

Research Article

Effect of Wrapped Carbon Nanotubes on Optical Properties, Morphology, and Thermal Stability of Electrospun Poly(vinyl alcohol) Composite Nanofibers

Naoual Diouri,¹ Mimouna Baitoul,¹ and Malik Maaza^{2,3}

¹ University USMBA, Faculty of Sciences Dhar El Mahraz, Laboratory of Solid State Physics, Group Polymers and Nanomaterials, Regional University Center of the Interface (CURI), P.O. Box 1796 Atlas, 30000 Fez, Morocco

² iThemba LABS, National Research Foundation, NANOAFNET, 1 Old Faure Road, Somerset West 7129, P.O. Box 722, Somerset, Western Cape Province, South Africa

³ UNESCO, UNISA Africa Chair in Nanosciences/Nanotechnology, College of Graduate Studies, University of South Africa (UNISA), Muckleneuk Ridge, P.O. Box 392, Pretoria, South Africa

Correspondence should be addressed to Mimouna Baitoul; baitoul@yahoo.fr

Received 29 October 2012; Accepted 19 May 2013

Academic Editor: Haiping Hong

Copyright © 2013 Naoual Diouri et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Electrospinning was used to elaborate poly(vinyl alcohol) (PVA) nanofibers in the presence of embedded multiwall carbon nanotubes (MWCNTs) in surfactant and polymer. MWCNTs were dispersed in aqueous solution using both sodium dodecyl sulfate (SDS) as surfactant and Poly(vinyl pyrrolidone) (PVP). Changing the surfactant and polymer concentration reveals that the maximum dispersion achievable is corresponding to the mass ratios MWCNTs : SDS = 1 : 5 and MWCNTs : SDS : PVP = 1 : 5 : 0.6 in the presence of the PVP. After the optimization of the dispersion process, the SEM image of the PVA/PVP/SDS/MWCNTs electrospun fibers presents high stability of the fibers with diameter around 224 nm. Infrared spectroscopy and thermal gravimetric analysis elucidate the type of interaction between the PVA and the coated carbon nanotube. The presence of PVP wrapped carbon nanotubes reduced slightly the onset of the degradation temperature of the electrospun nanofibers.

1. Introduction

Electrospun nanofibers present an exciting avenue for development of novel nanomaterials with well-defined functionalities which have attracted researchers' interest. Because of their unique physical, chemical properties and a specific surface approximately two order larger than flat films, nanofibers have great potential use in sensors [1–3], filtration for bacteria, medical applications, tissue scaffolding [4–8], textile fabric [9], and other applications in nanoscience and nanotechnology. Due to their electronic, mechanical, and thermal properties, CNTs enjoy an incomparable status in the panoply of nanomaterials finding large range of applications in composites. However, the fabrication of high quality polymer-CNTs nanocomposites with predictable and optimal performance requires homogenous dispersion of the CNTs in polymer matrix. This is a challenging task for their

utilization due to the highly nonwetting character of CNTs surface and strong tendency to form bundles by van der Waals attractive forces. Currently, different approaches are used to disperse CNTs, such as covalent or noncovalent functionalization. From the nondestructive point of view, in situ polymerization, polymers, and also surfactants are used to obtain homogenous CNTs dispersion in various solvents or matrices [10–12]. A series of cationic, anionic, and nonionic surfactants and polymers have been studied for their ability to suspend individual CNTs [13, 14]. The present work confronts the dispersion assisted by surfactant as well as polymer. In the first step, we investigate the dispersion of MWCNTs in aqueous solution using SDS as an anionic surfactant. Different concentrations of SDS compared to those of MWCNTs were used, and the second step consisted in improving the dispersion and its stabilization while using the PVP. After the optimization of the dispersion of MWCNTs, we elaborated

the nanocomposite fibers via electrospinning process. The optical properties and thermal stability of the electrospun nanofibers will be presented.

2. Experimental

2.1. Materials. Poly(vinyl alcohol) (Mw: 70000, 99% hydrolyzed), poly(vinyl pyrrolidone), and sodium dodecyl sulfate were purchased from Sigma Aldrich. Multiwall carbon nanotubes (CCVD method, purity >95%, outer mean diameter 10–15 nm, and length 0.1–10 μm) were purchased from Arkema France.

2.2. Dispersion of MWCNTs. In a typical dispersion procedure, two steps were realized in order to achieve better dispersion in the one hand and for preparing three suspensions of MWCNTs. The anionic surfactant SDS, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$, is first used for the exfoliation of the CNTs by varying the concentration to 10 wt% of MWCNTs aqueous solution. It can penetrate easily inside the aggregates of MWCNTs, and it was useful for improving the dispersibility. After the characterization with the UV-Vis spectroscopy, the solution with the ratio 1:5 of MWCNTs:SDS was chosen. However, this surfactant does not prevent individual nanotubes from agglomeration after sonication process. In order to achieve better stabilization of the dispersion, different amounts of the nonionic PVP ($\text{C}_6\text{H}_9\text{ON}$)_n which possesses both hydrophilic and hydrophobic groups have been added to this solution to further improve the dispersion. The temperature was around room temperature, and all solutions were ultrasonicated for 60 min. Moreover, rings in PVP contain a proton accepting carbonyl moiety, while PVA presents hydroxyl groups as side groups. Indeed, interactions by hydrogen bonding can be expected between hydroxyl groups of PVA and carboxyl groups of PVP.

2.3. Preparation of PVA/MWCNTs/SDS/PVP Nanofibers. PVA was dissolved in warm water by heating at 80°C under a continuous slight stirring for 2 h to prepare PVA solution with the desired concentration. The PVP/SDS/MWCNTs suspension was added to an aqueous solution of PVA to obtain a final solution of 12 wt% PVA and 0.3 wt% of MWCNTs. The solution of PVA/MWCNTs/SDS/PVP was briefly sonicated and stirred to remove trapped air bubbles and for effective mixing prior to electrospinning. After the complete homogenization of the nanocomposite, the solution was poured into the syringe. A voltage of 15 Kv was applied to the solution, and the solution jet emerging from the needle was collected on the stationary electrode (Figure 1).

2.4. Characterization. The dispersions of MWCNTs in the surfactant and polymer were characterized using UV-visible spectrophotometer—Cecil 2000 series which cover the full 190–1000 nm wavelength range with a narrow 1.8 nm optical bandwidth. The baseline correction was carried out using a quartz cuvette.

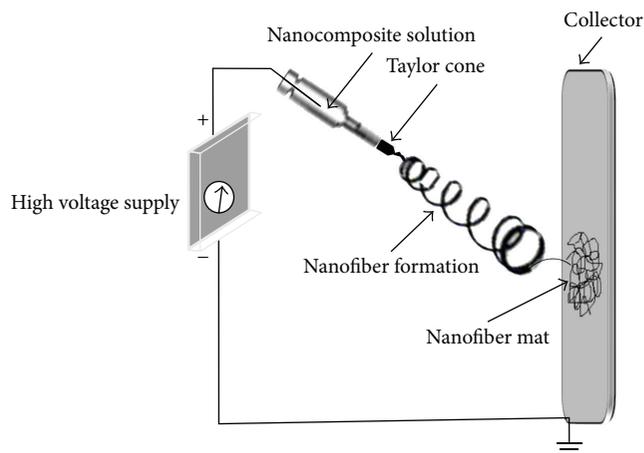


FIGURE 1: Scheme of the electrospinning process.

The morphology of electrospun nanofibers and their average diameter were characterized using environmental scanning electronic microscopy (ESEM) equipped with sonde EDAX for the surface microanalysis.

An analysis was carried out by ATR using PerkinElmer, Spotlight 400 FTIR Imaging system, while thermal analysis was accomplished using SETSYS Evolution.

3. Results and Discussion

3.1. Ultraviolet-Visible Spectroscopy. It has been demonstrated that carrier dynamics in carbon nanotubes bundles are dominated by the tunnel coupling between carbon nanotubes. These bundled carbon nanotubes are not active in the UV-Vis region and only individual carbon nanotubes absorb in the UV-Vis region [15]. Here, we describe combination of two concepts for dispersing MWCNTs by using SDS as surfactant and PVP.

To disperse MWCNTs, both maintaining stabilization and intrinsic properties of carbon nanotubes are required. We used the ionic surfactant to disperse MWCNTs because it is known to disperse them in aqueous solution via noncovalent method without affecting MWCNTs properties [16]. Since SDS molecules have featureless absorbance in the region, we were interested in this work. The mechanism of MWCNTs dispersion according to the duration and power of sonication has been studied by other researchers [15].

To obtain better dispersion, the solutions were resounded after the variation of the mass of SDS compared to that of the MWCNTs using the same conditions of sonication during all experiments.

The UV-Vis absorbance spectra (Figure 2(A)) show the prepared MWCNTs dispersion with different amounts of SDS. The MWCNTs have characteristic absorption peak around the wavelength of 290 nm corresponding to the intrinsic optical properties of graphite [17] and will thus be present in MWCNTs. Unlike optical transitions in a particle, the carbon nanotubes present different collective excitations of electrons, called π -plasmon, which involve the electron orbitals σ and exist at much higher energy. Since the size of carbon nanotubes is less than the wavelength of excitation in

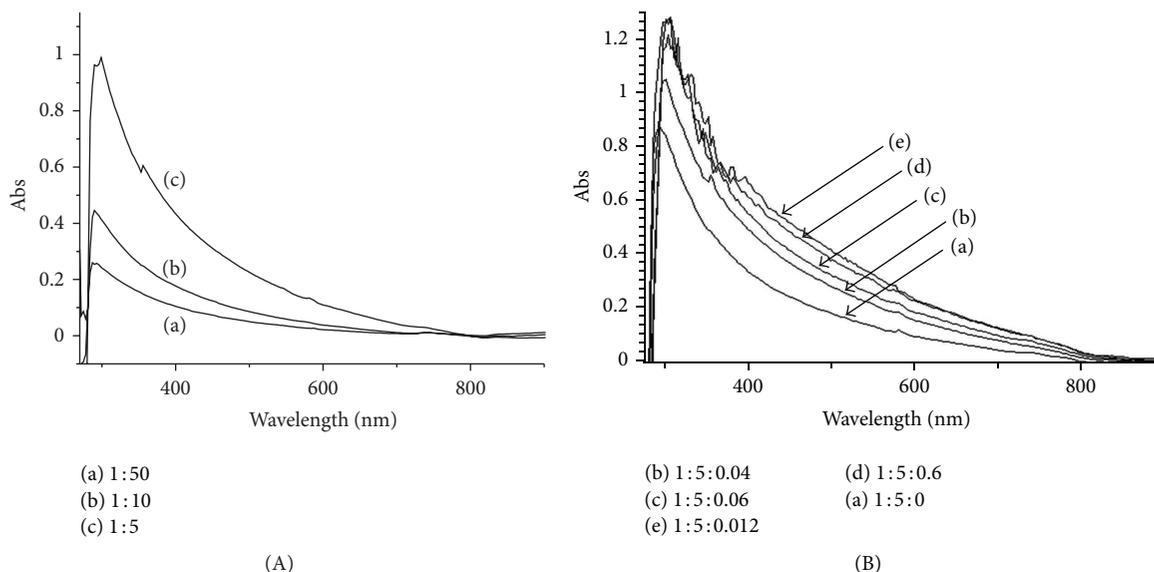


FIGURE 2: (A) UV-Vis optical absorbance spectra of aqueous solution of MWCNTs with different concentrations of SDS. (B) UV-Vis optical absorbance spectra of aqueous solution of MWCNTs-SDS with different concentrations of PVP.

the UV-Vis, there is a movement phase of the charge density and charge accumulation at the surface, and therefore π -plasmon carbon nanotubes can be coupled with light. But the distribution of charges at the surface of carbon nanotubes is not in mechanical equilibrium and oscillates around the equilibrium position. The plasmon resonance corresponds to a strong increase in absorption at the resonant frequency. Indeed, when we reduced the mass of SDS compared to that of MWCNTs which was fixed at 1 mg, from 50 mg to 5 mg of SDS, the intensity of absorbance was significantly increased, and the best absorbance was achieved for the mass ratio of MWCNTs : SDS—1 : 5.

To study the effect of the PVP on the dispersion of MWCNTs in the presence of SDS, we have taken the same quantities used for the MWCNTs : SDS, 1 : 5, which gave the best dispersion, and different amounts of PVP were added. All suspensions of MWCNTs-SDS-PVP were prepared in the same conditions as the previous suspensions.

The UV-Vis spectra of all suspensions (Figure 2(B)) show that when the mass of PVP increased from 0.04 mg to 0.6 mg compared to the mass of MWCNTs : SDS—1 : 5 the solutions absorbance has improved considerably and the characteristic absorbance band of the MWCNTs is shifted to higher wavelengths. This redshift can be explained by the improvement of the density fluctuations of π -plasmon of internal and external surfaces of MWCNTs [18]. So, we can deduce that the dispersion of MWCNTs is enhanced with the addition of the PVP until a certain threshold. For the mass increasing from 0.6 mg to 1.2 mg, the absorbance is found to saturate with even a slight drop. These optimized concentrations were used for the solutions used in electrospinning process.

3.2. SEM Analysis. The characteristics of the fibrous structures produced via the electrospinning process were observed by SEM micrograph.

Nanofibers diameter and morphology can be controlled by several processing parameters including solution viscosity (as controlled by changing the polymer concentration), voltage, feed solution conductivity, and capillary-to-collector distance. In addition, the spinning process is expected to align CNTs or their bundles along the fiber direction due to combination of dielectrophoretic forces caused by dielectric or conductivity mismatch between the CNTs and the polymer solution and high shear forces induced by spinning.

The selected SEM representative images (Figure 3) show the as-spun PVA (Figure 3(a)), PVA/SDS/MWCNTs (Figure 3(b)), and PVA/SDS/PVP/MWCNTs (Figure 3(c)) fibers deposited on the glass substrate at 20 000x magnification. The treatment of the images with Image J software shows that the diameter average was varying from 230 nm for the pure PVA to 210 nm for PVA/SDS/MWCNTs. The decrease of the fibers diameter indicates that the incorporation of the MWCNTs into the fibers increases the conductivity of the matrix solution, which favors the stretching of the solution under electric field during the electrospinning. Furthermore, for PVA/SDS/PVP/MWCNTs composite nanofibers, the fibers diameter decreases to be 224 nm due to the increase of solution viscosity. It should be noted that the fibers structures were completely stabilized and any beads were observed.

3.3. FTIR Spectroscopy. To determine the interaction between PVA, MWCNTs, and PVP, FTIR measurements of pure PVA, PVA/SDS/MWCNTs, and PVA/SDS/PVP/MWCNTs fibers were conducted.

The FTIR spectrum of pure PVA fibers (Figure 4(a)) shows the main characteristic bonds as follows.

The C-H stretching vibration is observed at 3283 cm^{-1} . The symmetric and antisymmetric $-\text{CH}_2$ vibrations appear at, respectively, 2940 cm^{-1} and 2912 cm^{-1} . The peaks located

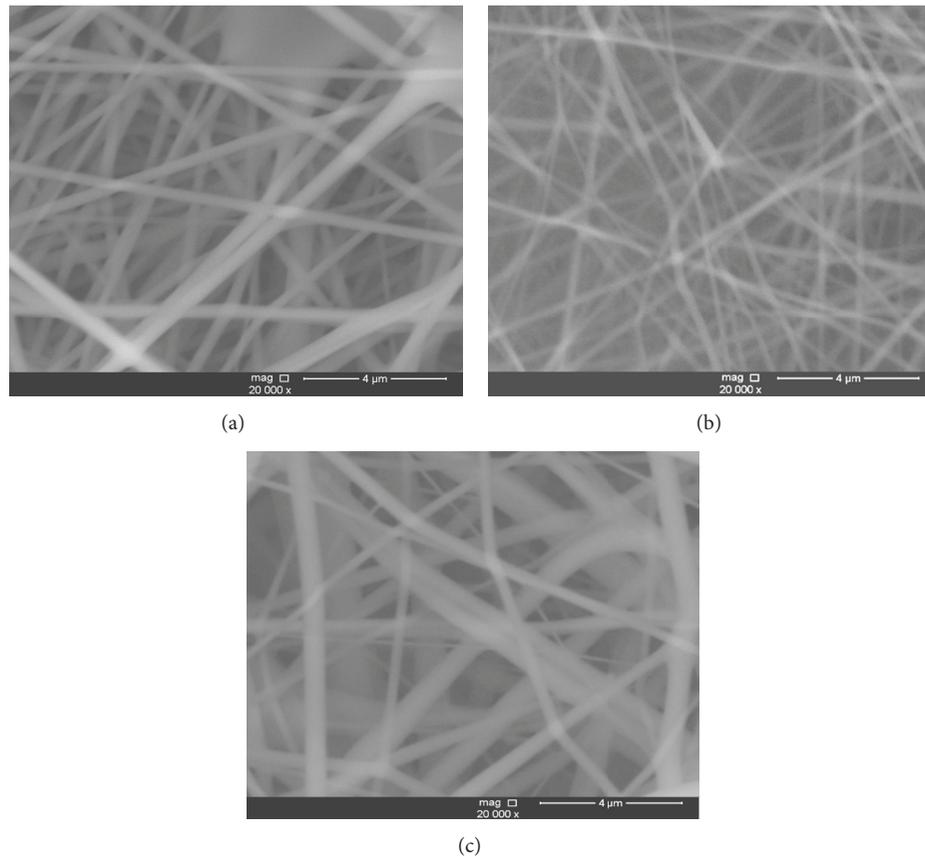


FIGURE 3: SEM images of PVA fibers (a), PVA/SDS/MWCNTs (b), and PVA/SDS/PVP/MWCNTs (c).

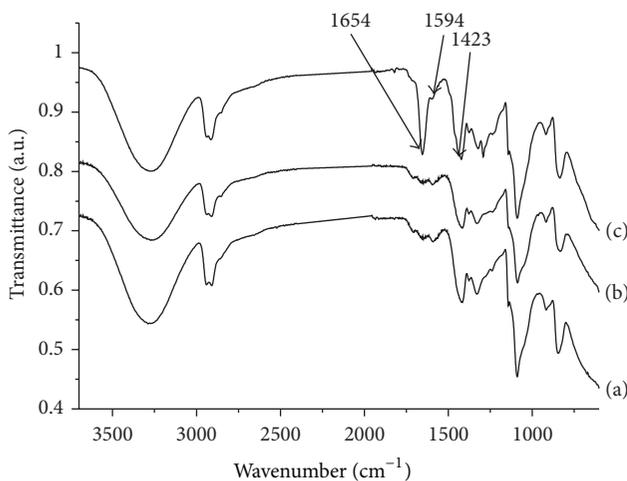


FIGURE 4: FTIR spectra of PVA (a), PVA/SDS/MWCNTs (b), and PVA/SDS/PVP/MWCNTs (c).

at 1417 cm⁻¹ and 1330 cm⁻¹ are attributed to the -CH deformation vibration. At 1089 cm⁻¹, we observe a characteristic peak of C-O stretching vibration. In addition, the peak of O-H stretching vibration appears at 919 cm⁻¹ [19, 20].

Compared to the PVA spectrum (Figure 4(a)), it could be observed that any additional band was observed in the PVA/SDS/MWCNTs spectra (Figure 4(b)). This indicates

that any covalent bond was created between PVA and MWCNTs coated with SDS. Consequently, we confirmed that MWCNTs were dispersed in the PVA via noncovalent functionalization.

Concerning the PVA/SDS/PVP/MWCNTs nanocomposite fibers, the FTIR spectra of the fibers (Figure 4(c)) showed a characteristic peak of PVP at 1423 cm⁻¹ which is assigned to the deformation of CH₂ in PVP. The shoulder at 1594 cm⁻¹ is characteristic of C=C (aromatic) and C-N stretching. The additional peak located at 1654 cm⁻¹ is assigned to the C=O vibration [21–23]. The appearance of this band is due to the interaction of MWCNTs with PVP.

3.4. Thermal Analysis. Thermal gravimetric analysis (TGA) was carried out at a heating rate of 10°C·min⁻¹ in nitrogen atmosphere.

The thermal decomposition of the three samples was multistage processes; it exhibits two degradation steps. In the first region, as can be seen, the three samples displayed a similar behavior with degradation temperature close to 240°C. In fact, the degradation of isobutyl groups [24, 25] was located at about 246°C for the neat PVA fibers (Figure 5(a)). This temperature was decreased slightly for the PVA/SDS/MWCNTs fibers (Figure 5(b)) to be 239°C, and the shift is due to the presence of SDS in the bulk PVA polymer matrix [26], while the PVA/SDS/PVP/MWCNTs fibers (Figure 5(c)) degradation temperature was decreased

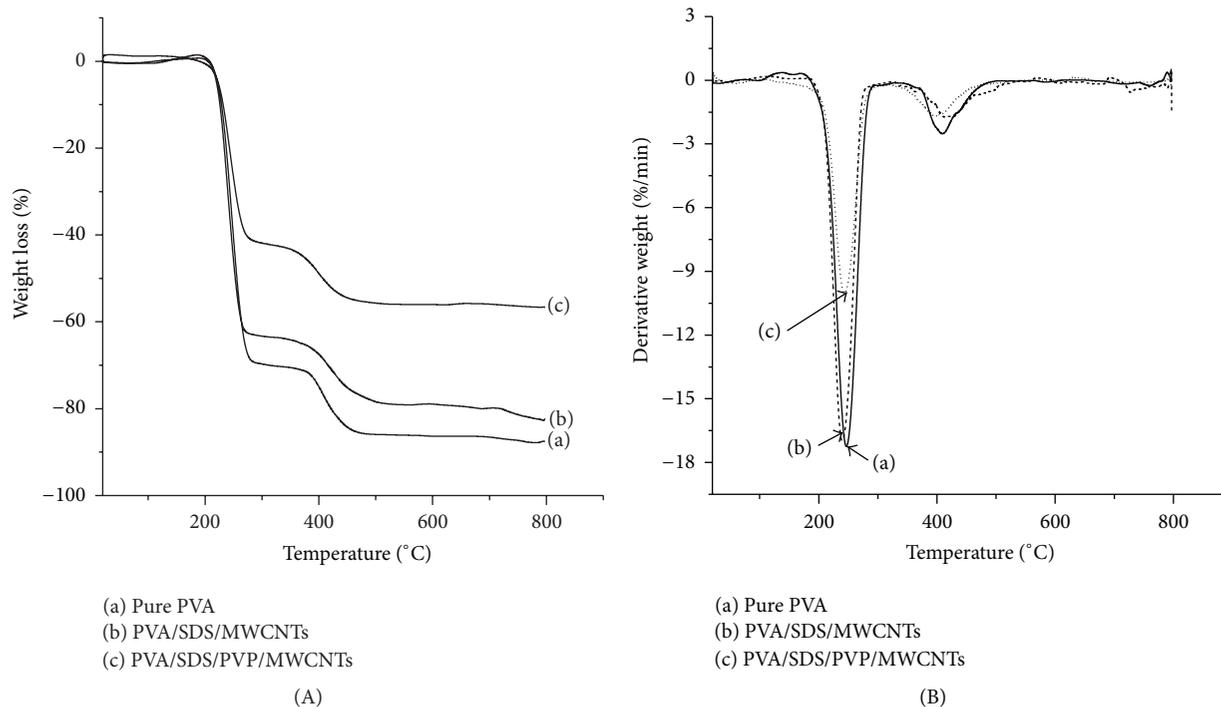


FIGURE 5: TGA and derivative TGA curves of (a) pure PVA, (b) PVA/SDS/MWCNTs and (c) PVA/SDS/PVP/MWCNTs.

TABLE 1: TGA results of weight loss of pure PVA, PVA/SDS/MWCNTs, and PVA/SDS/PVP/MWCNTs fibers.

	Pure PVA fibers		PVA/SDS/MWCNTs fibers		PVA/SDS/PVP/MWCNTs fibers	
Temperature (°C)	246.5	408.9	239.8	413	242.7	396
Weight loss (%)	70	17	63.5	18.7	43.7	14

from 246°C to 242°C compared to the pure PVA fibers. This change reflects the specific multiple hydrogen bonding interaction between PVA and PVP [27].

The second stage appearing around 400°C is corresponding to the cleavage of C–C backbone of side and main chains of PVA [25]. According to Figure 4, all these transitions were accompanied with a weight loss as listed in Table 1.

All samples show a small loss in weight at around 100°C which is assigned to the detachment of residual water (from fibers preparation). For the neat PVA, the major weight loss (70 wt%) is at 193°C, and this continued to increase rapidly with temperature, until a stable plateau region appeared between 351 and 477°C, while the difference between the weight loss of pure PVA and PVA/SDS/MWCNTs fibers indicated the interfacial interaction between the matrix and MWCNTs. When the PVP was incorporated into the composite, the weight loss decreased considerably due to the interaction of PVA with the MWCNTs coated by the PVP through hydrogen bonding interaction between PVA and PVP.

4. Conclusion

PVA electrospun nanofibers containing SDS/PVP/MWCNTs were fabricated, using different concentrations of the SDS

and PVP in order to achieve a stable dispersion lasting for several months. Our results showed clearly that the absorption of the wrapped MWCNTs in aqueous solution increased with the concentration of SDS and PVP and the best absorption was achieved for MWCNTs : SDS : PVP—1 : 5 : 0.6. SEM images of PVA/SDS/PVP/MWCNTs nanofibers showed that the diameter was decreasing to around 224 nm and the interaction between the PVA and the coated carbon nanotubes with PVP was elucidated by FTIR and TGA.

Conflict of Interests

The authors declare no conflict of interests.

References

- [1] B. Ding, M. Wang, J. Yu, and G. Sun, “Gas sensors based on electrospun nanofibers,” *Sensors*, vol. 9, no. 3, pp. 1609–1624, 2009.
- [2] R. Dersch, M. Steinhart, U. Boudriot, A. Greiner, and J. H. Wendorff, “Nanoprocessing of polymers: applications in medicine, sensors, catalysis, photonics,” *Polymers for Advanced Technologies*, vol. 16, no. 2-3, pp. 276–282, 2005.
- [3] M. Bognitzki, T. Frese, M. Steinhart et al., “Preparation of fibers with nanoscaled morphologies: electrospinning of polymer

- blends," *Polymer Engineering and Science*, vol. 41, no. 6, pp. 982–989, 2001.
- [4] Q. Li, S. Mahendra, D. Y. Lyon et al., "Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications," *Water Research*, vol. 42, no. 18, pp. 4591–4602, 2008.
 - [5] K. H. Hong, J. L. Park, I. N. Hwan Sul, J. H. Youk, and T. J. Kang, "Preparation of antimicrobial poly(vinyl alcohol) nanofibers containing silver nanoparticles," *Journal of Polymer Science B*, vol. 44, no. 17, pp. 2468–2474, 2006.
 - [6] K. Yoon, K. Kim, X. Wang, D. Fang, B. S. Hsiao, and B. Chu, "High flux ultrafiltration membranes based on electrospun nanofibrous PAN scaffolds and chitosan coating," *Polymer*, vol. 47, no. 7, pp. 2434–2441, 2006.
 - [7] J. Jagur-Grodzinski, "Polymers for tissue engineering, medical devices, and regenerative medicine. Concise general review of recent studies," *Polymers for Advanced Technologies*, vol. 17, no. 6, pp. 395–418, 2006.
 - [8] Z. Rożek, W. Kaczorowski, D. Lukáš, P. Louda, and S. Mitura, "Potential applications of nanofiber textile covered by carbon coatings," *Journal of Achievements in Materials and Manufacturing Engineering*, vol. 27, pp. 35–38, 2008.
 - [9] J. Nader, C. Bhuvanesh, M. Apparao et al., "Functional fabric with embedded nanotube actuators/sensors," Tech. Rep., National Textile Center Annual Report, 2004.
 - [10] A. Martinez, S. Uchida, Y.-W. Song, T. Ishigure, and S. Yamashita, "Fabrication of Carbon nanotube-poly-methylmethacrylate composites for nonlinear photonic devices," *Optics Express*, vol. 16, no. 15, pp. 11337–11343, 2008.
 - [11] B. Vigolo, A. Penicaud, C. Coulon et al., "Macroscopic fibers and ribbons of oriented carbon nanotubes," *Science*, vol. 290, no. 5495, pp. 1331–1334, 2000.
 - [12] H. Aarab, M. Baïtoul, J. Wéry et al., "Electrical and optical properties of PPV and single-walled carbon nanotubes composite films," *Synthetic Metals*, vol. 155, no. 1, pp. 63–67, 2005.
 - [13] O. Matarredona, H. Rhoads, Z. Li, J. H. Harwell, L. Balzano, and D. E. Resasco, "Dispersion of single-walled carbon nanotubes in aqueous solutions of the anionic surfactant NaDDBS," *Journal of Physical Chemistry B*, vol. 107, no. 48, pp. 13357–13367, 2003.
 - [14] L. Liu, F. Zhao, F. Xiao, and B. Zeng, "Improved voltammetric response of malachite green at a multi-walled carbon nanotubes coated glassy carbon electrode in the presence of surfactant," *International Journal of Electrochemical Science*, vol. 4, no. 4, pp. 525–534, 2009.
 - [15] J. Yu, N. Grossiord, C. E. Koning, and J. Loos, "Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution," *Carbon*, vol. 45, no. 3, pp. 618–623, 2007.
 - [16] N. Diouri and M. Baitoul, "Studies of multiwall carbon naotubes dispersion in poly vinyl alcohol," *Mediterranean Journal of Electronics and Communications*, vol. 6, pp. 127–131, 2010.
 - [17] M. E. Hughes, E. Brandin, and J. A. Golovchenko, "Optical absorption of DNA-carbon nanotube structures," *Nano Letters*, vol. 7, no. 5, pp. 1191–1194, 2007.
 - [18] L. Zeng, W. Wang, J. Liang et al., "The changes of morphology, structure and optical properties from carbon nanotubes treated by hydrogen plasma," *Materials Chemistry and Physics*, vol. 108, no. 1, pp. 82–87, 2008.
 - [19] X. M. Sui, C. L. Shao, and Y. C. Liu, "White-light emission of polyvinyl alcohol/ZnO hybrid nanofibers prepared by electrospinning," *Applied Physics Letters*, vol. 87, no. 11, Article ID 113115, 2005.
 - [20] L. Zhang, P. Yu, and Y. Luo, "Dehydration of caprolactam-water mixtures through cross-linked PVA composite pervaporation membranes," *Journal of Membrane Science*, vol. 306, no. 1-2, pp. 93–102, 2007.
 - [21] R. F. Bhajantri, V. Ravindrachary, B. Poojary, I. Ismayil, A. Harisha, and V. Crasta, "Studies on fluorescent PVA + PVP + MPDMAPP composite films," *Polymer Engineering and Science*, vol. 49, no. 5, pp. 903–909, 2009.
 - [22] S. F. Wei, J. S. Lian, and Q. Jiang, "Controlling growth of ZnO rods by polyvinylpyrrolidone (PVP) and their optical properties," *Applied Surface Science*, vol. 255, no. 15, pp. 6978–6984, 2009.
 - [23] S. Sethia and E. Squillante, "Solid dispersion of carbamazepine in PVP K30 by conventional solvent evaporation and supercritical methods," *International Journal of Pharmaceutics*, vol. 272, no. 1-2, pp. 1–10, 2004.
 - [24] Y.-W. Chang, E. Wang, G. Shin, J.-E. Han, and P. T. Mather, "Poly(vinyl alcohol) (PVA)/sulfonated polyhedral oligosilsesquioxane (sPOSS) hybrid membranes for direct methanol fuel cell applications," *Polymers for Advanced Technologies*, vol. 18, no. 7, pp. 535–543, 2007.
 - [25] E. D. Wang, T. S. Zhao, and W. W. Yang, "Poly (vinyl alcohol)/3-(trimethylammonium) propyl-functionalized silica hybrid membranes for alkaline direct ethanol fuel cells," *International Journal of Hydrogen Energy*, vol. 35, no. 5, pp. 2183–2189, 2010.
 - [26] C. Bartholome, P. Miaudet, A. Derré et al., "Influence of surface functionalization on the thermal and electrical properties of nanotube-PVA composites," *Composites Science and Technology*, vol. 68, no. 12, pp. 2568–2573, 2008.
 - [27] A. B. Seabra and M. G. De Oliveira, "Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blended films for local nitric oxide release," *Biomaterials*, vol. 25, no. 17, pp. 3773–3782, 2004.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

