Synthesis and Characterization of PVdF/PVP-Based Electrospun Membranes as Separators for Supercapacitor Applications

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Abstract: Electrospun polyvinylidene fluoride (PVdF)/polyvinylpyrrolidone (PVP) nanofiber embedded with carbon black nanoparticles (<50nm) were fabricated and characterized for supercapacitor separators. Carbon black nanoparticles with different weight percentages (0, 0.25, 0.5, 1, 2, and 4wt%) were added to a mixture of N, N-dimethylacetamide (DMAC)/acetone and sonicated for a well dispersion. Then, PVdF and PVP were added, and the solution was heated on a hot plate to make a polymeric solution prior to the electrospinning process. The morphology of the electrospun nanofibers was characterized by scanning electron microscopy and transmission electron microscopy. Fourier transform infrared spectroscopy was carried out on the PVdF/PVP films to identify changes in the crystalline phase during the process. The annealed nanofibers samples were also examined by X-ray diffraction unit. These investigations demonstrated that the many physical properties were significantly improved, which may be useful for supercapacitor separators. Supercapacitors will become one of the most suitable energy storage devices in the near future, and the separator is one of the major components of the supercapacitors.

Keywords: Electrospun Nanofibers, PVdF, carbon black nanopowders, characterization, supercapacitor separators.

1. INTRODUCTION

Supercapacitors, ultrasupercapacitors, and electro-chemical double-layer capacitors are the most promising energy storage devices with long cyclic functions and high power densities. They have attracted considerable attention because of their low electrical resistivity, large surface area, and superb charging-discharging rate compared to conventional storage devices. They have displayed excellent performance in a wide range of applications such as power backup in some electrical devices and a power source for hybrid vehicles [1-7]. Previous studies have focused on increasing the energy density of supercapacitors by finding suitable materials for the separator/electrode and lowering the overall cost [8]. A large variety of materials, such as metal oxides or materials with carboneous compositions such as porous carbon, activated carbon fibers, carbon aerogels, carbon nanotubes, and graphene, are the most frequently used substances in supercapacitors [5-11]. Carbon-based nanocomposites with conducting polymers have high capacitance values and better cyclic performance in supercapacitors. They possess high capacitance values due to their functional groups containing phosphorus, nitrogen, and oxygen, which are referred to as the pseudocapacitance effect [12].

Electrospinning is an effective technique for producing woven and non-woven micro/nanoscale fibers from a polymeric solution. Polymeric separators fabricated by the electrospinning possess a unique texture with micro and/or nanosize fiber arrangements, flexibility, and high surface area and porosity. This can be a promising material for various types of separators. Typically, electrospinning consists of a syringe, syringe pump, high voltage power supply, and collector. The process parameters can be optimized to prepare separators having extraordinary properties. The resultant fibers generally have large surface area, flexibility and uniform porosity [13, 14]. Fibers produced by this method can be used for many industrial applications, such as sensors, filtration, biomedical, reinforcement of composite, solar cells, fuel cells, batteries, supercapacitors, and membrane technology [15, 16].

The main focus of this study was the fabrication and characterization of nanofiber separators for supercapacitors, providing a nanoporous structure resulting in a conductive membrane that can be soaked with liquid electrolyte. Polyvinylidene fluoride polymer was used in this study. Among many polymers, PVdF has shown better results due to its high electrochemical stability and particularly excellent electrical properties, which can be useful for supercapacitor applications, although the flexibility of PVdF is not sufficient due to the high crystallinity of its structure and may eventually, cause some difficulties [17]. PVdF is well known for its polymorphism and, depending on its processing

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conditions, can display five different polymorphs. PVdF possesses several phases, the most stable and prevalent being the α-phase (non-polar phase). The important pyroelectric and piezoelectric features of the β-phase (polar phase) of PVdF provide better material properties [18]. The most common technique for transitioning from the non-polar α-phase to the polar β-phase is with thermal treatment [19]. Electric double-layer (EDL) capacitors prepared with electrospun nonwoven PVdF- polyhexafluoropropylene (PHFP) membrane separators have exhibited excellent cycling efficiency and specific capacity [20].

Carbon black nanopowders are generally used as conductive materials in many types of batteries and supercapacitors. Highly conductive carbon black is described as a highly branched and open structure having a small particle size and high porosity. The specific resistivity of carbon black is typically in the range of 10^{-1} to 10^{-2} Ωcm. High porosity and/or finer carbon blacks have more particles per unit weight and, hence, reduce the average inter-aggregate gap width due to their greater number [21]. The surface area of carbon blacks is commonly considered to be more accessible than other types of high surface area carbon [22]. The purpose of this study was to fabricate and characterize PVdF/PVP separators incorporated with carbon black nanoinclusions for supercapacitors using the electrospinning technique.

2. EXPERIMENTAL

2.1. Materials

PVdF and PVP with molecular weights of 180,000g/mole and 120,000g/mole, respectively, were purchased from Sigma-Aldrich and used without any modification or purification. Carbon black (ELFTEX8) was purchased from the Cabot Company and used as reinforcement nanoparticles. N, N-dimethylacetamide (DMAC) and acetone were purchased from Fisher Scientific and together used as the solvent. Figure **1** shows SEM and TEM images of carbon black powders used in this experiment. As can be seen, they are mainly aggregated and need to be dispersed well prior to the electrospinning process. TEM images further confirm that the carbon black particles are attached together. The particles have nearly spherical shapes, and the average size is less than 50nm. Agglomerated carbon black powders are observed in the TEM images.

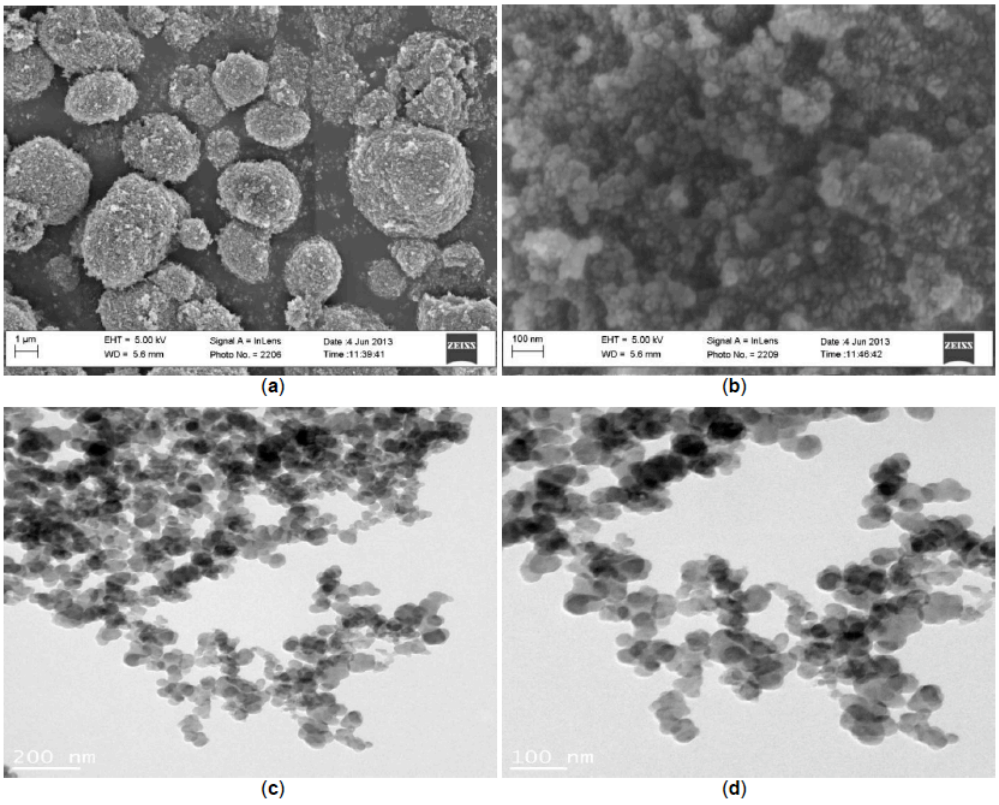


Figure 1: (**a**) SEM image of carbon black powder at low magnification, (**b**) SEM image of carbon black powder at high magnification, (**c**) and (**d**) TEM images of carbon black powder.

2.2. Preparation of Electrospun Fibers

Carbon black nanopowders with different weight percentages (0, 0.25, 0.5, 1, 2, and 4wt%) were dispersed in a DMAC/acetone solvent and sonicated for 90 minutes. Then PVdF and 2wt% of PVP were added separately to the dispersions. Ratio of 80:20 was chosen during the dispersion and dissolution processes. The solution was constantly stirred at 550rpm and 60°C for five hours before electrospinning. The dispersed solution was transferred to a 10ml plastic syringe connected to a capillary needle having an inside diameter of 0.5mm. The electrospinning parameters of voltage, distance between tip and collector, and syringe pump speed were 25 kV DC, 25cm, and 2ml/hr, respectively. Electrospun fibers were then collected on an aluminum screen and dried in an oven at 60°C for eight hours to remove all residual solvents. Electrospun PVdF/PVP fibers were annealed at 90°C for three hours.

3. RESULTS AND DISCUSSION

3.1. SEM Investigation

The morphology and size distribution of electrospun PVdF/PVP nanofibers were characterized using a field-emission (FE)-SEM instrument (Oxford Instruments, INCA system) equipped with energy-dispersive X-ray (EDX) spectroscopy at an accelerating voltage of 5 and 15 kV. Before SEM observations, the samples were coated with gold spatter. The SEM images of PVdF/PVP nanofibers incorporated with carbon black nanopowders shown in Figure **2** indicate that all PVdF

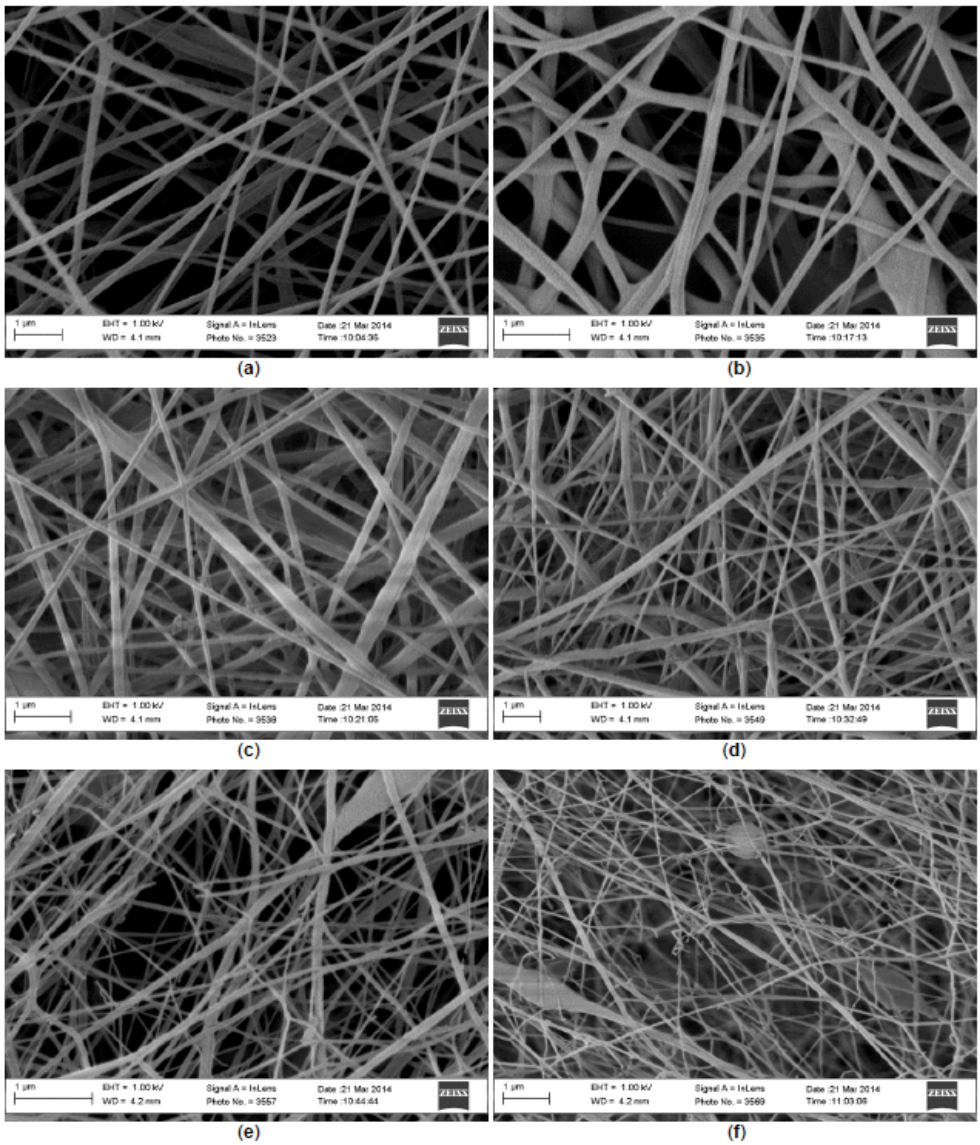


Figure 2: SEM images: (**a**) electrospun PVdF/PVP fibers, and incorporated with (**b**) 0.25wt%, (**c**) 0.5wt%, (**d**) 1wt%, (**e**) 2wt%, and (**f**) 4wt% carbon black.

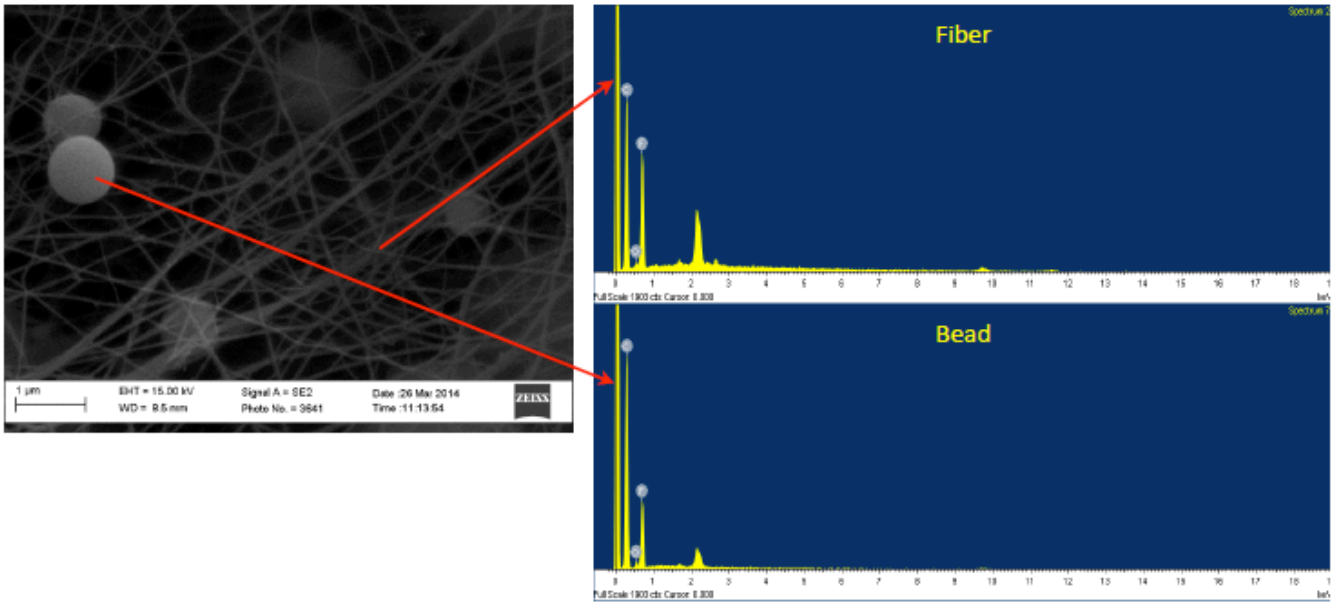


Figure 3: EDX results of fibers and beads of PVdF/PVP with 4wt% carbon black.

nanofibers are nanosize, and fiber diameters are in the range of 100 to 200nm. A good combination of PVdF/PVP and carbon black nanopowders is observed in all samples. However, some round-shaped beads were formed during electrospinning, especially in the 4wt% carbon black, which may be due to the high carbon loadings in the polymeric solution.

EDX spectroscopy was applied to determine the composition of fibers and beads in the structure. Figure **3** shows the EDX spectroscopy results of beads and fibers, indicating that both consist of carbon (C) and oxygen (O) elements, and the EDX scan on the surface of the beads and fibers shows that the carbon concentration in the beads is higher than the carbon concentration in the fibers. However, the fibers presented a higher fluorine (F) concentration. Surface EDX elemental data also provided information on the distribution of C, F and O atoms in the fibers and beads. The loading percentage may create some beads during the electrospinning process. EDX results of the electrospun PVdF/PVP nanocomposite fibers and beads provided in Table **1** confirm the agglomeration of carbon particles.

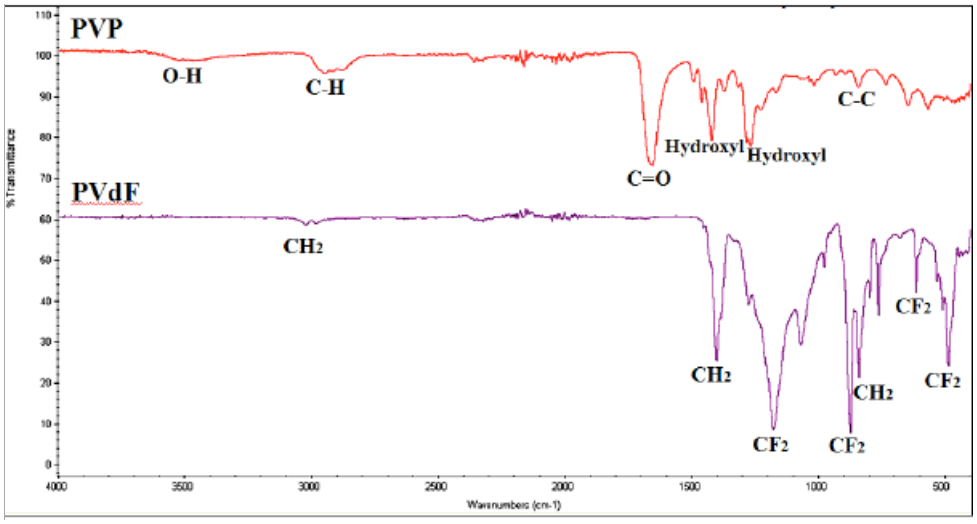
Table 1: EDX Results of Electrospun PVdF/PVP Nanocomposite Fibers and Beads

Element	Fiber Composition (%)	Bead Composition (%)
Carbon (C)	65.54	73.84
Oxygen (O)	2.10	3.13
Fluoride (F)	32.36	23.03

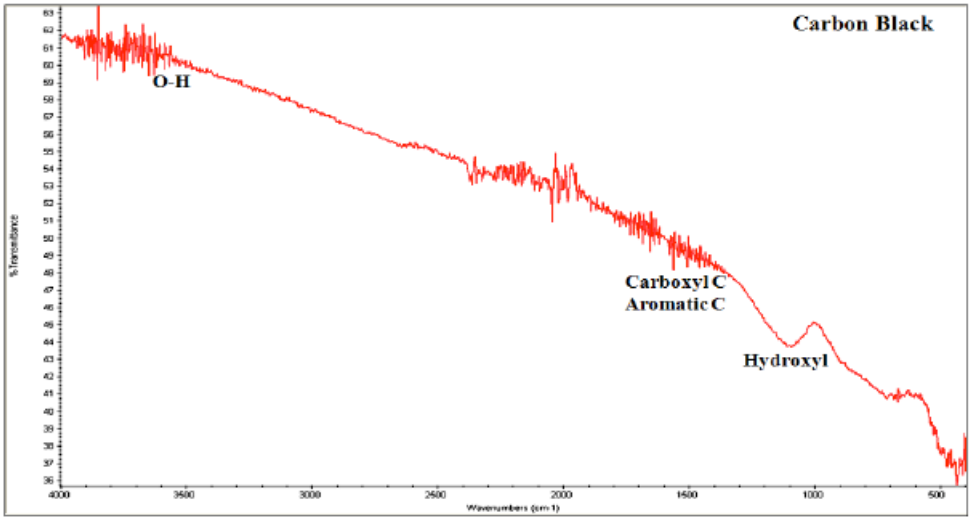
3.2. FTIR and Raman Spectroscopy Results

In this study, the chemical structures of electrospun PVdF/PVP nanofibers were characterized by FTIR to specify the spectral regions. The FTIR spectra of PVdF/PVP nanofibers incorporated with carbon black powders were recorded using a Thermal Nicolet Avatar 360 IR spectrometer in the range of 4,000 to 400cm^{-1}. Results of pure PVdF, PVP, and carbon black materials are shown in Figure **4**.

In the FTIR spectra of pure PVdF, the corresponding crystalline α-phase peak was observed at 490cm^{-1}, representing the wagging and bending vibrations of the CF_2 group [23]. Other peaks of the crystalline α-phase were also detected at 615 and 763cm^{-1}. The absorption band at 763cm^{-1} is related to a rocking vibration [24]. The band at 615cm^{-1} shows a mixed mode of C-C-C skeletal vibration and CF_2 vibration [24, 25]. A characteristic β-phase peak at 840cm^{-1} is assigned to a mixed mode of CH_2/CF_2 stretching vibrations [25, 26]. The band at 745cm^{-1} is defined as a rocking mode. The very strong band appearing at 1,184cm^{-1} is mainly formed by the CF_2 symmetric stretching mode [26]. The CH_2 group is described in two frequencies between 2,800 and 3,100cm^{-1}. Peaks at 1,435, 2,978 and 3,016cm^{-1} confirm stretching of the CH_2 group [24]. The symmetric and asymmetric stretching vibrations of the CH_2 group are located at 3,016cm^{-1} and 2,978cm^{-1}, respectively. Asymmetric vibrations are generally stronger than symmetric vibrations since the



(**a**)



(**b**)

Figure 4: FTIR spectrum: (**a**) pure PVP and PVdF, and (**b**) carbon black.

asymmetric situation leads to minor changes in dipole moment [24, 26].

The FTIR spectrum of PVP displayed strong peaks at 1,286 and 1,447cm^{-1}, which are attributed to the bending vibrations of the hydroxyl group. The band at 2,900cm^{-1} is due to the C-H stretching vibration [27]. The C=O vibration groups show a prominent peak at 1,663cm^{-1} [28]. The infrared peak at 760cm^{-1} is attributed to C-C bending. The broad peak of O-H stretching is observed at 3,500cm^{-1} [27].

The FTIR spectra of carbon black show band overlapping, which is attributed to carboxyl C and aromatic C between 1,700 and 1,500cm^{-1}. The presence of the phenolic hydroxyl group is considered to be in the range of 1,000 to 1,200cm^{-1}. Carbon black appears at the low absorbance of O-H stretching vibrations around 3,400 to 3,450cm^{-1}, probably from the phenolic groups [29]. Figure **5** illustrates the FTIR spectra of PVdF/PVP nanofibers by adding different percentages of carbon black nanopowders.

All nanofiber samples showed CF_2 and CH_2 groups from 490 to 1435cm^{-1} and C=O vibration groups at 1,663cm^{-1} related to PVdF and PVP spectrums, respectively. The presence of 0.5, 1, and 2wt% of carbon black resulted in sharp peaks of C≡N and C≡C bondings at 2,300 to 2,400cm^{-1}. CH_2 group stretching was identified in the range of 2,978 to 3,016cm^{-1} to all PVdF/PVP nanofibers; however, a prominent peak was shown for the 4wt% of carbon black. A strong peak at 3,500 to 3,700cm^{-1} in the 4wt% of carbon black samples is attributed to the O-H group. Surface functional groups—O-containing and N-containing groups—in the samples can considerably enhance the

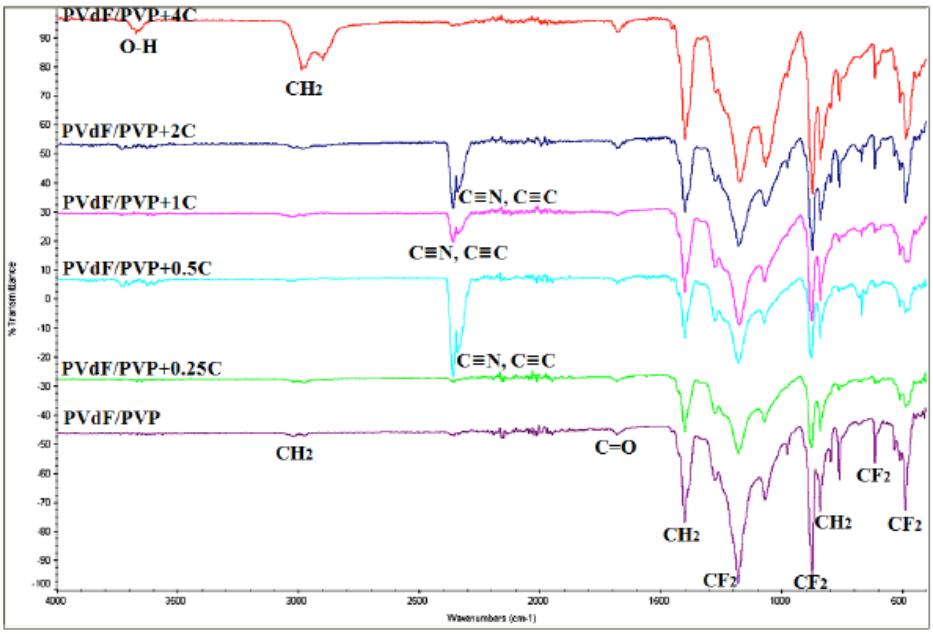


Figure 5: FTIR spectra of PVdF/PVP nanofibers as a function of different percentages of carbon black nanoinclusions.

total capacitance values through additional Faradaic reactions called the pseudocapacitance effect [30-34].

Raman spectra were recorded by employing a HORIBA Scientific Xplora spectrometer in the range of 400 to 4,000cm^{-1}. A laser operating at 542nm radiation was used as the excitation source. Raman spectroscopy is the most suitable, simple, and quick method to provide details about molecular structures. In contrast to FTIR, Raman spectroscopy data provide more information for the low bands, which are not visible with FTIR analysis alone. Raman spectra of PVdF have been studied to observe different phases that are not identified with FTIR. Raman spectroscopy results confirmed FTIR observations [35, 36]. The Raman spectra of electrospun PVdF/PVP nanofiber are shown in Figure **6**. As can be seen, most of the bands correspond to the α-phase of PVdF.

The strong and intense band at 799cm^{-1} is related to the CH_2 rocking vibration [35]. Raman scattering around 810cm^{-1} shows the γ-phase of PVdF, which

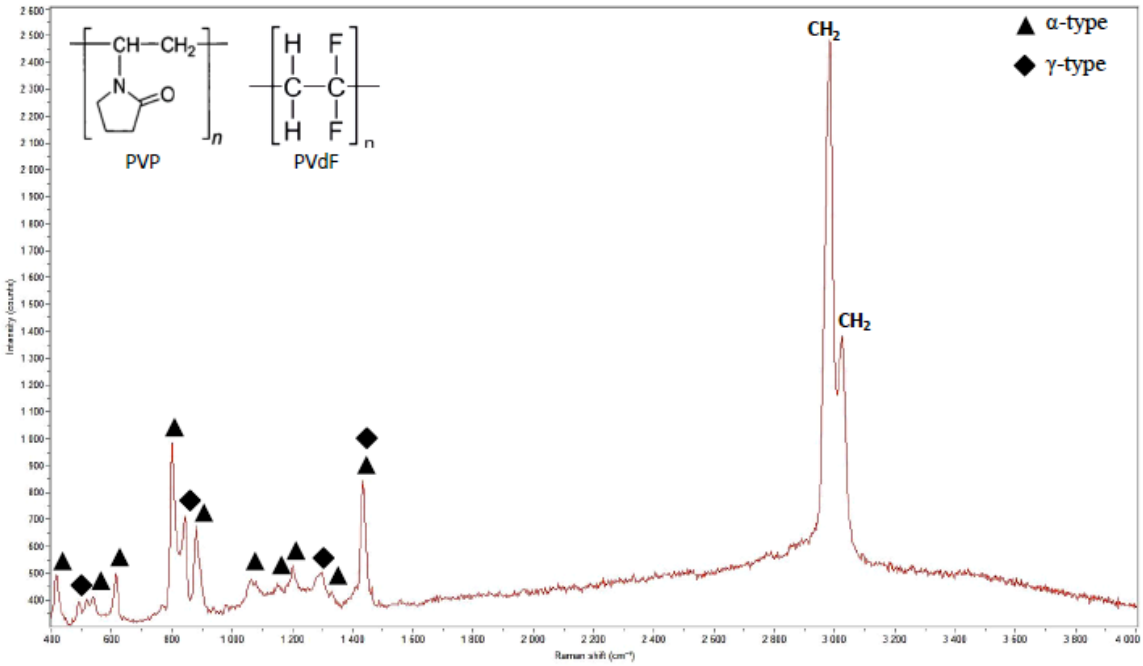


Figure 6: Raman spectra of PVdF/PVP nanofiber.

gives a high frequency for the liberation lattice mode due to the strong molecular force [37]. The peak at 442cm^{-1} is assigned to the CF_2 rocking mode of the α-phase. The intense Raman peak at 878cm^{-1} is due to the symmetric stretching vibration of the C-C bond [38]. The weak bonding at 490 and 1,280cm^{-1} corresponds to the γ-phase of PVdF, whereas the peak at 893cm^{-1} is attributed to the α-phase. The strong band at 1,440 is a mixture of α-phase and γ-phase crystals [39]. The presence of PVP in the PVdF matrix shows strong peaks at 2,980 and 3,020cm^{-1}, which are attributed to the asymmetric stretching of CH_2 chains [40].

3.3. XRD Analysis

X-ray results were collected with a Philips X'Pert system (Cu K α radiation, λ = 1.5418 Á). Figure **7** shows the wide-angle X-ray diffractometry (WAXD) diagram of annealed pure PVdF/PVP and annealed PVdF/PVP with 4wt% carbon black fibers.

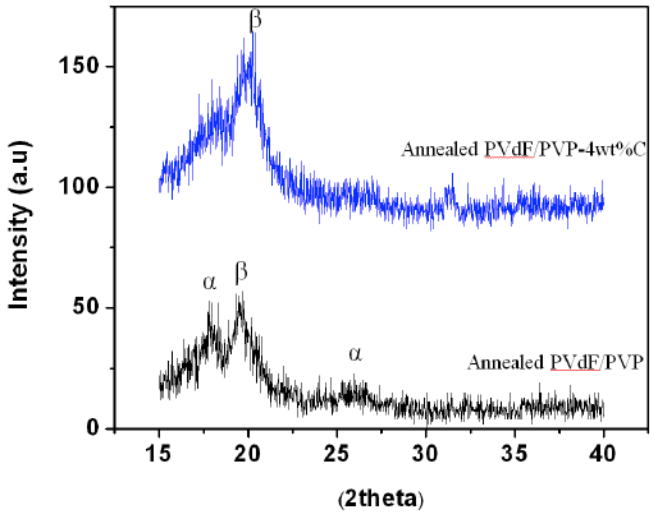


Figure 7: WAXD pattern of annealed pure PVdF/PVP and annealed PVdF/PVP with 4wt% carbon black nanofibers.

No peaks were detected in the pure PVdF/PVP samples without annealing. As can be seen, the diffraction patterns of the PVdF/PVP electrospun fibers displayed two peaks at 2 theta around 18° and 20°, corresponding to α-phase and β-phase crystals, respectively [41-43]. The small peak around 27° is observed only for the α-phase [43]. Adding 4wt% of carbon black exhibited a single peak around 21°, corresponding to (110) and (200) reflection of the β-phase crystal of PVdF, and the α-phase showed low intensity [44].

In addition, PVdF/PVP fibers with 4wt% carbon black showed higher intensities of the β-phase peak than pure PVdF/PVP, and 2 theta of this form also slightly shifted to higher angles. The addition of carbon black resulted in further enhancement of the β-phase content of PVdF. Moreover, the XRD spectra in both samples displayed an amorphous structure of the fibers.

4. CONCLUSIONS

Electrospun nanofibers of PVdF/PVP incorporated with different percentages of carbon black nano-powders were fabricated, characterized and analyzed in detail. SEM images showed that all the PVdF/PVP nanofibers were at nanosize (between 100 and 200nm). EDX elemental data also provided information on the distribution of C, F, and O atoms in the fibers and beads, which indicates a high concentration of carbon atoms in the beads of the fibers. FTIR results displayed some functional oxygen and nitrogen groups in samples that can considerably enhance the total capacitance values through additional Faradaic reactions called the pseudo-capacitance effect. Raman spectroscopy spectra also displayed different forms of PVdF. Wide XRD diagrams of annealed PVdF/PVP samples confirmed the presence of α-phase and β-phase crystals. However, the addition of carbon black further enhanced the β-phase content of PVdF. Overall; this study may open up new possibilities to produce new separators for the future applications of supercapacitors.

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