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Morphological Study of Hybrid Nanofibers Based on Polyaniline/Carbon Nanofibers Prepared by Electrospinning Method

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Abstract

Uniform and thin polyaniline/carbon nanofiber (PANi/CNF) hybrid nanofibers has been prepared using electrospinning method. Three polymer solutions with different components were examined for synthesis of PANi/CNF electrospun nanofibers. The SEM technique and FT-IR analysis were used to characterize the hybrid nanofibers. Effects of process parameters and used materials on the morphology and diameter of PANi/CNF hybrid nanofibers were experimentally studied in the each of polymer solutions. The resulting nanofibers obtained from the polymer solution containing commercial PANi with combination of dichloroacetic acid (DCAA) and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPSA) were more uniform and thinner than prepared fibers from other polymer solutions. The average diameter of synthesized hybrid nanofibres using the polymer solution containing AMPSA/DCAA was about 100 nm.

Keywords: Electrospinning, Carbon nanofibers, Hybrid nanofibers, Polyaniline.

Contents

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Abbreviations

PANi Polyaniline
CNF Carbon nanofiber
DCAA Dichloroacetic acid
PVA Polyvinyl alcohol
PSS Polysulfonated styrene
PEO Polyethylene oxide
PMMA Polymethyl methacrylate
CNTs Carbon nanotubes
DI Deionized water
NMP N-Methyl-2-pyrrolidone
APS Ammonium peroxydisulfate
AMPSA 2-acrylamido-2-methyl-1-propane sulfonic acid
PANiEB Emeraldine base form of polyaniline

1. Introduction

Many studies have examined conductive polymer nanostructures in the form of nanofibers and nanotubes and have reported the advantages of these nanostructures compared with conventional conductive polymers in many applications such as catalyst support [1] supercapacitors [2] sensors [3] electronic devices [4] gas-separation membranes and etc [5]. Among the conducting polymers, polyaniline has been studied extensively because of its attractive properties such as high conductivity, excellent environmental stability, inexpensive monomer, good processability which makes it very applicable [6]. Electrospinning is a physical method for fabrication of polymer nanofibers with multi-compositions. Polyaniline electrospun nanofibers, in addition to having properties of traditional polyaniline, also have unique functionality such as high porosity, high specific surface area and excellent mechanical performance [7]. Hence, these fibrous polyanilines have improved performance considerably in cases where a larger surface area is needed, such as catalyst supports, sensors and etc. Furthermore, polyaniline alone can not be electrospun into nanofibrous structures due to its limited solubility and molecular weight. Studies have demonstrated that for preparation of polyaniline electrospun nanofibers, it can be blended with spinnable polymers such as polyvinyl alcohol (PVA) [8] polysulfonated styrene (PSS) [9] polyethylene oxide (PEO) [10] polymethyl methacrylate (PMMA) [11] and etc. The resulting nanofibers of the mixing of polyaniline with a spinnable polymers in electrospinning method, can have drawbacks in terms of electrical conductivity. Therefore, some studies have investigated the electrospinning of polyaniline with nanoparticles or carbon nanotubes as additives and have reported that the fiber properties were improved Yu, et al. [12]. Shin, et al. [13] have reported that the introduction of carbon nanotubes (CNTs) to PANi/PEO nanofibers can improve the electrical properties of the electrospun polyanline nanofibers. Mottaghitalab et al. [14-16] investigated the influence of addition of single- and multi-wall CNTs to the PANi electrospun nanofibers and observed that CNTs can improve the conductivity, morphological stability and mechanical strength of fabricated nanofibers. PANi/CNT fibers were studied as electrode material by Wang, et al. [4] and they reported that CNT can improve the electrical properties of the fibers. The electrospinning of PANi-C combined with PVA (as spinnable polymer) has been reported by Sujith, et al. [17] and they found that morphology of the resulting nanofiber was stable. Compared to CNTs, carbon nanofibers have been investigated less in studies but nevertheless carbon nanofibers can offer unique properties such as chemical stability ,good electronic conductivity and high surface area [18]. Hybrid of the nanostructured carbon materials(e.g. CNF and CNT) and conductive polymers can offer more suitable properties such as higher surface area and higher electron conductivity compared with their single component [19]. So far, the synthesis and applications of PANi/CNT electrospun nanofibers have been reported but, to the best of our knowledge, no studies have examined the hybrid of PANi/CNF electrospun nanofibers. In present study, the preparation of a novel hybrid system has been investigated based on polyaniline/carbon nanofiber (PANi/CNF) electrospun nanofibers using three different polymer solutions. Preparation method of each polymer solutions and synthesis of PANi/CNF hybrid nanofibers via electrospinning method were described. At first, the synthesized polyaniline were used to preparation of spinning solution, then commercial polyaniline were examined. Finally, commercial polyaniline with a combination of 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPSA) and dichloroacetic acid (DCAA) were used in polymer solution for synthesis of hybrid nanofibers and in the each step PVA was used as an auxiliary polymer. Also, electrospinning process parameters were examined for each polymer solution to the synthesis of uniform and thin nanofibers. The morphological characteristics of the synthesized nanofibers by three polymer solutions were studied in the different values of electrospinning parameters by scanning electronic microscopy (SEM).

2. Experimental

2.1. Preparation of Dedoped PANi

In order to prepare the dedoped PANi, 1 gr ammonium peroxydisulfate (APS) was added to 100 ml of sulphuric acid (1 M) and the mixture was stirred for 15 min. 1 ml distilled aniline monomer (Merck) was injected into the previous solution and was stirred for 5 h. During the reaction, the color of solution was changed into dark green. After 5 h, the resulting polymer were centrifuged, then the precipitated was washed several times with deionized (DI) water. To prepare emeraldine base form of polyaniline (PANiEB), ammonia solution was added to the precipitate from the previous step that was placed on the magnetic stirrer, and during the addition, the color of product was changed to dark blue. The final solution was filtered and washed with DI water then dried in vacuum oven at 60℃.

2.2. Preparation of Spinning Solution

2.2.1. Spinning Solution of Synthesized PANi

At first, in order to remove metallic impurities, CNF (from Sigma Aldrich, platelet type) was treated with a mixture of HNO_3 /H_2SO_4 (1:3 by volume) and used in subsequent steps. 0.03 gr synthesized PANi was dissolved in N-Methyl-2-pyrrolidone (NMP) and stirred at 50℃. In another container, solution of 10% (w/v) Polyvinyl alcohol (PVA, M_w=720000 g mol^{-1}, Merck) in DI water was stirred at 70℃ to obtain a viscous solution. Then, a solution containing PVA was added to PANiEB solution. A weighted amount of treated CNF was dispersed in ethanol by ultrasonic bath for 30 min and then added to the previous mixture. This mixture was stirred for 10 min at 50℃. To obtain a homogeneous solution and then Filtered. This filtered mixture was transferred to electrospinning set up [20].

2.2.2. Spinning Solution of Commercial PANi

Commercial PANiEB (from Sigma Aldrich Grade, Conductivity: 30 S/cm) was used to preparation of this polymer solution. The amount of materials and preparation method of polymer solution is the same as previous step, except the type of polymer, that commercial emeraldine base form of polyaniline was used.

2.2.3. Spinning Solution of Commercial PANi with AMPSA/DCAA

0.2 g of AMPSA (Sigma Aldrich) was dispersed in 10 ml DCAA (98%, Merck) by ultrasonic bath until a colorless solution was produced then treated CNF was added to this solution and again was dispersed through an ultrasonic bath for 30 min. Gray powder obtained by mixing 0.4 gr of commercial PANiEB and 0.3 gr of AMPSA were added to the previous solution and was stirred under nitrogen atmosphere. The resulting mixture was filtered and then transferred to electrospinning system [16].

2.3. Electrospinning

The resulting spinning solution of each steps was transferred to a 2 ml plastic syringe separately and flow rate of the spinning solution was controlled by a syringe pump. An aluminum foil as fibers collector was placed horizontally below the syringe. An electric potential difference was applied through a high DC voltage power supply set between the aluminum foil and the syringe tip. Finally, electrospinning technique for different spinning solutions in the range of process parameters are listed in Table 1 to 3 were performed. The spinning voltage, distance from tip to collector and flow rate of spinning solution, have changed according to data presented in these tables to produce uniform nanofibers.

2.4. Characterization of Hybrid Nanofibers

The morphological studies of PANi/CNF hybrid nanofibers and estimating the average fiber diameter were performed using scanning electron microscopy technique (SEM). SEM images of synthesized hybrid nanofibers for each of the spinning solutions have been investigated, in the range of process parameters presented in Table 1 to 3. The chemical structures of the synthesized hybrid nanofibers was characterized by the Fourier transform infrared (FTIR) spectroscopy analysis.

Table-1. Values of the applied process parameters for the spinning solution containing commercial PANi

Values of process parameters					
V [a]	14	17	19	20	22
Q [b]	0.25	0.5	0.75	1	1.5
d [c]	6	9	14	16	19

[a] Applied voltage (kv). [b] Flow rate of polymer solution (ml/hr). [c] Tip to collector distance (cm).

Table-2. Values of the applied process parameters for the spinning solution containing synthesized PANi

Values of process parameters					
V [a]	14	16	18	20	22
Q [b]	0.25	0.5	0.75	1	1.5
d [c]	5	9	13	16	19

[a]Applied voltage(kv). [b] Flow rate of polymer solution(ml/hr). [c] Tip to collector distance(Cm).

Table-3. Values of the applied process parameters for the spinning solution containing commercial PANi with combination of AMPSA/DCAA

Values of process parameters					
V [a]	15	16	18	20	22
Q [b]	0.25	0.5	0.75	1	1.5
d [c]	7	10	13	17	20

[a] Applied voltage(kv). [b] Flow rate of polymer solution(ml/hr). [c] Tip to collector distance(Cm).

3. Results and Discussion

3.1. Surface Morphology of PANi/CNF Hybrid Nanofibers

The effect of changes in the values of process parameters on the morphology of fibers are shown in Figures 1 to 7. As shown in the SEM images, small changes in parameters can lead to significant changes in the fibers morphology. A constant concentration of the polymer solution was considered for all experiments and the effects of changes the spinning voltage, flow rate of polymer solution and tip to collector distance on the fibers morphology was investigated. In the case of nanofibers obtained from synthesized polyaniline, as shown in Fig.1 (a) no fibers were formed at lower voltages (12 kv). With increasing the electrospinning voltage (19 kv), fibers with the beads or

belt-like structures have been observed, which is shown in Fig.1 (b). There were more probability to formation of high density of bead in the excessive values of voltage, because the polymer jet wasn't stable and controllable.

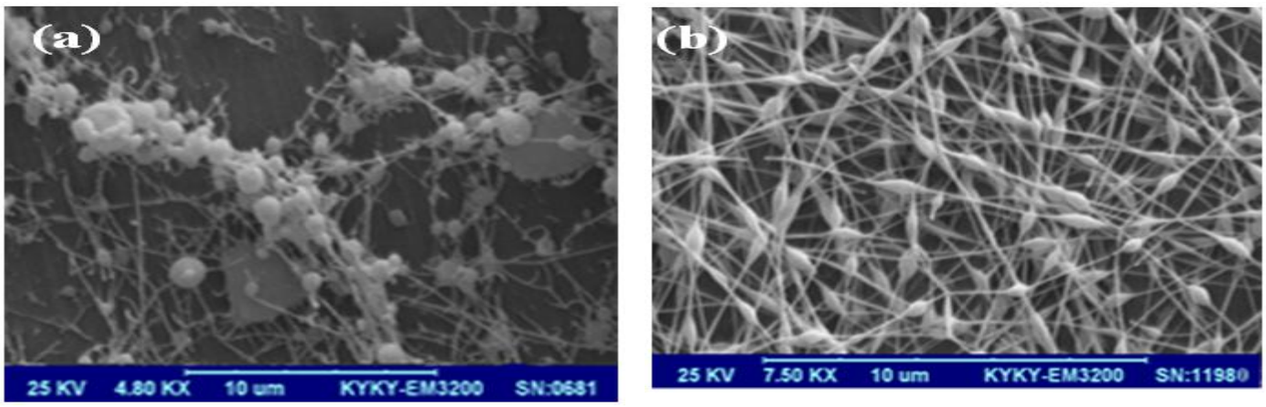

Figure-1. The effect of a low (a) and high (b) voltage on the morphology of nanofibers containing synthesized PANi

The effect of the tip to collector distance on the fibers morphology has shown in the Fig. 2 (a), (b). As can be seen, in lower distances (5 cm) defective fibers with bead-like structure have been formed because increasing the electrical field and the high electrostatic repulsion on the fibers. Also, there wasn't enough time to evaporation of solvent prior to reaching of fibers to the Al foil in the lower distances.

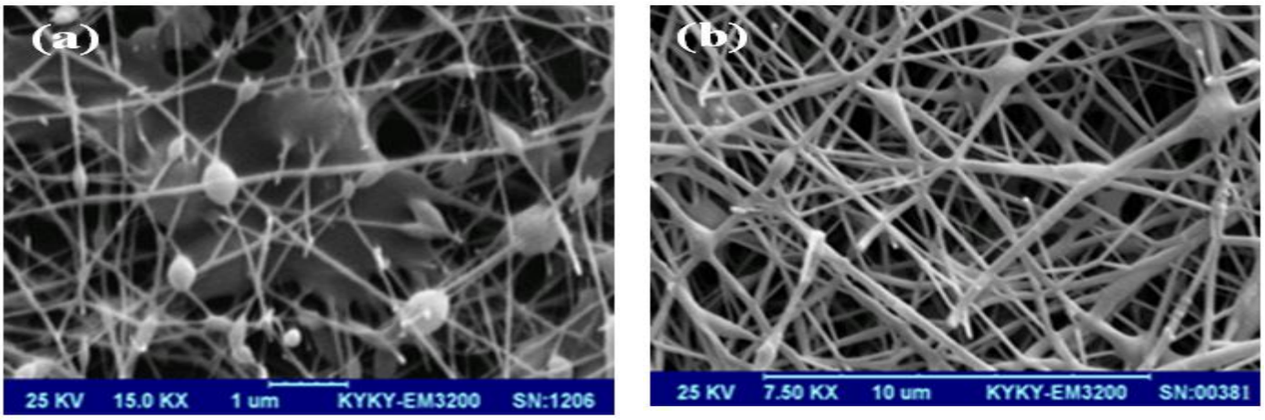

Figure-2. The effect of a low (a) and high (b) distance on the morphology of nanofibers containing synthesized PANi

It has been observed that with increasing of flow rate of polymer solution from syringe, solvent don't have enough time to evaporate and the remaining solvent on the surface of fiber causes fibers to stick together, so that they form a spider web together (Fig. 3a). In the lower flow rate (0.5 ml/hr) the morphological structure has changed and less beads have been observed (Fig. 3b). Resulting nanofibers from synthesized polyaniline in the different process conditions weren't uniform and beed-free and this might be due to the type of used polymer and its solubility limitations in NMP.

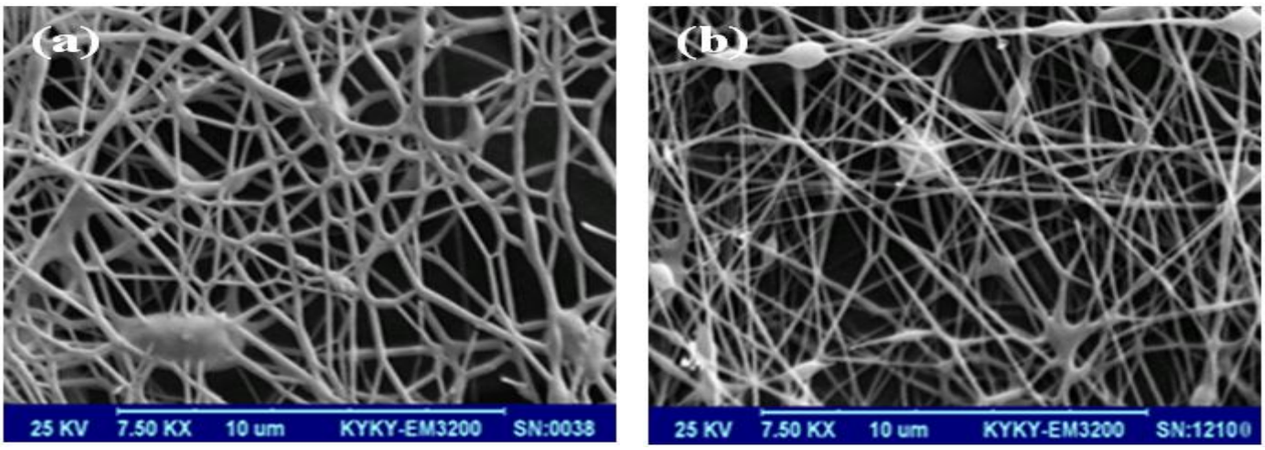

Figure-3. The effect of a high (a) and low (b) flow rate of polymer solution on the morphology of nanofibers containing synthesized PANi

Also, the effect of process parameters on the morphology of the resulting fibers from commercial polyaniline have been investigated. The corresponding SEM images are shown in Fig.4 to 6. The effect of flow rate on the morphology of fibers is shown in Fig.4 (a) and (b). As can be seen, with decreasing of the flow rate, node density has declined and fibers with uniform morphology have been obtained. As observed in Figures 5 (a) and (b) by reducing the distance from tip to collector, the electrical field is increased and the instability of the polymer jet has led to the formation of nodes. As shown in Fig. 6 (a) and (b), a higher voltage will lead to a further stretching in the polymer

jet, increasing the Coulomb forces in the jet stream and an increase in the electrical field that these factors have led to a decrease in fiber diameter.

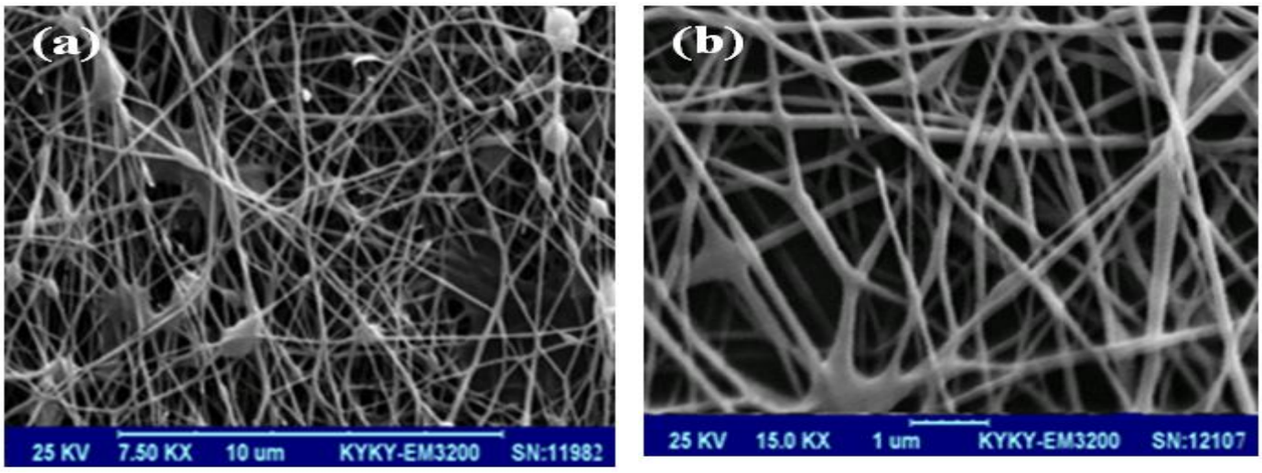

Figure-4. The effect of a high (a) and low (b) flow rate of polymer solution on the morphology of nanofibers containing commercial PANiEB

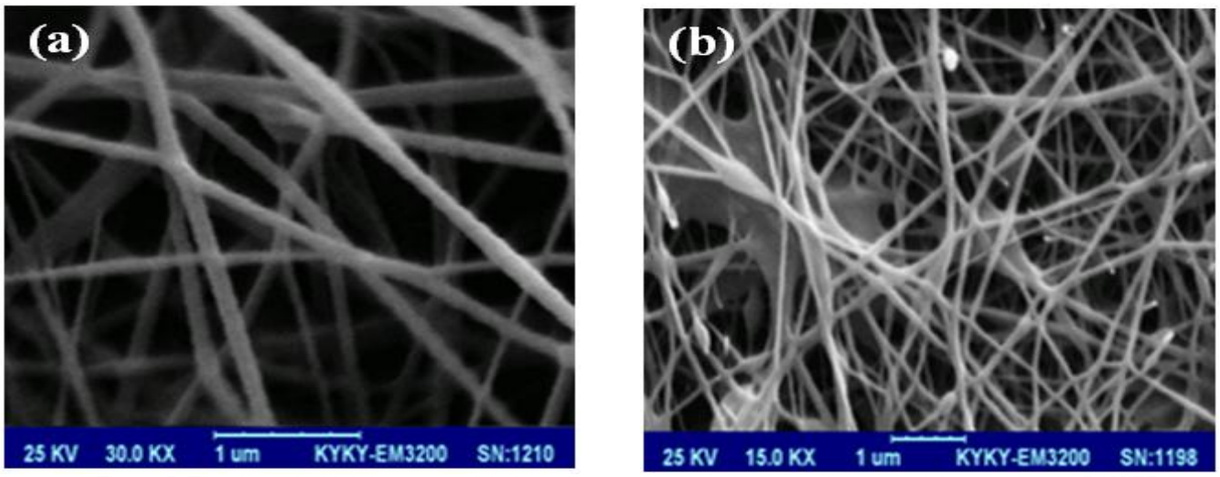

Figure-5. The effect of a high (a) and low (b) distance on the morphology of nanofibers containing commercial PANiEB

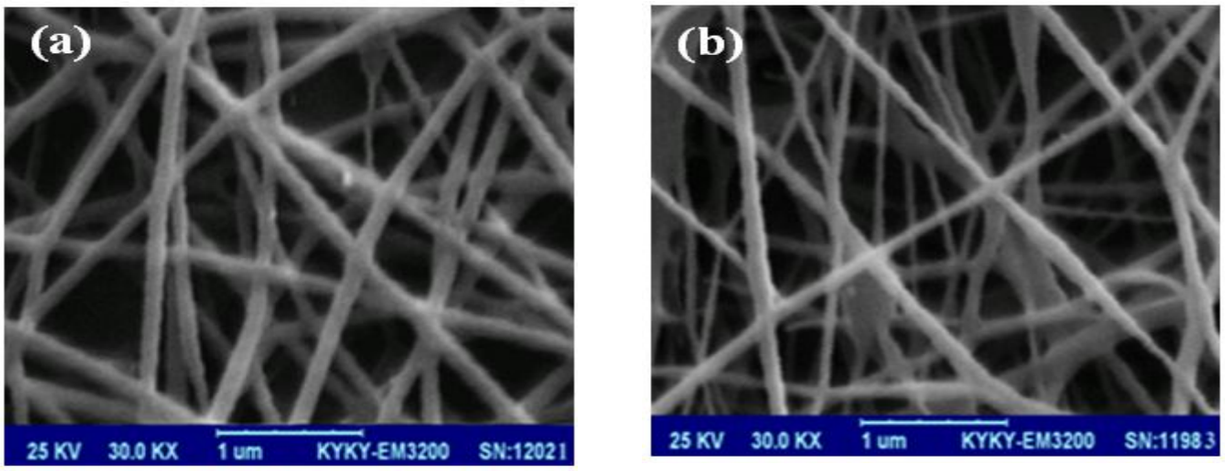

Figure-6. The effect of a low (a) and high (b) voltage on the morphology of nanofibers containing commercial PANiEB

The comparison between the SEM images of resulting nanofibers from commercial and synthesized PANi were indicated that prepared nanofibers from commercial PANi were more uniform and thin. In this study, use of commercial PANi with a combination of AMPSA / DCAA in the polymer solution was another method for preparation of nanofibers, that morphology of the resulting nanofibers are shown in Figure 7. Presence of the combination of AMPSA / DCAA in the polymer solution has created a suitable solvent system for dissolution of PANi. The dispersion of CNF has improved by DCAA solvent and also addition of AMPSA to this solution helps to the stability of the carbon nanofibers [16]. AMPSA was applied as the doping agent for emeraldine base form of polyaniline (PANiEB). The resulting nanofibers from this method were prepared in the voltage of 22 kv, the flow rate of 1 mm/hr and tip to collector distance of 13 cm. Uniform and thin PANi/CNF electrospun nanofibers with an average diameter of about 100 nm were prepared by this polymer solution. The comparison among SEM images of obtained fibers from the three methods have indicated that uniform fibers with a narrow diameter distribution can be prepared using the third method and this might be due to compatibility of the components present in the third method.

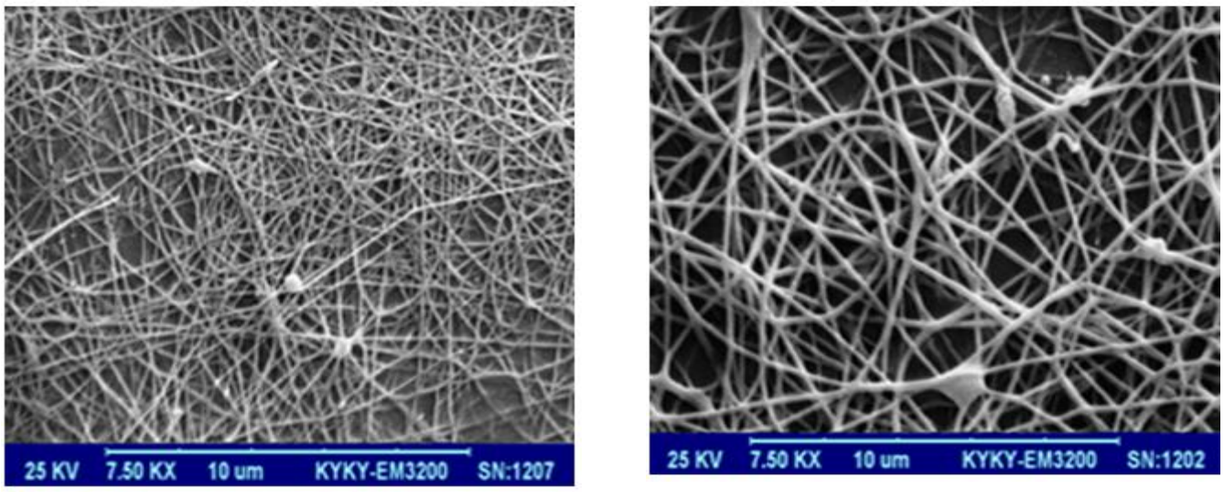

Figure-7. The obtained nanofibers from polymer solution containing PANiEB with the combination of AMPSA/DCAA

3.2. FTIR Analysis

Fourier-transform infrared (FT–IR) spectroscopy was utilized to study the chemical structure of PANi/CNF hybrid nanofibers. The FTIR analysis of the PANi/CNF electrospun nanofibers was recorded in the range of 400-4000 cm^{-1}. As shown in Fig.8, the peaks at 1570 cm^{-1} and 1420 cm^{-1} suggests the presence of C=C stretching vibration of the quinonoid and benzenoid rings of polyaniline. The peak observed at 1328 cm^{-1} can be attributed to C-N stretching vibration and the peaks 1092 cm^{-1} and 845 cm^{-1} can be assigned to the in-plane and out-of-plane deformation of C–H. A broad peak around 3317 cm^{-1} can be attributed to the stretching of -OH- groups and peaks at 2936 cm^{-1} and 2895 cm^{-1} indicating stretching of C–H band in structure of PVA.

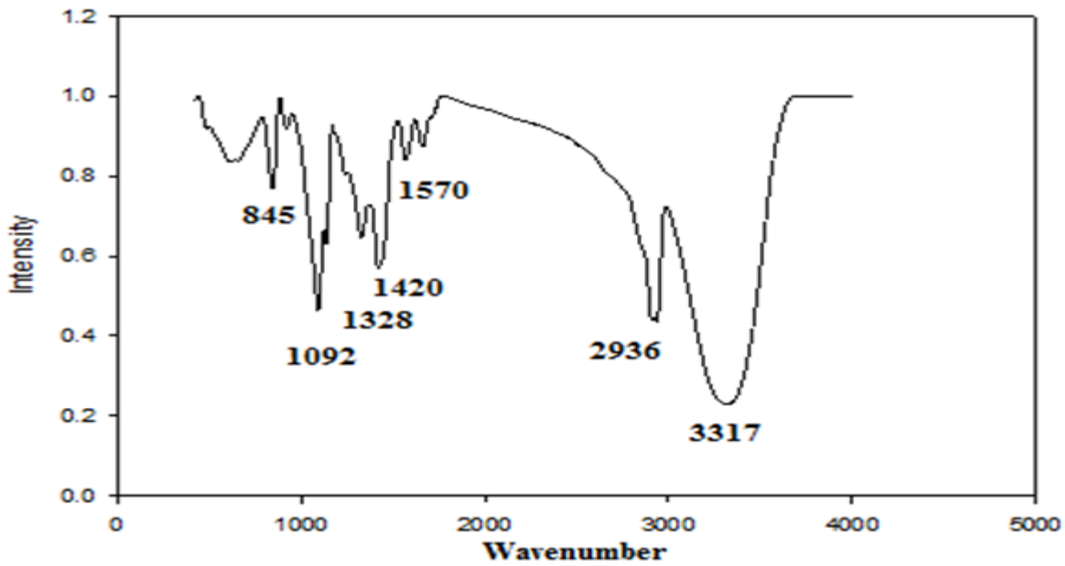

Figure-8. FTIR spectra of PANi/CNF hybrid nanpfibers

4. Conclusions

Three polymer solutions with different components were applied to produce PANi/CNF electrospun nanofibers by electrospinning method. The effect of process parameters on the obtained fiber morphology of the three polymer solutions, were examined and SEM images have indicated that uniform and thin nanofibers can be prepared using a polymer solution containing a combination of commercial PANiEB and AMPSA/DCAA. The average fiber diameter from this polymer solution was about 100 nm. Combination of AMPSA / DCAA has created a suitable solvent system for dissolution of PANi and a better dispersal of CNF in the polymer solution. The possible role of CNF in improving the conductivity of nanofibers have been reported in the results of our previous work on the use of these fibers in the fuel cell electrodes.

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