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Method Article

Fabrication and characterization of TiO_2 and MWCNT coated electrospinning nanofibers for UV protection properties

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A B S T R A C T

This paper aimed to fabricate UV protective nanofibers by the use of specific nanoparticles. The DMF/TiO_2 (Titanium dioxide), DMF/MWCNT (Multi-Walled Carbon Nano Tubes), and DMF/MWCNT+TiO_2 (MWCNT: TiO_2 mass ratio= 1:1) solutions were transferred into a syringe with a stainless steel needle with gauge 21. The electrospinning process was performed for 3 h at the optimized conditions. The surface morphology of nanofibers was characterized by field emission scanning electron microscopy (FESEM). Fourier transform infrared spectroscopy (FTIR) was utilized to characterize functional groups of oxidized MWCNTs and investigate the successful load of nanoparticles at the fiber surface. The UV protection property of nanofibers was investigated by measuring UV rays' transmittance through the composite web. The data of Spectroscopy was used to compute the UV protection factor (UPF).

(1) The effect of CNT,TiO_2, and CNT+TiO_2 nanoparticles on ultraviolet protection property was analyzed separately and simultaneously.

(2) The different concentrations of nanoparticles, including 1,5,10, & 15 wt%, were used to fabricate UV protective nanocomposites.

(3) The electrospinning condition was optimized as a 15 cm distance between the needle tip and collector, 20 KV voltage, 250 RPM drum rotation, and 1.2 ml/h feeding rate to access the best nanofibers.

A R T I C L E I N F O

Method name: Electrospinning
Keywords: Electrospinning, Nanofiber, Polyacrylonitrile, UV protection, UPF, MWCNT, TiO_2
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Specifications table

Subject Area	Materials Science
More specific subject area	Electrospinning of UV protective nanofibers
Method name	Electrospinning
Name and reference of original method	Doshi, J. and Reneker, D.H., 1995. Electrospinning process and applications of electrospun fibers. *Journal of electrostatics, 35*(2–3), pp.151–160. Merati, A.A., Mousavi Shoushtari, A. and Mirzaei, J., 2017. A comparison between the UV protection of PAN/ZnO and PAN/MWNT composite nanofiber mats. *The Journal of the Textile Institute*, 108(12), pp.2086–2089. Im, J.S., Kim, M.I. and Lee, Y.S., 2008. Preparation of PAN-based electrospun nanofiber webs containing TiO2 for photocatalytic degradation. *Materials Letters, 62*(21–22), pp.3652–3655.
Resource availability	Not applicable

Material

PAN (MW=150,000) and MWCNT produced via chemical vapor deposition process (OD:10–15,ID:2–6 nm, length:0.1–10 μm, purity≥90%) were obtained from Sigma-Aldrich chemical company. N,N-Dimethyl formamide (DMF) was supplied from Baker and was used as the solvent. Acid sulfuric and acid nitric were purchased from Merck and applied for reflux. The type of TiO_2 nanoparticles used in this study was Degussa P25.

Functionalization of MWCNT

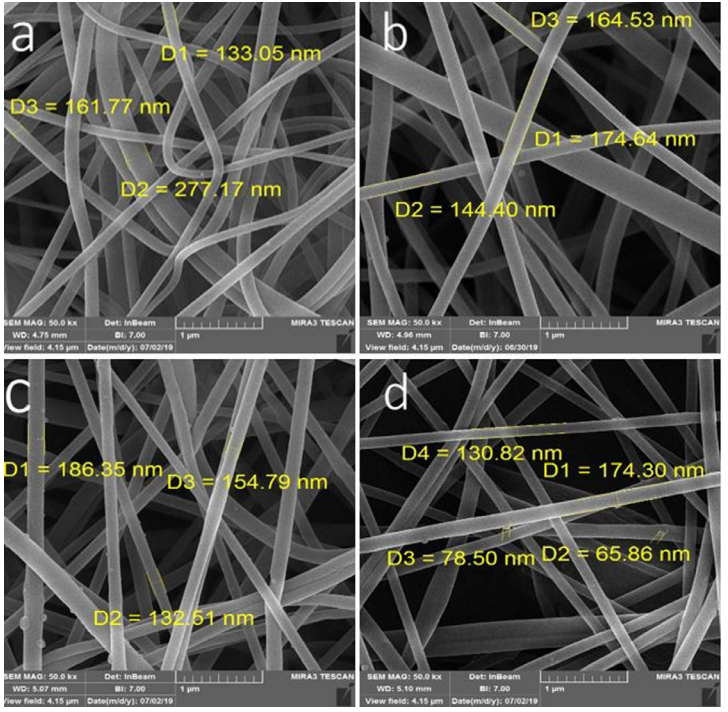
Carbon nanotubes cannot be dispersed in DMF. To obtain homogeneous and stable MWCNT/DMF dispersion, 1 g of MWCNTs were refluxed in the mix of 24 and 8 ml of sulfuric acid and nitric acid, respectively, for 3 h at 45 °C to supply functional groups. The blend was washed with freshly prepared deionized water, and the pH value was measured with pH-indicator paper to access the pH 7. The mixture was centrifuged for 100 min at 4000 rpm to separate the precipitated phase (functionalized MWCNT). The collected nanoparticles were placed in the oven for 48 h to get dry. An FTIR analyzer examined the functionalization of nanotubes [11].

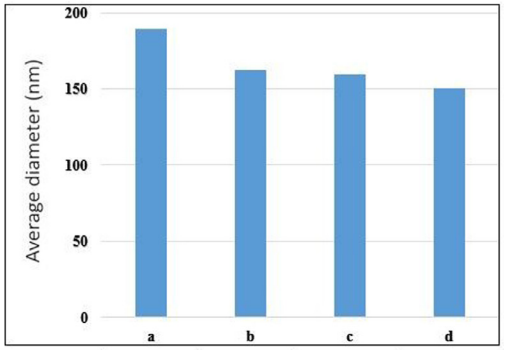
Membrane electrospinning

In order to fabricate PAN nanofibers, 0.316 g of PAN powder was added to 3 ml of DMF and stirred at 50 °C for 2 h to prepare 3 ml of 10 wt% PAN/DMF solution. To obtain DMF/TiO_2, DMF/MWCNT, and DMF/MWCNT+TiO_2 (MWCNT: TiO_2 mass ratio= 1:1) mixtures, nanoparticles at different concentrations of 0,1,5,10, & 15 wt% (relative to PAN weight) were added to DMF and sonicated at 50 °C for 80 min. The prepared mixtures were blent with PAN solution and stirred for 45 min. The solutions were transferred into a syringe with a stainless steel needle (syringe volume: 2 ml, needle gauge: 21). The reason for choosing a low volume syringe was to prevent the deposition of nanoparticles during the electrospinning process. Nanofibers were collected on aluminum foil. The electrospinning process was performed for 3 h at the following conditions include a 15 cm distance between the needle tip and collector, 20 KV voltage, 250 RPM drum rotation, and 1.2 ml/h feeding rate. Each experiment was carried out three times, and the mean value of all tests was reported [16,17].

Characterization of membrane

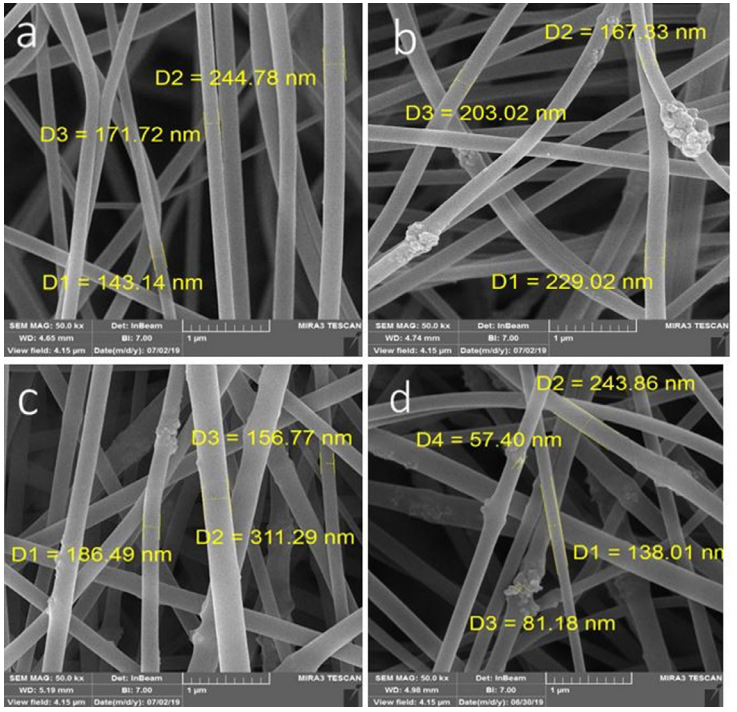
The surface morphology of nanofibers was characterized by field emission scanning electron microscopy (FESEM). For this purpose, samples were covered with a thin layer of gold to prevent nanofibers' electrical charge, and then the microscopy images of nanofibers were taken. The diameters of 50 different nanofibers were determined using Image J software. The SEM images of PAN/CNT, PAN/TiO_2, and PAN/CNT/TiO_2 are presented in Figs. 1–3, respectively.

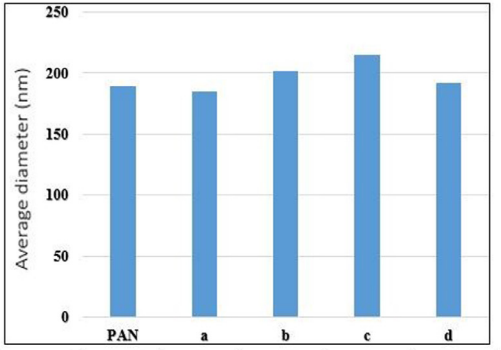




sample	PAN	1% CNT	5% CNT	10% CNT
Average diameter	189.26	162.29	159.83	150.63
SD	26.25	13.17	20.2	22.54

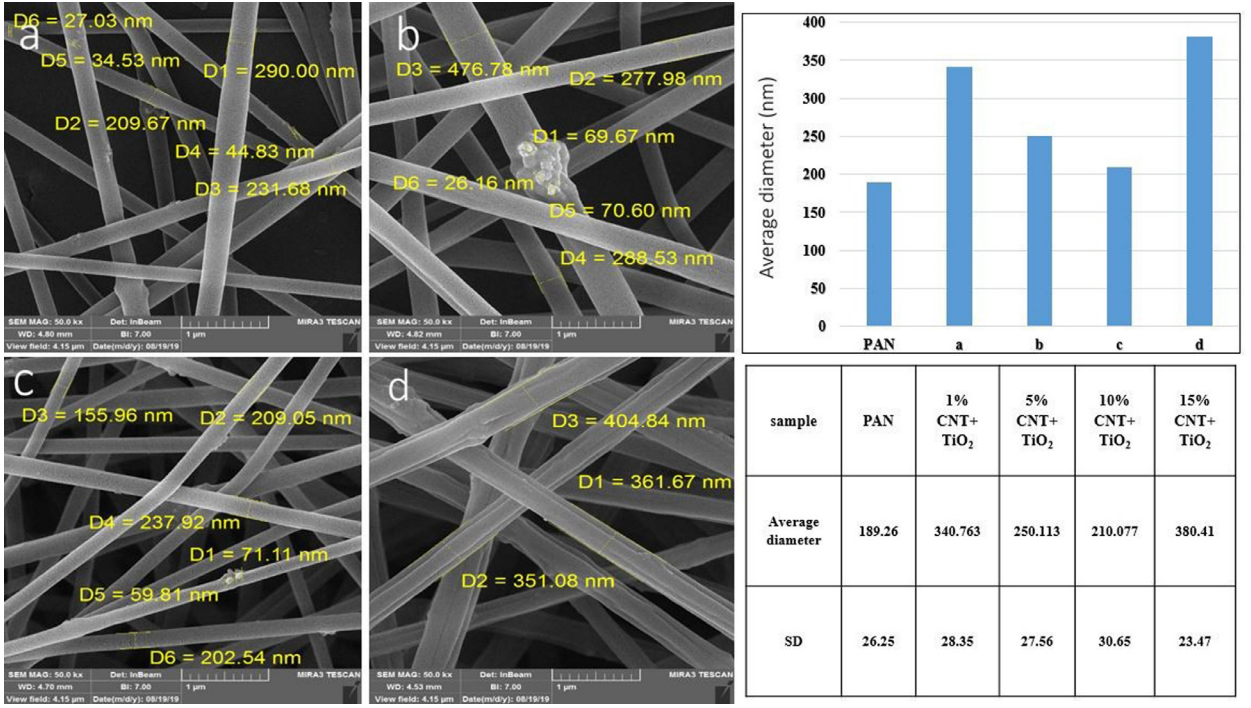
Fig. 1. Appearance of **a:** pure PAN nanofibers, **b:** PAN/MWCNT (1wt%), **c:** PAN/MWCNT (5wt%), **d:** PAN/MWCNT (10wt%) nanofibers.





sample	PAN	1% TiO_2	5% TiO_2	10% TiO_2	15% TiO_2
Average diameter	189.26	184.54	201.79	215.18	191.93
SD	26.25	24.41	25.97	17.99	16.84

Fig. 2. Appearance of **a:** PAN/TiO_2 (1wt%), **b:** PAN/TiO_2 (5wt%), **c:** PAN/TiO_2 (10wt%), **d:** PAN/TiO_2 (15wt%) nanofibers.



sample	PAN	1% CNT+ TiO_2	5% CNT+ TiO_2	10% CNT+ TiO_2	15% CNT+ TiO_2
Average diameter	189.26	340.763	250.113	210.077	380.41
SD	26.25	28.35	27.56	30.65	23.47

Fig. 3. Appearance of **a:** PAN/MWCNT/TiO_2 (1wt%), **b:** PAN/MWCNT/TiO_2 (5wt%), **c:** PAN/MWCNT/TiO_2 (10wt%), **d:** PAN/MWCNT/TiO_2 (15wt%) nanofibers.

Table 1
The transmittance and UPF of nanofiber webs.

Protection level	UPF	Average transmittance(%)	Sample
Not ratable	8.72	11.53	PAN
Good protection	16.09	6.34	1%CNT
Very good protection	32.19	3.07	5%CNT
Excellent protection	47.86	2.11	10%CNT
Good protection	15.01	6.65	1%TiO_2
Very good protection	26.71	3.75	5%TiO_2
Excellent protection	42.31	2.33	10%TiO_2
Excellent protection	133.34	0.71	15%TiO_2
Excellent protection	90.55	1.07	1% CNT+TiO_2
Excellent protection	170.31	0.57	5% CNT+TiO_2
Excellent protection	331.54	0.27	10% CNT+TiO_2
Excellent protection	685.81	0.15	15% CNT+TiO_2

Fourier transform infrared spectroscopy (FTIR) was utilized to characterize functional groups of oxidized MWCNTs and the successful load of nanoparticles at the fiber surface [1,7,12,13]. The pattern obtained from the FTIR of a specific compound contains unique peaks due to the presence of specific functional groups and chemical bonds. The FTIR of oxidized MWCNTs and the nanoparticle-coated nanofibers were presented in Figs. 4 and Fig. 5, respectively.

The UV protection property of nanofibers was investigated according to the American Association of Textile Chemists and Colorists (AATCC) Test Method 183–2004. The transmittance of UV rays through the composite web was measured by Lambda 900UV/VIS/NIR of PerkinElmer Co in 280–400 nm wavelengths. The Spectroscopy data were used to compute the UV protection factor (UPF) according to standard AS/NZS/4399:1996 of Australia/ New Zealand by Eq. (1).

$$UPF = \frac{\int_{280}^{400} E_\lambda S_\lambda d_\lambda}{\int_{280}^{400} E_\lambda S_\lambda d_\lambda \Gamma_\lambda} \tag{1}$$

where E_λ is the relative erythemal spectral effectiveness, S_λ is the solar spectral irradiance (W/cm2/nm), d_λ is the measured wavelength interval (nm) and T_λ is the average transmittance of the specimen (%). The related data are presented in Fig. 6 and Table 1.

Method validation

The FTIR study of nanofibers showed significant peaks in specific wavenumbers, which indicates PAN and MWCNT and TiO_2 nanoparticles in the structure of nanocomposites. According to SEM images, nanoparticle concentration influences the nanofiber diameter. At the PAN/MWCNT samples, the MWCNT content enhancement leads to the solution's more electrical conductivity. High conductivity induces more charges at the jet surface and more electrostatic repulsive force between jet sprays. The increase in jet energy results in overcoming surface tension and the decrease of nanofiber diameter.

On the other hand, this trend may be related to the increased viscosity of the solution resulting from carbon nanotubes' addition [14] Increased viscosity enhances the bonding between molecular chains and prevents the jet from releasing. As shown in Fig. 1, this has resulted in a decrease in PAN/MWCNT nanofibers' diameter. According to Fig. 2, the diameter of nanofibers increased as the TiO_2 content increased. A load of TiO_2 nanoparticles in each part of the fibers leads to an increase in thickness.

Meanwhile, in the sample with 15 wt% TiO_2, the diameter of nanofibers was lower. Since the amount of nanoparticles in this sample is highest, the nanoparticles are not entirely dispersed in the polymer solution. The other reason for this decrease can be attributed to the effect of the high concentration of nanoparticles on the formation of nanofibers' irregular and non-uniform morphology. As presented in Fig. 3, at the PAN/MWCNT/TiO_2 samples, the diameter change was descending due to

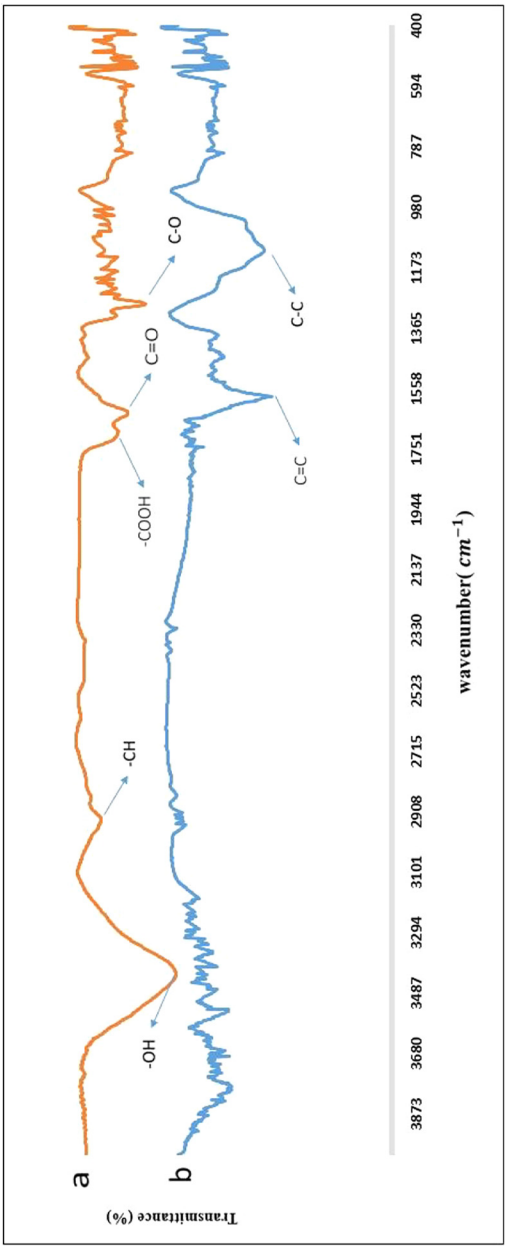


Fig. 4. FTIR spectra of **a:** functionalized MWCNT, **b:** unfunctionalized MWCNT.

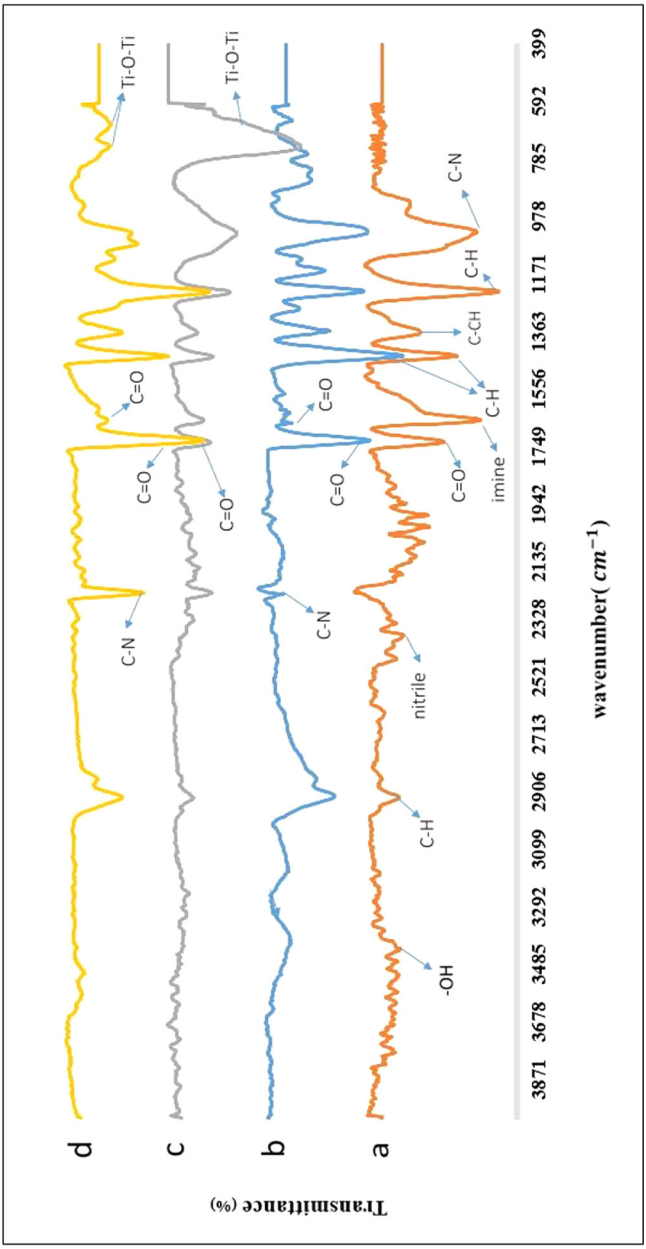


Fig. 5. FTIR spectra of **a:** PAN, **b:** PAN/MWCNT, **c:** PAN/TiO_2, **d:** PAN/MWCNT/TiO_2 nanofibers.

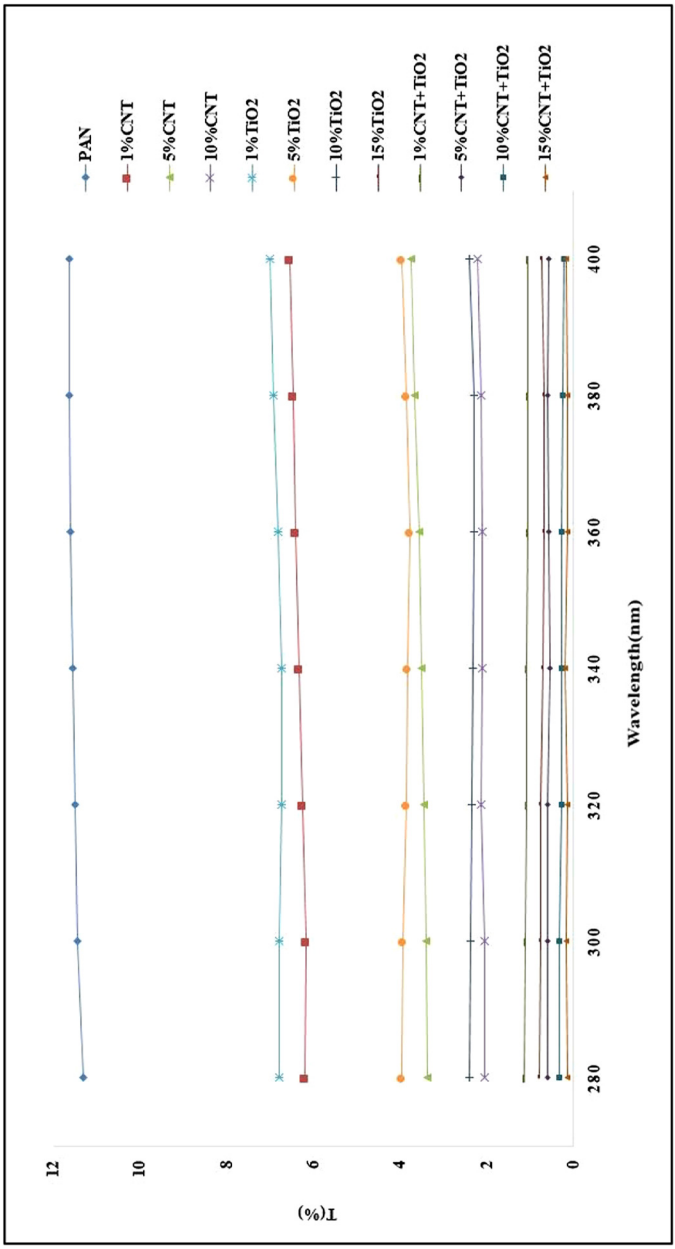


Fig. 6. UV transmission of PAN and nanoparticle coated mats.

the solution's high electrical conductivity and viscosity; however, at the 15 wt% MWCNT+TiO_2 sample, the diameter had a rise as the result of high nanoparticle loading.

The results showed that a load of nanoparticles increases UV protection compared to pure PAN nanofibers, in which the MWCNT coated webs have better performance than TiO_2 coated samples [4]. However, the PAN/MWCNT/TiO_2 composites provide the best protection and are classified as excellent protection at all concentrations. The lower UV blocking activity of pure TiO_2 than MWCNT is due to the recombination of electron-hole pairs, which reduces the number of electrons and holes to be trapped and participate in the reactions. In CNT/TiO_2 hybrids, the photogenerated electrons in the conduction band of TiO_2 transfer to the CNTs during photo-irradiation of the composite and prevent the recombination electron-hole pairs in the TiO_2. Therefore, CNTs leave the holes in the valence band of the TiO_2, which can move to the surface and react. Another advantage of the TiO_2/CNT hybrid is the formation of a high surface area. The bonding between TiO_2 and CNTs enhances the photon absorption ability compared to pure CNTs or neat TiO_2 [9,10].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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