. The results obtained from this study were also compared to the trends reported by previous studies.

2. Experimental

2.1. Materials and fabrication of PAN fibers

Polyacrylonitrile (PAN) in powder form was obtained from Aldrich, USA. Meanwhile, acrylamide (AM) purchased from Sigma–Aldrich, Germany was used as an additive. Dimethylformamide (DMF) purchased from Merck, Germany was employed as the solvent. The method to prepare uniform spinning dope of PAN and AM in DMF was reported earlier (Ismail et al., 2008; Yusof & Ismail, 2012a; Yusof et al., 2012). Eighteen weight percent of PAN/DMF solution was prepared, into which 5% of AM was added. The slurry was heated continuously at 70 °C until a highly viscous dope solution became ready for the spinning process. Then, the homogeneous dope was degassed in an ultrasonic bath (Branson Ultrasonics) for 24 h to remove the gas bubbles present in the dope. The dry-jet-wet spinning technique was used to produce PAN fibers. The high interest regarding environmental issues has resulted in the development of PAN fiber fabrication in a solvent-free coagulation process using 100% tap water in the coagulation bath (Ismail et al., 2008; Yusof & Ismail, 2012a; Yusof et al., 2012). The spinning conditions used in this study are listed elsewhere (Yusof & Ismail, 2012a). The AM/PAN fibers have a round shape cross-section with a fiber diameter around 100 μm.

2.2. Pyrolysis process

The stabilization process was carried out under tension in an air flow condition by heating at a rate of 2 °C/min until 275 °C, before constant heating carried on for 30 min. This is an important step in preparing the fibers so that they can withstand higher temperatures without decomposing during the carbonization treatment by further orienting and then cross-linking the molecules (Sedghi et al., 2008; Yusof & Ismail, 2012b). The quality of the resulting activated carbon fibers depends strongly upon the degree of stabilization (Yusof & Ismail, 2012b).

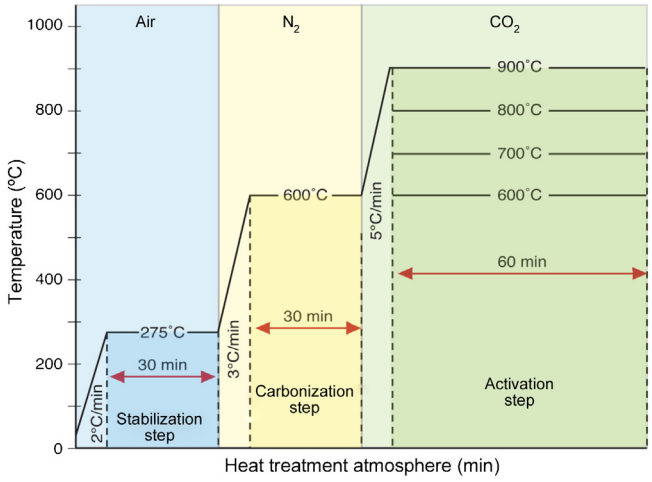

Fig. 1. Heat treatment protocol for preparation of ACFs.

The carbonization process was carried out without tension in a high-purity nitrogen stream with a flow rate of 0.2 L/min at a heating rate of 3 °C/min until 600 °C was reached. Then the temperature was kept at 600 °C for 30 min, which is known as the soaking time. The activation step of the fibers was done with the introduction of carbon dioxide gas with a flow rate of 0.2 L/min at a heating rate of 5 °C/min and at various activation temperatures of 700, 800 and 900 °C for 1 h of activation time. The fibers made at the activation temperature of 700, 800 and 900 °C are named as ACF 700, ACF 800, and ACF 900, respectively. For the case of ACF 600, the fiber is made at the 600 °C activation temperature for 1 h in the carbon dioxide gas atmosphere. It is noted that neither tension nor load was applied to the fiber during this process. The details of the heat treatment protocol can be illustrated in Figure 1.

2.3. Characterization

2.3.1. Observation of surface and surface pores by the atomic force microscopy (AFM)

The surface morphology and roughness (R_a) of the ACFs were observed by atomic force microscopy (AFM). The samples were washed in ethanol to remove all traces of glycerol. Small pieces were cut from each fiber, fixed onto magnetic disks by using double side adhesive tape and then attached to a magnetic sample holder, located on top of the scanner tube. In order to analyze the fibers internal surface, the fibers were cut longitudinally by means of a sharp razor (Hallmark Blades Ltd., Sheffield, UK). Samples intended for observation of the internal surface were sectioned on the bias so that their cylindrical shape was retained and not strained during observation.

The laser beam of the AFM was focused on a preselected spot of the surface prior to the engagement of the cantilever. AFM was operating in a tapping mode at the surface of the ACFs. Surface scanning was done at an ambient temperature under the air environment using a NanoScope III AFM equipped with a 1533D scanner (Digital Instruments, Santa Barbara, CA). The R_a was measured by visual inspection of the line profile from different areas of the carbon fiber using the NanoScope software.