Electrospun Nanocomposite Membranes Incorporated With PVdF/PVP and Carbon Blacks for Supercapacitor Applications

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Abstract. Supercapacitors are new generation of energy storage devices using high surface area conductive or semiconductive materials. The supercapacitors show a better performance compared to the other chemical storage devices because of the high power densities and long cyclic life. Metal oxides, carbon fibers, carbon nanotubes, aerogel and graphene nanoflakes are some of the examples which have high surface area, storage capacitance and electrical conductivity. This study is mainly focused on the effects of carbon black inclusions on the physical properties of the polymeric membranes (or separators). Carbon black nanoparticles were incorporated with polyvinyl fluoride (PVdF) / polyvinylpyrrolidone (PVP) at different concentrations, and then electrospun at various conditions, such as distance, electrical potential, and pump speed. SEM images proved the well-textured polymeric membranes at nanoscale. Surface hydrophobicity properties of the membranes were investigated. FTIR results showed the atomic bonding of nanofibers in the presence of nanoscale inclusions.

1. Introduction

Supercapacitors (also known as electrochemical capacitors or double layer capacitors) have been recently attracted much attention as high potential energy storage devices due to the long life cycle, high power density, low electrical resistivity and larger specific surface areas compared to the common batteries and other conventional capacitors/devices [1-3]. Polymer nanocomposite separators can present good cycling performances and high capacitances, and also show higher total capacitance due to the surface functional groups including phosphorus, nitrogen and oxygen [4].Among the polymers, PVdF has presented better results due to the high electrochemical stability in electrolyte; however, the flexibility of PVdF is insufficient due to high crystalinity, and may eventually causes some difficulties. PVdF also has excellent electrical properties which can be useful for the supercapacitors applications. PVdF has many phases and the most common one is α-phase. β-phase is the most important one because of the piezoelectric and pyroelectric benefits of the material [5].

Electrospinning is an easy and effective method of producing woven and non-woven micro/nanoscale fibers from many different polymeric materials. In this technique, a polymer solution is injected into a syringe and a continuous filament is drawn from the syringe by high electrostatic forces. With this electrostatic force, a charged polymer jet is ejected when the electrostatic field overcomes the surface tension of the solution, and then the filaments are eventually deposited on the surface of a collector or screen which is placed at a certain distance from the capillary tube [6].

This study is mainly focused on the effect of carbon nanopowders on the properties of separators which may be used for the supercapacitor fabrications.

2. Experiment, Results and Discussion

Carbon black (ELFTEX8), purchased from Cabot Co., was used as the reinforcement nanoparticles (15-60 nm). PVdFas a homopolymer and PVP powders purchased from Sigma-Aldrich and used without any purifications or modifications. DMAC (N, N-Dimethylacetamide) and acetone, purchased from Fisher Scientific, were usedas solvents. Carbon black nanoparticles with different weight percentages (0.25, 0.5, 1, 2 and 4 wt %) were dispersed in the solvent (DMAC/Acetone) for 90 minutes prior to the addition of PVdF+2wt% PVP, and then whole solution was stirred for five hours before the electrospinning process. The dispersed solutions were placed into the plastic syringe, and electrospun at 25 kV DC, 2 ml/hr pump speed and 25 cm separation distance to produce nanocomposite fibers. Figure 1 shows the SEM images of the nanocomposite fibers with 4 wt% of carbon black produced by electrospinning process. The SEM image indicates that the PVdF/PVP fibers are mostly at nanoscale and the average thickness of these fibers is between 100 nm and 200nm. However, some beads were formed during the electrospinning process. The contact angle values of PVdF/PVP nanofibers in the presence and absence of the carbon black nanopowders were determined using the Goniometer from KSV Instruments Ltd. The software of the instrument precisely calculates the contact angle and also takes pictures of water droplets on the PVdF/PVP fiber films.

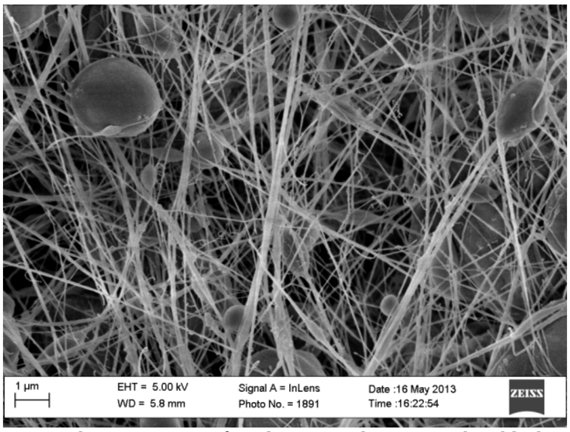

Fig. 1. The SEM image of PVdF/PVP with 4 wt% carbon black

Table 1 gives the water contact angles values of PVdF nanofibers. The contact angle values were decreased by adding 0.25, 0.5 and 1 wt% carbon black powders in the PVdF/PVP fibers. Adding 2 and 4 wt% carbon black showed higher values compare to PVdF/PVP nanofibers.

Table 1: The contact angle values of PVdF/PVP

Nanofiber Samples	Water Contact Angle (°)
PVdF/PVP	112.29
PVdF/PVP+0.25 wt% Carbon black	110.85
PVdF/PVP+0.5 wt% Carbon black	95.31
PVdF/PVP+1 wt% Carbon black	81.02
PVdF/PVP+2 wt% Carbon black	116.23
PVdF/PVP+4 wt% Carbon black	118.46

In this study, to characterize the chemical structure of the prepared PVdF/PVP nanofibers, Fourier transform infrared (FTIR) spectroscopy was employed. Fig. 2 shows the results of FTIR spectra of pure PVdF, PVP and carbon black samples. In the FTIR spectrum of PVdF, crystalline α-phase peak at 490 cm^{-1} indicated bending and wagging vibration of CF_2 group. Characteristic bands from β-phase have been identified at 840 and 745 cm^{-1} which are assigned mixed mode of CH_2/CF_2 stretching vibrations. Peaks at 1435, 2978 and 3016 cm^{-1} confirms CH_2 group.

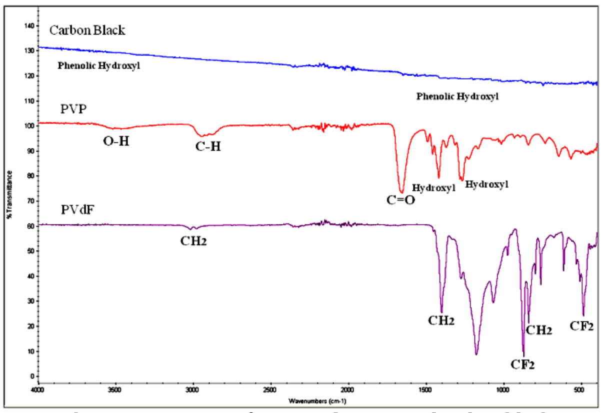

Fig. 2. The FTIR spectrum of pure PVdF, PVP and carbon black

FTIR results of PVP showed strong peaks at 1447 and 1286 cm^{-1}that are assigned to hydroxyl group. The C=O vibration groups at 1663 cm^{-1} and C-H bonding at 2900 cm^{-1} observed. Broad and intense bands of O-H stretching are seen at 3480 cm^{-1}. Peaks at 3430-3460 cm−1 are considered of presence of phenolic hydroxyl groups in carbon black.

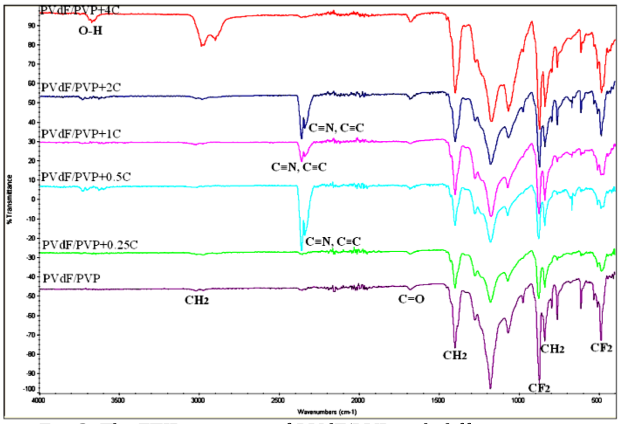

Fig. 3. The FTIR spectrum of PVdF/PVP with different percentage of carbon black

Figure 3 illustrates the addition of 0.25 wt% of carbon black caused no changes to FTIR spectra of PVdF/PVP. C≡N and C≡C bonding are observed at 2300-2400 cm^{-1} in 0.5, 1 and 2 wt% of carbon black. Peaks at 3500-3700 cm^{-1} in 2 and 4 wt% of carbon black assigned to O-H group.

3. Conclusions

PVdF/PVP nanofibers incorporated with various percentages of carbon black nanopowders were produced using electrospinning methods. The fibers were characterized by using SEM and FTIR. The sizes of PVdF/PVP fibers were in nanosize. Contact angle measurements showed improving wettability of nanofibers in the presence of carbon black. FTIR results showed oxygen functional groups which increase total capacitance values due to pseudo-capacitance effects.

4. References

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