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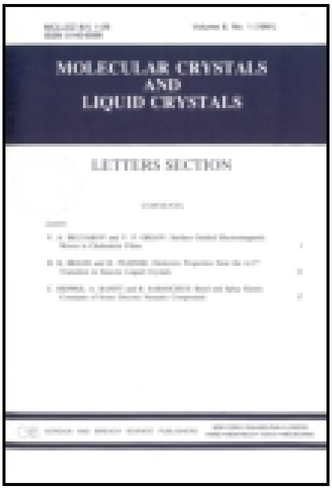

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Plasma and $KMnO_4$ Oxidation of Polyacrylonitrile Nanofiber

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The effect of plasma and chemical methods on the stabilization of Polyacrylonitrile (PAN) nanofiber prepared by electrospinning technique, has been investigated at various oxygen contents (10%, 20%, and 30%) and $KMnO_4$ solutions (3% and 5%). Fourier transform infrared (FT-IR) analysis of plasma and chemical oxidized samples indicated that the treated nanofibers were oxidized under different contents of oxygen plasma and $KMnO_4$ contents by increasing the peak intensities of C=O stretching band and OH– stretching vibration mode, respectively. Additionally conversion of C≡N bands into C=N ones in the copolymer chain was observed in both plasma and chemical methods, but changes in chemical stabilized samples were not very sensible. Field emission scanning electron microscopy (FE-SEM) images revealed that the surfaces of the plasma treated nanofibers were extremely etched. Furthermore a higher reduction in the average oxidized nanofiber diameters was observed using plasma method.

Keywords FT-IR; PAN; SEM; Stabilization

1. Introduction

PAN and copolymers of PAN have been widely studied for almost a century for commercial technological exploitations. Recently, considerable efforts have been devoted to its processing and fiber forming technologies. Among the various precursors for producing carbon nanofibers (CNFs), PAN is the most commonly used polymer, mainly due to its high carbon yield (up to 56%), flexibility for tailoring the structure of the final CNF products and the ease of obtaining oxidized products due to the formation of a ladder structure via nitrile polymerization [1–5]. The chemistry of PAN is of particular interest because of its use as a precursor in the formation of CNFs for different applications, including porous structured CNFs of high surface area for electronics and energy storage applications as well as graphite reinforcement filaments for organic materials in high strength and high stiffness composites. PAN also has many advantages such as large original modulus, high tensile strength, anti-acid, alkali, corrosion, good dispersing, large oil-absorbency, and stable with chemicals. PAN and its copolymers are most common precursors for the production of CNFs because of their excellent characteristics, such as spinnability, being

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environmentally friendly and commercial viability. Although there are other materials such as rayon or pitch that can be used to produce CNFs, but experimental results show that PAN copolymers result in carbon fibers with a better performance in comparison to PAN homo polymer [6–9]. The preparation of CNFs from PAN precursor involves three main steps of which the oxidative stabilization step is the most important for obtaining high-quality CNFs. Results show that good oxidative stabilization of PAN fiber is necessary to obtain high-quality CNFs.

Recently, remarkable efforts have been done in the fields of processing and fiber forming technologies. It is generally accepted that a major limitation to the tensile strength of PAN-based carbon fibers is the presence of surface defects and large fiber diameters. There has been a trend toward thinning precursor fibers with small diameters providing uniformity of thermal stabilization in very short times and carbon fibers with fewer defects per unit volume. Hence, ideal oxidation stabilization would allow the removal of surface defects and attenuation of fiber diameter. Conversion of PAN fibers to carbon fibers requires a critical thermal stabilization stage which has great influence on the final properties of the carbon fibers. For example, the chemical stabilization process is commonly performed in air between 180 and 300°C [10,11]. During this process, PAN undergoes a number of physical and chemical changes that converts the linear PAN molecular chains to an aromatic ladder structure suitable for further conversion to carbon fibers [12,13]. Cross-linking of PAN will impart some of its important physical properties, such as insolubility and resistance to swelling in common organic solvents. Also stabilization process is very effective way to stabilization of PAN and is done in a very short time in comparison of chemical method.

2. Experimental Details

2.1. Material

The material used in this work was terpolymer polyacrylonitrile. It contains 93% acrylonitrile, 6.1% methyl acrylate and 0.9% methylallyl sulphonate. The molecular weight of the polymer is 300,000–500,000. The concentration 15% wt PAN/DMF solution were stirred by an electromagnetically driven magnet at room temperature for 30–50 hr in order to obtain homogeneous solution.

2.2. Electrospinning Nanofiber

In a typical process, an electrical potential is applied between a droplet of polymer solution or melt held at the end of a capillary and a grounded collector. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution or melt is ejected. The jet becomes longer and thinner, because of the bending instability or splitting until it solidifies or collects on the collector. The nanometre's diameter size promises a high specific surface area and durable physical properties on the compression process [14–20]. The solution was immediately collected into a 15 mL syringe equipped with an 18 gauge stainless steel needle tip. The syringe was fixed on an electric syringe pump set to maintain a constant feedrate of 0.5 mL/hr. A high voltage power supply (Gamma ES40P-20 W/DAM) was employed to apply positive charge to the needle, and a grounded metal plate covered with aluminium foil as the collector. The voltage used for electrospinning was 18 KV. The distance between the needle tip and collector was 19 cm. Nanofiber was produced with an

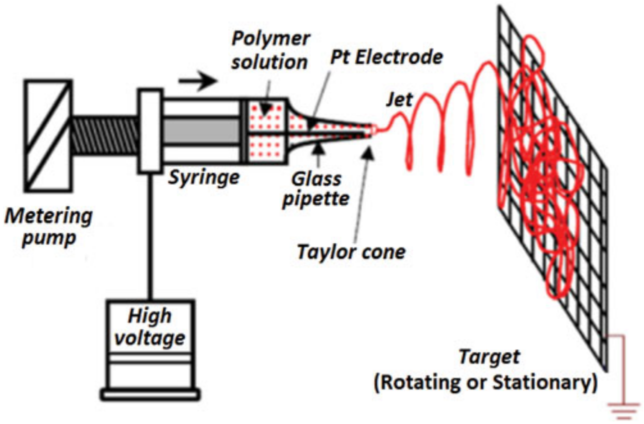

Figure 1. Schematic diagram of electrospinning apparatus.

average diameter of 377 nm. A schematic diagram of electrospinning apparatus is presented in Fig. 1.

2.3. Chemical Stabilization by $KMnO_4$ Solution

In the chemical stabilization PAN samples were put in a $KMnO_4$ solution and heated to a temperature in the range of 180–300 °C for over an hour. After heating results show that C≡N band was changed to C = N and some functional groups were produced too. It is necessary to note that heating the solution in high temperature and using a larger amount of catalyst damage the polymer. Chemical modification's schematic of PAN to modified PAN is shown in Fig. 2.

2.4. Low-Pressure DC Plasma Treatment

The schematic diagram of the plasma configuration is shown in Fig. 3. The reactor is a Pyrex cylinder of 12 cm length and 15 cm diameter, with two internal electrodes separated

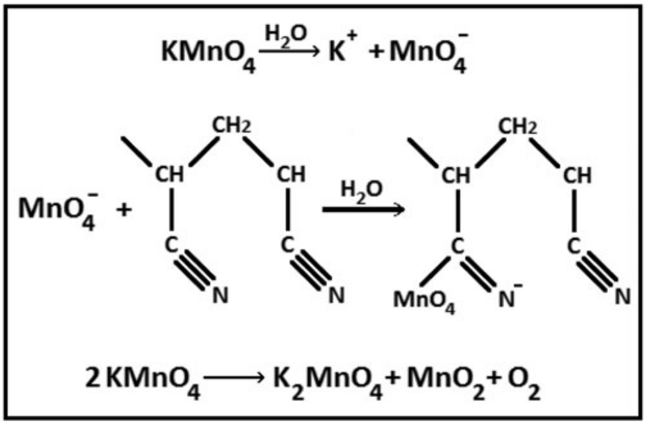

Figure 2. Modification schematic of chemical oxidation of PAN.

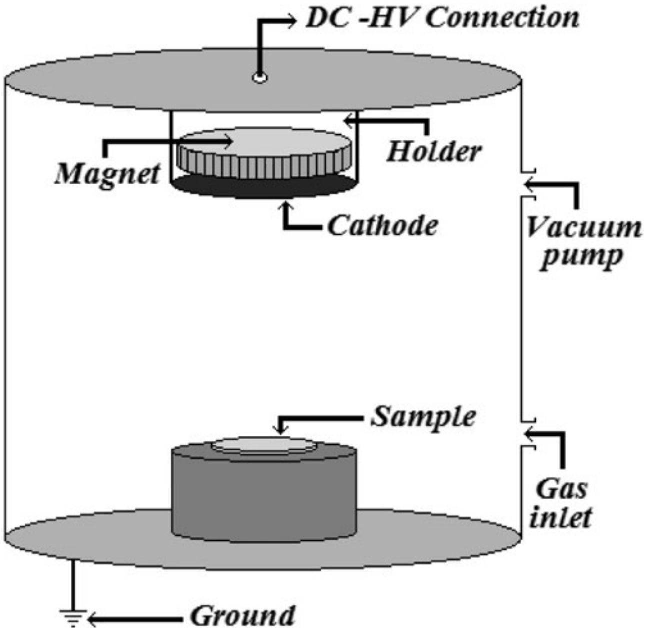

Figure 3. Schematic of chemical oxidation of PAN.

by 5 cm. The polymer samples were located at the bottom of the chamber using a metal support. Samples were treated under 10%, 20%, and 30% of oxygen for 15 min of plasma.

Before beginning the experiment, the chamber was evacuated up to 5×10^{-5} mbar by rotary and turbo pumps. After that mixed gas was fed in to the chamber via a needle valve at low pressure. The chamber keeps the vacuum between 5×10^{-2} mbar during the process. By using high voltage, the gas was ionized and converted to plasma by the DC power supply.

Plasma as a full ionized gas interacts in numerous ways with a polymer surface [21]. The results show that bulk properties of the polymers were unchanged because the attack by atomic oxygen is limited to the surface of the polymer. In many instances, a simple ablation of the surface was observed, but in some cases, especially polyethylene and polypropylene, a highly oxidized surface layer was created. In rather severe conditions, the polymer surface is subject to etching effects, where by the polymer is continuously degraded, physical etching occurs under strong ion bombardment. Plasma irradiation on the polymer surface make C–H, CH_2 bands are broken and free radicals are produced, which interact with the ambient oxygen. In this way, oxygen containing groups (carbonyl, carboxyl, etc.) are created, which increased the polymer surface polarity.

3. Results and Discussion

Fourier transform infrared (FT-IR) spectroscopy has proven to be an excellent technique to study the structural evolution of PAN fibers during the oxidation. In the present work, the main functional groups of extruder PAN fibers were identified and characterized by the FT-IR technique. Figure 4 shows the FT-IR patterns of untreated sample and plasma oxidized samples with different oxygen contents. Based on FT-IR analysis of oxidized samples using plasma treatment, the intensities of $C = O$ and COOH– bands (wavelength of

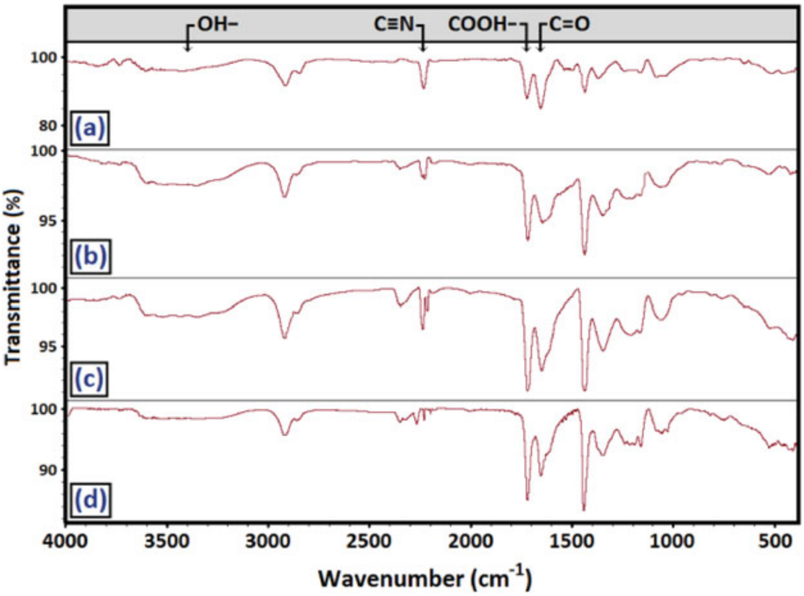

Figure 4. FT-IR spectra of (a) untreated sample and oxidized PAN nanofibers by plasma with (b) 10% oxygen, (c) 20% oxygen, and (d) 30% oxygen.

1500–2000 cm^{-1}) were increased with increasing the plasma oxygen content. Additionally, a reduction in the extent of cyclization reaction is observed with further increase in oxygen contents which implies lower conversion of C≡N bands into C=N ones in the copolymer chain. A gradual decrease in the formation of the amine bands C=N at 2358 cm^{-1} is observed at higher oxygen content which implies the lower extent of cyclization. Seemingly, with increase in oxygen flow under plasma oxidative environment, the extent of oxidation is more dominate than the extent of cyclization reaction.

Because of the chemical reactions involved, cyclization, dehydrogenation, aromatization, oxidation, and cross-linking occur and as a result of the conversion of C≡N to C=N band a fully aromatic cyclized ladder-type structure form. It has also been reported that during chemical stabilization, according to Fig. 5. the OH– (3000–3500 cm^{-1}) bands are increased drastically. Also the intensities of oxygen containing groups namely, C=O and COOH– groups were increased with $KMnO_4$ content. As can be seen from Fig. 5. intensity cyanide band (C≡N) in 2240 cm^{-1} is creased, decreasing C≡N means that crosslinking is occurring and result in fully aromatic polymer ladder-type structure forms. By increasing catalyst content in chemical stabilization, OH– band is increased drastically and C≡N band is decreased, but its decreasing amount in plasma stabilization is very higher than the chemical stabilization.

Morphological properties of untreated sample and oxidized PAN nanofibers using plasma and chemical methods have been investigated by FE-SEM micrographs. Figure 6 shows FE-SEM images of untreated sample, oxidized PAN nanofibers by plasma with various oxygen contents and obtained samples by chemical method.

From Fig. 6. observe that after both plasma and chemical oxidation, fibers become rougher. As it is observable from Fig. 6. the plasma oxidized nanofibers are etched. For example, the oxidized PAN nanofiber by plasma with 30% oxygen content, due to the existence of strong ion bombardment, is extremely etched (see Fig. (6-d)).

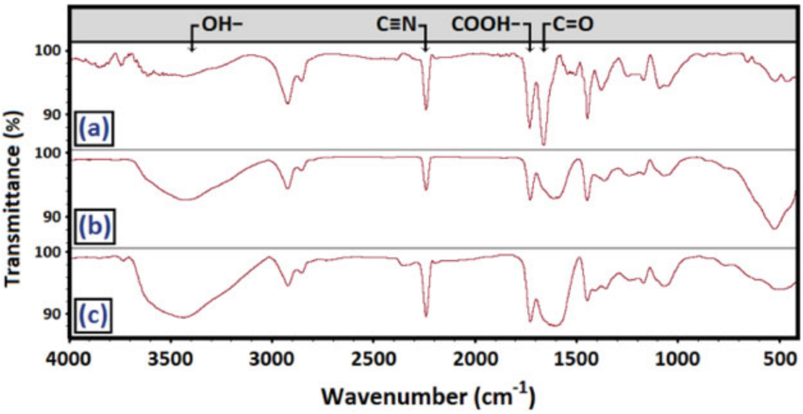

Figure 5. FT-IR spectra of (a) untreated sample and oxidized PAN nanofibers by (b) 3% $KMnO_4$ and (c) 5% $KMnO_4$.

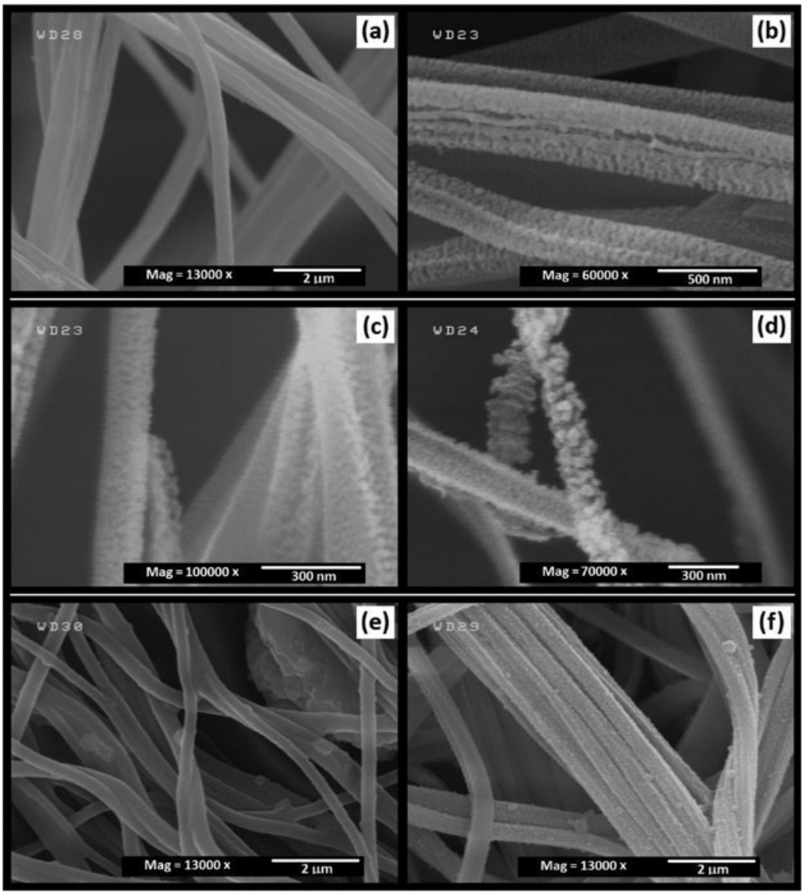

Figure 6. FE-SEM images of (a) untreated sample, oxidized PAN nanofibers by plasma with (b) 10% oxygen, (c) 20% oxygen, (d) 30% oxygen and oxidized PAN nanofibers by chemical method with (e) 3% $KMnO_4$ and (f) 5% $KMnO_4$.

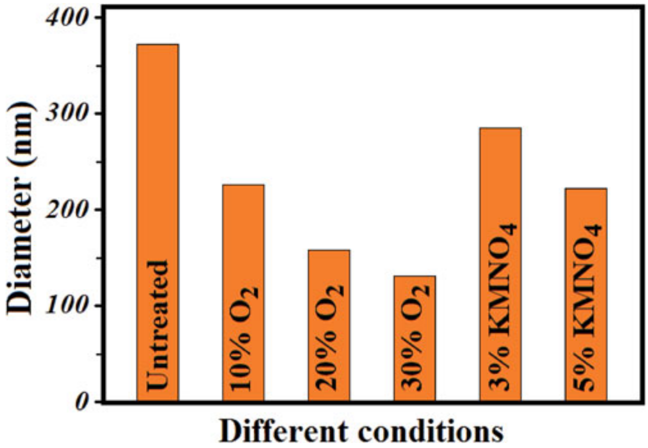

Figure 7. Average diameter of oxidized PAN nanofibers.

The diameter of the oxidized PAN nanofibers investigated by obtained results from FE-SEM images. Figure 7 shows the average diameter of obtained samples with various conditions.

As it is observable from Fig. 7, reduction in the average diameter is observed in oxidized PAN samples in both of methods. However, plasma treatment leads to more reduction of the diameter of the oxidized PAN nanofibers with respect to chemical method. The diameter of the oxidized PAN nanofiber decreases about 65% as a result of plasma treatment (with 30% oxygen content) and 41% by the chemical oxidative stabilization (with 5% $KMnO_4$).

Conclusion

The PAN nanofibers were oxidized under plasma treatment (with 10%, 20%, and 30% oxygen contents) and chemical method (with 3% and 5% $KMnO_4$ contents). Based on the FT-IR analysis, the intensities of oxygen containing groups namely, C=O, COOH– and OH– groups were increased with plasma exposure time and oxygen content in the oxidation. Decreasing in diameter of oxidized nanofibers can be result of producing some polar bands such as OH–, COOH–, and C=O. Producing these polar bands, make the polymer chains attract each others, this can be reduced diameter of fiber. However, the extent of cyclization reaction in the conversion of C≡N bands into C=N ones was decreased at higher oxygen contents and $KMnO_4$. Decreasing C≡N bands and crosslinking, make the distance between fibers has been decreased and this make the nanofiber's diameter will be decreased. According to the FE-SEM observations, some clues were formed on the surface of the treated nanofibers under plasma physical etching or strong ion bombardment with increasing the exposure time and oxygen content. The average fiber diameters were reduced from 377 nm in the PAN nanofiber to 180, 150 and 130 nm in the oxidized one under 10%, 20%, and 30% of oxygen content. More over the average fiber diameters were reduced from 377 nm in the PAN nanofiber to 288 and 220 nm in the oxidized one under 3%, and 5% $KMnO_4$ contents. Results show that the plasma stabilization is very effective than the chemical stabilization. Plasma stabilization is done in a very short time in comparison to the chemical method.

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