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Optimum stabilization processing parameters for polyacrylonitrile-based carbon nanofibers and their difference with carbon (micro) fibers

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ABSTRACT

Carbon nanofiber webs have high electrical and thermal conductivity, porosity and surface area, etc. making them favorable in many applications. In this paper, three types of polyacrylonitrile (PAN) co-polymers are electrospun (average diameter of 150–500 nm) and carbon nanofibers are produced (average diameter of 110–300 nm). The effects of chemical composition and processing parameters on the formation of graphitic structure, morphology and electrical conductivity of the carbon nanofibers are studied. Unlike carbon fibers in micro scale, using PAN without acidic comonomers is suitable for production of carbon nanofibers. Common processing parameters for stabilization of PAN microfibers are not applicable to PAN nanofibers. Nanofibers stabilized using common microfibers procedure cannot tolerate high carbonization temperatures. While, thermal stabilization at higher temperature (300 °C) results in proper stabilized structure with ability to tolerate carbonization conditions. Progress of stabilization reactions higher than 98% is inappropriate for obtaining electrically conductive nanofiber webs, whereas 85–90% progress is considered adequate for development of proper structure during carbonization to obtain optimum electrical conductivity. Formation of nanofiber mats in shape of an interconnected sponge-like structure is believed to be necessary for obtaining much higher electrical conductivity (17–26 S/cm compared to 1–8 S/cm). Reducing fiber diameter from micro to nanoscale, the effect of processing parameters as well as the rate of thermochemical reactions can be different.

1. Introduction

Carbon microfibers possess high mechanical strength and modulus, low density, excellent electrical and thermal conductivities; therefore, they have been widely used for numerous applications particularly for the development of large load-bearing composites [1–5]. PAN copolymers are the best precursors for the production of carbon micro and nanofibers [6–9]. Production of carbon microfibers from PAN precursor fibers includes stabilization in air (200–350 °C), followed by high temperature carbonization (800–2000 °C) in high purity nitrogen atmosphere [10–13]. Beside other important structural modifications to improve mechanical properties of carbon fibers, reduction of fiber diameter is also one of the effective methods to minimize structural defects of carbon fibers and improve mechanical properties. Therefore, obtaining carbon fibers with smaller diameter is one of the important objectives in carbon fiber industry. Moreover, reduction of fiber diameter results in increased surface area per unit mass, which facilitates the stabilization of precursor fiber and prevents from formation of core – shell structures [2,4,14,15].

Carbon nanofibers are receiving increasing attention because of their large length to diameter ratio, high strength, elastic modulus, and relatively low density. Therefore, they are used in composite reinforcement and nanocomposites [1,16–19]. Furthermore, carbon nanofiber webs have high thermal and electrical conductivity, porosity and surface area as well as uniform pore size distribution,

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high chemical stability and excellent corrosion resistance, which makes them proper templates for nanotubes, filters, gas storage systems (mainly hydrogen), fuel cells, rechargeable batteries, catalyst supports, supercapacitors, etc. [1,6,7,16–18,20–27]. The electrospun nanofibers produced from PAN copolymers are uniform, with high degree of molecular orientation. Their structural defects are also less than PAN homopolymer nanofibers. These nanofibers are approximately 30 times finer than PAN microfibers. Additionally, the electrospun PAN nanofiber webs have relatively uniform pore size distribution, high interconnectivity of pores and high porosity [3–5,27–29].

Highly polar nitrile groups in PAN homopolymer make spinning process difficult [30]. Stabilization process of PAN homopolymer fibers is performed at relatively high temperatures, where the reactions are difficult to control due to sudden heat release [3,9]. Incorporation of comonomers into PAN chains reduces the nitrile – nitrile interactions and increases the solubility of the polymer. Hence, polymer chains can be more readily oriented beside each other and fiber orientation would improve. In addition, presence of comonomers facilitates the thermochemical reactions during oxidative stabilization by reducing the activation energy and initiation temperature of the reactions. Moreover, the temperature range of exothermic reactions is broadened, which improves the uniformity and mechanical properties of stabilized fibers and resulting carbon fibers [2,9,31–33]. Stabilization is the most complicated and time-consuming process in the production of carbon fibers. It is a thermo-mechanical and multi-step process usually carried out in air atmosphere in the temperature range of 200–350 °C, especially in production of carbon microfibers [9–11,34–36]. During this process, chemical and physical changes such as cyclization, dehydrogenation, oxidation, crosslinking and chain fragmentation take place in fibers. The linear structure of PAN is converted into an infusible ladder-like structure that can tolerate higher temperatures in carbonization process [1,10,11,31,34–42]. If PAN fibers are not properly stabilized, either obtaining carbon fibers will be impossible or low quality carbon fibers will be produced [43]. It is accepted that a maximum stabilization progress of about 60% in case of PAN microfibers is preferable for production of carbon microfibers, whereas higher progress of reactions leads to fiber damage in carbonization process [9,35]. High performance carbon microfibers are usually made from copolymers of PAN. Acidic comonomers such as itaconic acid are used to decrease initiation temperature of the cyclization reactions in the stabilization process, whereas esteric comonomers such as methyl acrylate are used to improve solubility, spinnability and stretchability of the fibers [2]. Coleman and Sivy [43] studied degradation rate of PAN copolymers containing vinyl acetate, acrylamide and methacrylic acid by FT-IR spectroscopy. They observed that the degradation rate strongly depends on chemical composition of the comonomers. The effect of different comonomers on stabilization reactions of PAN nanofibers has also been investigated. But the research on this subject is limited compared to PAN microfibers. Cetiner et al. [30] showed that presence of vinyl acetate comonomer in PAN copolymers, decreases PAN nanofiber diameter and provides excellent mechanical stability for the resulting carbon nanofibers. Liu et al. [2] compared nanofibers of PAN dipolymer (including itaconic acid comonomers) with PAN terpolymer (including itaconic acid, and methyl acrylate comonomers). They observed that PAN dipolymer nanofibers have higher macromolecular regularity, better orientation of macromolecular chains and crystals, and more dimensional stability. Therefore, the structural defects during thermal treatments decreases and nanofibers have desirable structural and thermochemical properties. The difference in the content and composition of comonomers affects the sequence and progress of stabilization reactions [10,35,44]. Duan et al. [45] showed that PAN copolymer nanofibers containing 8 wt% monobutyl itaconate (MBI) have higher cyclization degree than PAN copolymer nanofibers containing 5 wt% MBI in similar stabilization conditions.

After stabilization, carbonization process is carried out in an inert atmosphere at temperatures as high as 800–2000 °C. During this process, structural changes including crosslinking, and integration of cyclized segments convert the ladder-like structure of the stabilized fibers to the graphitic structure of carbon fibers [12,13]. Raman spectroscopy is used to study the microstructure of carbon nanofibers and formation of ordered graphitic structures [4,5,46,47]. A number of researchers showed that at higher carbonization temperatures, the conversion of disordered carbonaceous (turbostratic) structures to ordered graphitic structures are increased and the graphite crystal size is enhanced [4,5,19,20,46–50]. Electrical conductivity as one of the important properties of carbon nanofibers, is usually lower than 20 S/cm [20]. At low temperatures soon after stabilization, the basic structural units of carbon nanofibers are isolated due to existence of heteroatoms and voids. At higher temperatures, as the number of the heteroatoms decreases during carbonization process and the void sizes decrease, these basic structural units are bonded to each other. Once the microdomains become continuous, and the layers of turbostratic carbon appear across the nanofibers, constituting a conducting channel, the nanofibers start to be conductive. This usually takes place above 800 °C [51,52]. Several factors can increase the electrical conductivity of carbon nanofiber webs, such as higher proportion of graphitic structure, bigger size of graphitic crystallites, higher chain orientation and less structural defects (such as holes and fractures) within the individual nanofibers as well as more connection points and higher compression between nanofibers in the web [5,13,46,51,53,54]. Some researchers showed that electrical conductivity of carbon nanofibers increases with temperature and time of the carbonization process. They both result in more graphitic and ordered structure within the individual nanofibers and increased connections between carbon nanofibers in the web. Increasing the temperature of carbonization process leads to a reduction in the voids between basic structural units of individual carbon nanofibers by joining graphite-like sheets. The distorted sheets of structural units of individual carbon nanofibers are bonded to one another, wherever the boundaries of adjacent sheets meet [5,48,51,52,54–56]. However, Kim et al. [46] observed that despite the increase in graphitic microstructures from carbonization temperature of 2000–2800 °C, the electrical conductivity of carbon nanofiber webs is decreased from 55.41 to 20.15 S/cm. This is attributed to the reduced number of connection points within carbon nanofiber webs.

Compared to carbon microfibers, not many research works have been done on the production of carbon nanofibers from different PAN precursors with different chemical compositions. Due to substantial difference in fiber dimensions between micro and nanofibers, the results obtained for carbon microfibers are not expected to be completely applicable to nanofibers. Accordingly, in this work three different types of PAN copolymers, which are used to produce commercial PAN fibers and two of them (P_2 and P_3) are used to produce industrial carbon microfibers [34,44], are employed to make PAN nanofibers. Two different procedures -one of them used to produce carbon microfibers in industry-are employed for the stabilization of nanofibers, followed by carbonization. In order to investigate the effect of processing parameters in production of carbon nanofiber webs, different analysis techniques including, Fourier Transform Infrared Spectrometry (FT-IR), Differential Scanning Calorimetry (DSC), Field-Emission Scanning Electron Microscopy (FE-SEM), Raman Spectroscopy and Electrical Conductivity measurement are used.