The essential conditions for developing high electrical conductivity capability in carbon nanofibers

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Abstract
Carbon nanofiber webs have high electrical and thermal conductivity, porosity, surface area and good mechanical properties promising great potential for different applications. In this paper, three types of chemically different polyacrylonitrile (PAN) copolymers were electrospun in various concentrations and nanofibers with average diameter between 220 and 530 nm were produced. After stabilization and carbonization of PAN nanofibers, carbon nanofibers with diameter in the range of 110 to 300 nm were produced. The effects of chemical composition and processing parameters on the formation of the sponge-bond interconnected morphology and electrical conductivity of the carbon nanofibers were studied. The results revealed that the progress of stabilization reactions higher than 98% is inappropriate, whereas the stabilization progress in the range of 87% was considered adequate for the development of a proper structure for obtaining high electrical conductivity during carbonization process. Formation of nanofiber mats in shape of a network interconnected sponge-like structure was believed to be necessary for obtaining much higher electrical conductivity (16.70 S/cm compared to 1.10 and 2.33 S/cm in the case of nanofiber mats without interconnections and sponge-like structure).

Keywords— Carbon nanofibers, Electrical conductivity, Morphology, PAN nanofibers, Stabilization.

I. INTRODUCTION

Carbon microfibers have been widely used for numerous applications particularly for the development of large load-bearing composites. Obtaining carbon fibers with smaller diameter is one of the important objectives in carbon fiber industry, because 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 [1-3]. Carbon nanofibers are receiving increasing attention because of their large length to diameter ratio, high strength, elastic modulus, and relatively low density [1].

PAN copolymers are the best precursor for the production of carbon nanofibers [4-7]. Incorporation of comonomers into the PAN chains reduces the nitrile – nitrile interactions, increases the solubility of the polymer, facilitates the thermochemical reactions during oxidative stabilization by reducing the activation energy and the initiation temperature of the reactions. Moreover, the temperature range of exothermic reactions is broadened, which improves the uniformity and mechanical properties of precursor fibers and resulting carbon microfibers [2, 8-12]. During the stabilization, which is the most complicated and time-consuming process in the production of carbon nanofibers and carried out in air atmosphere in the temperature range of 200 – 350 °C, chemical and physical changes such as cyclization, dehydrogenation, oxidation, crosslinking and chain fragmentation take place. The linear structure of PAN is converted into an infusible ladder-like structure which can tolerate higher temperatures in carbonization process [1, 7, 10, 13, 14]. If PAN fibers are not properly stabilized, either obtaining carbon fibers will be impossible or the produced carbon fibers will have low quality [15]. High performance carbon
fibers are usually made from PAN copolymers. 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, spinning and stretchability of the fibers [2].

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 converts the ladder-like structure of the stabilized fibers to the graphitic structure of carbon fibers [9, 16]. A number of researchers showed that the conversion of disordered carbonaceous (turbostratic) structures to ordered graphitic structures as well as graphite crystal size are increased in carbon nanofibers carbonized at higher temperatures [17-20]. Electrical conductivity is one of the important properties of carbon nanofibers, which is usually lower than 20 S/cm [21]. Several factors can increase the electrical conductivity of carbon nanofibers, such as higher proportion of graphitic structure, higher chain orientation, more connection points between nanofibers, bigger size of graphitic crystallites, less structural defects (like holes and fractures) as well as increased compression between nanofibers [9, 17, 20, 22-24]. Some researchers showed that electrical conductivity of carbon nanofibers increases with temperature and duration of the carbonization process. They both result in a more graphitic and ordered structure and increased connections between carbon nanofibers [17, 22, 25, 26].

Less research has been done on the production of carbon nanofibers from various PAN copolymers with different chemical compositions. In this work, three types of PAN copolymers were used to obtain PAN nanofibers by electrospinning and stabilization and carbonization thermal treatments were employed to produce carbon nanofibers. Different analysis techniques including Differential Scanning Calorimetry (DSC), Field Emission Scanning Electron Microscope (FE-SEM) and electrical conductivity were used to investigate carbon nanofibers properties and the effect of processing parameters on PAN nanofibers during thermal treatments.

II. METHODS AND PROCEDURES

A. Materials

Three types of polyacrylonitrile copolymers with different chemical composition were used to produce PAN nanofibers (Table I). N, N-dimethylformamide solvent (99.5%, Merck) was used to prepare electrospinning solutions.

| Polymer Code | Manufacturer company | Chemical composition | Monomer feed in polymerization reactor (%) | [n] (dL/g) | Mv (g/mol) |
|--------------|----------------------|----------------------|------------------------------------------|-----------|------------|
| P1           | Polycryl Co.         | AN-MA-SMS            | 95-4.5-0.5                               | 1.441     | 112452     |
| P2           | Courtaulds Co. Ltd   | AN-MA-IA             | 95-4-1                                   | 2.216     | 202000     |
| P3           | Jilin Chemical Fiber Group, Co. Ltd | AN-MAA-AM    | 95-1.5-3.5                               | 2.174     | 197000     |

P: PAN Copolymer, AN: Acrylonitrile, MA: Methyl Acrylate, IA: Itaconic Acid, MAA: Methacrylic Acid, AM: Acrylamide, SMS: Sodium Methallyl Sulfonate.

B. Nanofiber production

After preparation of the electrospinning solutions (10 wt%) from each copolymer, electrospinning process was carried out at room temperature with a positive high voltage of 11 kV, solution flow rate of 0.25 ml/h. The distance between the spinneret and the fixed metal collector was 15 cm. The electrospun PAN nanofibers were stabilized using two different procedures in air atmosphere from the room temperature to 300 °C with the heating rate of 5 °C/min, followed by holding the temperature at 300 °C for 90 minutes to allow the stabilization to complete. Then stabilized nanofibers were carbonized in pure nitrogen atmosphere at 1250 °C with the heating rate set at 40 °C/min and the samples were held at the final temperature for 5 minutes. Nomenclature of PAN nanofibers (PF), stabilized PAN nanofibers (SF) and carbon nanofibers (CNF) are listed in Table II.
TABLE II
NOMENCLATURE OF INITIAL PAN NANOFIBERS, STABILIZED PAN NANOFIBERS AND CARBON NANOFIBERS

| Polymer Code | PAN nanofibers | Stabilized nanofibers | Carbon nanofibers |
|--------------|----------------|-----------------------|-------------------|
| P₁           | PF₁           | SF₁                  | CNF₁              |
| P₂           | PF₂           | SF₂                  | CNF₂              |
| P₃           | PF₃           | SF₃                  | CNF₃              |

C. Characterization

Thermal behavior of PAN nanofibers (temperature range of 50-450 °C) and stabilized PAN nanofiber (temperature range of 50-600 °C) was studied using a Mettler To ledo DSC 802 in air and at a heating rate of 5 °C/min. In order to estimate the progress of the stabilization reactions, cyclization index (CI) was calculated using the following equation [27-31]:

\[
CI = \frac{\Delta H_{PF} - \Delta H_{SF}}{\Delta H_{PF}} \times 100
\]  

(1)

Where \( \Delta H_{PF} \) and \( \Delta H_{SF} \) are the reactions enthalpy of initial PAN and stabilized PAN nanofibers, respectively.

A Hitachi U-4080 field-emission scanning electron microscope (FE-SEM) was employed in order to examine the surface morphology of PAN and carbon nanofibers. The average diameter of nanofibers was calculated using Image J software. Diameter measurements were done in 100 different points randomly selected in the micrographs of each sample. The average diameter ± standard deviation of each sample is presented [2, 32].

Electrical conductivity of carbon nanofiber webs was measured by standard four-point probe method using the Keithley 196 System DMM_2:

\[
\sigma = \frac{L}{R \times A}
\]  

(2)

Where \( L \) is distance between two electrodes in “cm”, \( R \) is the web resistance in “Ω” and \( A \) is the area of carbon nanofibers sheet in “cm²”.

III. RESULTS

A. DSC study of PAN and stabilized nanofiber Webs

DSC curves of the initial and stabilized PAN nanofibers are shown in Fig. 1. The presence of acidic comonomers in PF₂ and PF₃ nanofibers leads to initiation of cyclization reactions through ionic mechanism [10, 33-36]. As a result, the exothermic peak becomes broader and its initiation temperature decreases compared to PF₁ nanofibers (Fig. 1). Unlike PF₂ and PF₃, PF₁ nanofiber does not contain acidic comonomers. Despite similar stabilization conditions, the progress of stabilization reactions in PF₁ nanofibers is approximately 87%, whereas the progress of stabilization reactions in PF₂ and PF₃ nanofibers containing acidic comonomers is more than 98%, demonstrating maximum progress of stabilization reactions in these fibers (Table III).

B. Morphology study of PAN and carbon nanofiber webs

Field emission scanning electron microscopy (FE-SEM) images of PAN and carbon nanofiber webs are shown in Fig. 2 and their statistical data are reported in Table III. The produced initial PAN nanofiber webs were uniform and bead-free.

TABLE III
CHARACTERIZATION OF PAN AND CARBON NANOFIBERS.

| PAN nanofibers | Average diameter of PAN nanofibers (nm) | Cyclization Index (%) | Carbon nanofibers | Average diameter of carbon nanofibers (nm) | Electrical conductivity of carbon nanofibers (S/cm) |
|----------------|----------------------------------------|-----------------------|-------------------|---------------------------------------------|-------------------------------------------------|
| PF₁           | 233                                    | 87.25                 | CNF₁              | 110                                        | 16.90                                           |
| PF₂           | 240                                    | 98.59                 | CNF₂              | 178                                        | 2.33                                            |
| PF₃           | 529                                    | 99.17                 | CNF₃              | 312                                        | 1.10                                            |

In similar spinning conditions, the diameter of PF₁ nanofibers is lower than those of PF₂ and PF₃ nanofibers in various concentrations of electrospinning solution. This can be attributed to the lower molecular weight of PF₁ polymer compared to PF₂ and PF₃ (Table I). Lower diameter of PF₁ nanofibers may lead to a better diffusion of
oxygen into nanofiber structure during stabilization process. Oxygen has an important role in initiation and progress of stabilization reactions. Despite the absence of acidic comonomers in PF₁ nanofibers, better diffusion of oxygen results in proper oxidation of these nanofibers during stabilization process.

The morphology of CNF₁ nanofibers is completely different compared to CNF₂ and CNF₃ nanofibers. Most nanofiber strands in CNF₁ are merged and formed a sponge-like network structure. However, the morphology of CNF₂ and CNF₃ has not changed considerably. Only a number of fractures has been introduced in the structure due to the thermal treatment.

**Fig. 1.** DSC curves of PAN and stabilized PAN nanofibers. (a) PF₁ and SF₁, (b) PF₂ and SF₂, (c) PF₃ and SF₃.

**C. Electrical conductivity of carbon nanofiber webs**

Electrical conductivity of CNF₁ nanofiber webs is significantly higher than CNF₂ and CNF₃ nanofiber webs (Table III). The significantly higher electrical conductivity of CNF₁ nanofibers compared to CNF₂ and CNF₃ can be attributed to formation of connection points between nanofibers during thermal treatment, resulting in a sponge-like compact network structure of carbon nanofibers mats (Fig. 2).

The electrical conductivity of carbon nanofiber webs are mainly influenced from the compactness of structure and formation of connection points due to thermal treatment. The more compact nanofiber mats increases the probability of presence of connection points and enhancement of carbon nanofiber webs electrical conductivity. In CNF₁ nanofibers (Fig. 2), a number of nanofiber strands are merged together and a sponge-like network structure is created.
PF$_2$ and PF$_3$ nanofibers show higher progress in stabilization reactions due to the presence of acidic comonomers. However, the electrical conductivity of their carbon nanofibers is lower than CNF$_1$ nanofibers. Therefore, it can be concluded that obtaining proper carbon structure, specially higher electrical conductivity, requires an optimum stabilization process with optimum progress in stabilization reactions and formation of a sponge-like interconnected network of carbon nanofibers.

IV. CONCLUSION

Carbon nanofiber webs were produced from three different types of PAN precursor through the stabilization and carbonization of electrospun PAN nanofiber webs. The results showed that despite the common viewpoint in production technology of carbon fibers in micro scale, presence of acidic comonomers in the copolymer structure is not necessary for production of carbon fibers at nanoscale. The results revealed that progress of stabilization reactions higher than 98% is inappropriate, whereas the stabilization progress in the range of 87% leads to development of proper graphitic structure during carbonization process and formation of nanofiber mats in shape of an interconnected sponge-like network structure with much higher electrical conductivity. Therefore, it can be concluded that the formation of interconnected structure in carbon nanofiber web is essential for obtaining high electrical conductivity.

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