

Vibration electrospinning of Polyamide-66/Multiwall Carbon Nanotube Nanocomposite: introducing electrically conductive, ultraviolet blocking and antibacterial properties

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Fabrication of electro-conductive fiber is a novel process. Nanocomposites of multiwall carbon nanotube/polyamide66 were produced by electrospinning with different amounts of multiwall carbon nanotube. Field emission scanning electron microscope and Fourier transform infrared spectroscopy of samples proved the existence of multiwall carbon nanotube distribution in polyamide 66 nanofibers. Results showed that electro conductivity of electrospun multiwall carbon nanotube/polyamide 66 nano fiber has increased in comparison with electrospun polyamide 66. Moreover, UV blocking of samples was investigated which has shown that using multiwall carbon nanotube in polyamide 66 increases UV blocking of fibers. Furthermore, anti-bacterial activity of nanocomposite showed that these nanocomposites have antibacterial property against both *Staphylococcus Aureus* and *Escherichia Coli* bacteria according to AATCC test method.

Keywords: MWCNT, PA66, Electrospinning, Electrical Conductivity, UV-Blocking, Antibacterial.

INTRODUCTION

During the past decades, nanotechnology has exposed a novel section among the materials. The application of nanotechnology has quickly grown in several areas, particularly in textile industry^{1–3}. Producing ultrafine fiber such as nanofiber is carried out through electrospinning which is the most usual and best-known technique that can overcome the surface tension of polymer in order to create sub-micrometer fibers⁴. The main characteristics of electrospinning include high aspect ratio, specific surface area, dimensional stability, high porosity and small diameter^{5–7}. This method is a conventional approach for fabricated nanocomposite⁸.

Electrospinning process contains a polymer solution which is charged and by overcoming the surface tension, a thin layer of web polymer is formed on a surface ejection of polymer solution, causing the elongation of polymer and firmed ultra-thin fiber^{9–11}.

Electrospinning nanofibers have many medical applications such as wound dressing¹², drug delivery, dental restoration, as well as engineering applications such as filtration, and tissue. Poor mechanical properties of these fibers (like Young's modulus) can be enhanced by combining nano-materials such as carbonaceous nano-materials with these fibers¹³.

Multi-walled carbon nanotubes (MWCNTs) have attracted considerable attention because of their unique characteristics such as electrical, optical and mechanical properties^{8, 14, 15}, high surface to volume ratio, high conductivity, low mass density and small size^{16–18}.

The most processable fiber which has special properties such as high strength, toughness and elasticity, is polyamide-66 (PA66). It is a semi-crystalline polymer having oil and heat resistance. Formic acid and Metacrosol are two common solvents that can solve it at room temperature in order for electrospinning. Obviously, its poor humidity adsorption and non-electrical conductivity are among the disadvantages of this fiber. In order to overcome these

problems, blending of PA66 with MWCNT is suggested because by blending, its properties will be balanced¹⁹. Chang Jae Lee et al. reported the dispersion of CNT in the PA66 phase because of high affinity, and reported the higher electrical conductivity of PA66/carbon nanotube¹⁰. Clemente et al. reported the better dielectric, crystallinity and rheology properties of PA66/MWCNT²⁴.

In this paper, nanocomposites of MWCNT/PA66 with different concentration of carbon nanotubes were electrospun and its properties such as UV-blocking, antibacterial and electrical conductivity was investigated.

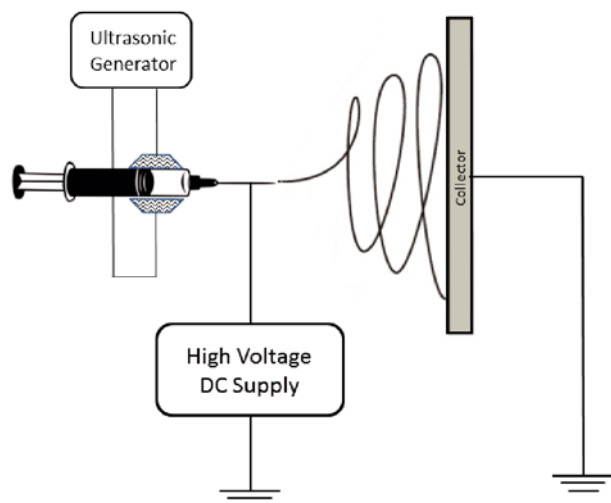
EXPERIMENTAL

Material and Methods

For the purpose of this study, we prepared PA66 granule from Aldrich (N66 74712) Company; Formic acid 99% from Merck, MWCNT with outside diameter of 20–30 nm and inside diameter of 5–10 nm and specific surface area of more than 110 m²/g from US Nano Company were prepared. A suspension containing different loadings of MWCNT in the solution of PA66/formic acid was prepared and was sonicated for 30 min at 50°C. A Euronda ultrasonic bath model Eurosonic 4D, 350 W, 50/60 Hz (Italy) was used. For electrospinning, the distance between nozzle and collector was 15 cm, pumping rate was 0.1 ml/h and spinning potential was 25 kV. More information on electrospinning parameters is given in Table 1. An ultrasonic generator was added to the device in order to obtain homogenate suspension during electrospinning (Fig. 1). This device provides vibration at 20 kHz. Without this device, nanomaterial might be aggregate, so ultrasonic device (vibrating electrospinning) can help to improve distribution of multi wall carbon nanotube during electrospinning. The Nanocomposites were collected on the Aluminum foil. The FTIR (Fourier Transform Infrared) spectra were obtained by BRUKER TENSOR27. The morphology

Table 1. Parameters of electrospinning

Parameter	Pumping rate [ml/h]	Voltage [kV]	Distance of nozzle to collector [cm]	Collector speed [rpm]	Traverse speed [m/min]	Temperature [C]
Value	0.1	25	15	150	0.3	28

**Figure 1.** Schematic diagram of the vibration electrospinning

of nanofibers was observed by field emission scanning electron microscope (FE-SEM) MIRA3-TESCAN. UV-blocking properties of samples were determined using Perkin Elmer Lambda UV-vis spectrophotometer. Electrical surface resistivity was investigated by Hioki digital multimeter model 3256-50, Japan.

RESULTS AND DISCUSSION

Microscopic analysis

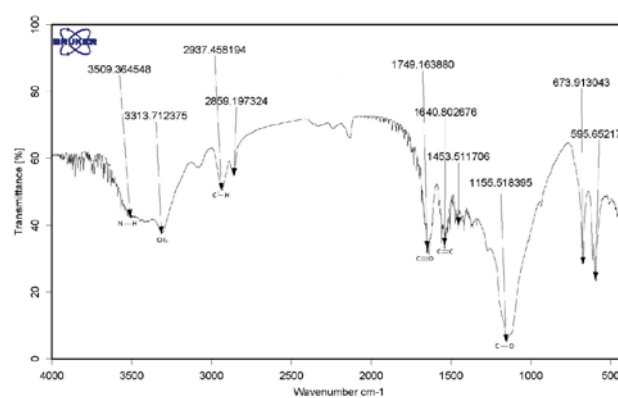
Figure 2 shows the morphologies of electrospun nanofibers and MWCNT's. According to FE-SEM images, the electrospun nanofibers were formed without any beads. Also it is possible to authenticate the MWCNTs on the surface of electrospun samples at higher magnification. The diameters of MWCNTs and nanofibers range between 20 to 32 nm and 24 to 55 nm, respectively. The average diameter of nanofibers was calculated according to Eq. (1)

$$D_n = \frac{\sum niDi}{\sum ni} \quad (1)$$

Where D_n is the diameter of fibers, and ni and Di are number and diameter of each fiber, respectively.

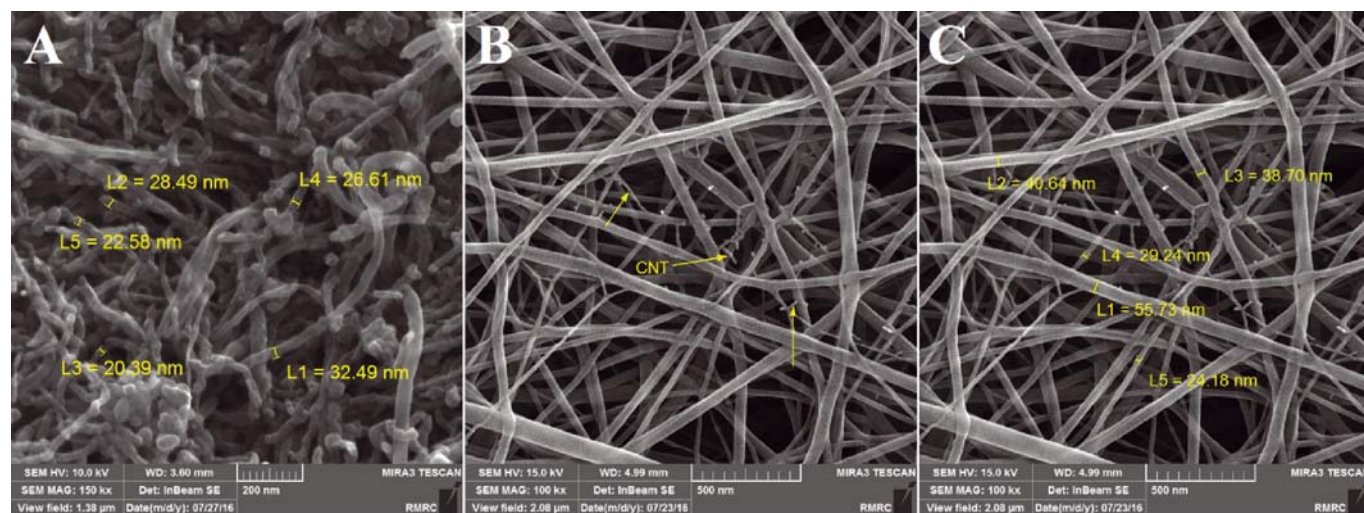
FTIR analysis

Functional groups of the samples were studied by FT-IR spectroscopy. As shown in Figure 3 the peak at 1640 m^{-1} shows the existence of C=C bond. For PA66, the characteristic peaks appear at 3509 cm^{-1} (N-H), 3313 cm^{-1} (CH_2) and 1749 cm^{-1} (C=O). Therefore, the results proved the existence of PA66 and carbon compound.

**Figure 3.** FT-IR spectrum of PA66/MWCNT electrospun nanocomposite

Electrical Conductivity

One of the most important physical properties of CNT/PA66 nano-composite is electrical conductivity. The electrical conductivity of raw sample (PA66 electrospun with 0.00% MWCNT) and treated samples were compared. Figure 4 shows the conductivity of various MWCNT loadings for electrospun fibers. As it can be seen, by increasing MWCNT from 0% to 1%, the electrical conductivity increases significantly. However, increasing MWCNT from 1% to 4% enhances the electrical conductivity but not as much as 0% to 1%. It can

**Figure 2.** FE-SEM images of (A) MWCNT, (B) distribution of MWCNTs on electrospun fibers, and (C) diameter of electrospun nanofibers

be explained by percolation theory. By observing Table 2, one can easily understand that the conductivity of raw sample was zero while the electrical resistance of treated samples was about $10^{10}\Omega/\text{square}$, $10^6\Omega/\text{square}$ for samples A, B and $10^3\Omega/\text{square}$ for samples C and D, respectively. In other words, by increasing the percentage of MWCNTs, the electrical conductivity is increased. It means that enhancing the MWCNT concentration had a perceptible effect on the electrical conductivity of PA66 nanofibers. This can be explained by better contact between MWCNTs. The polymer barrier between adjacent MWCNTs may reduce the conductivity of the samples. Chien et al. reported the electrical conductivity of polyacrylonitrile/carbon nanotube ranging from 10^2 to $10^5\Omega^{20}$. Mohiuddin and Hoa obtained a resistance of about $10^3\Omega$ for polyether ether ketone/CNT composite fiber²¹. In electrospun PA66/MWCNT fibers, the conductive pathways are formed through MWCNT network, and by the excellent conductivity of composite it comes to the conclusion of good dispersion of MWCNT in composite. The lower electrical resistance results in higher MWCNT content in nanocomposite which can be the result of enhancing the possibility of MWCNT contacts in the same area.

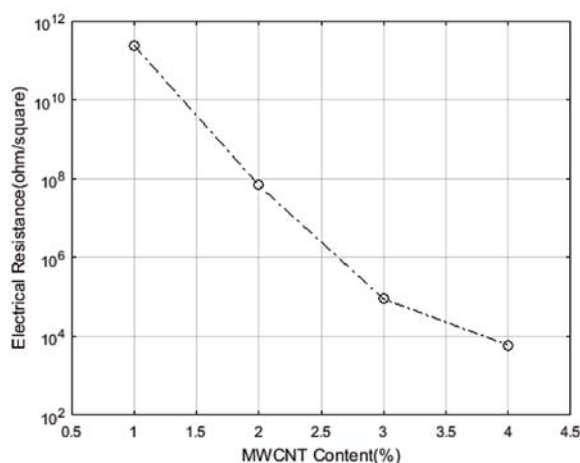


Figure 4. Conductivity of various MWCNT loadings for electrospun fibers

UV blocking

Many health problems of ultraviolet radiation have been proven such as cancers and erythema. Hence, UV-blocking fabrics have attracted much attention in the last decade. These fabrics are produced via different methods such as sol-gel, dry pad and finishing techniques²². UV-blocking property of fabrics is illustrated by UPF (ultraviolet protection factor). This factor is measured via Eq. 2. In this equation, $E\lambda$ is the relative erythral spectral effectiveness, $T\lambda$ is the spectral transmittance of the specimen, $S\lambda$ is the solar UV spectral irradiance and $d\lambda$ is the wavelength increment. The UV transmittance diagram of raw sample and treated samples are presented in Figure 5 (in the range of 200–400 nm). As it is shown, the transmittance spectrum of treated samples is lower than that of the raw sample. It means that UV

protection of PA66/MWCNTs is higher. This is due to UV absorption ability of carbon nanotubes. The UPF of the raw sample is 6, which has no protection against transmittance of UV irradiation. However, the measured UPF of the treated samples is 68, 105, 143, 189 for samples A, B, C and D, respectively. As a consequence, the samples with MWCNT have better UV protection compared to the raw sample due to UV absorption ability of MWCNT.

$$UPF = \frac{\int_{200}^{400} E\lambda \times S\lambda \times d\lambda}{\int_{200}^{400} E\lambda \times S\lambda \times T\lambda \times d\lambda} \quad (2)$$

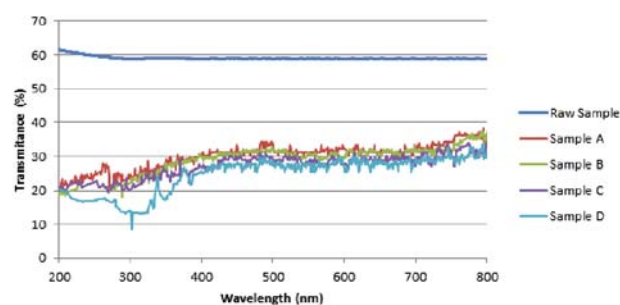


Figure 5. UV transmittance diagram of samples

Antibacterial properties

Using reactive oxygen species can cause to oxidation of proteins, nucleic acids lipids and DNA which can leads to bio cells destruction²⁵. Musico and Liu were reported that carbon compounds produce reactive oxygen species^{26–27}. Carbon compounds including graphene, mesopores carbon, graphene oxide and carbon nanotubes are well known because of their special properties like antibacterial activity^{27–30}. Antibacterial and antimicrobial properties of carbon materials such as fullerene and carbon nanotube have been reported by Krishnamoorthy and Zhang^{31–32}. The antimicrobial efficiency of the treated fabrics was tested against both Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria. The *S. aureus* bacterium is a pathogenic micro-organism causing many diseases such as toxic shock, purulence, abscess, fibrin coagulation, and endocarditic. Moreover, *E. coli* bacterium which causes urinary tract and wound infections is a popular test organism²³.

The result of the antibacterial test is reported in Figure 6. There is no meaningful reduction of bacteria on the raw sample while the samples treated with MWCNT had the proper antibacterial activity against both *S. aureus* and *E. coli* bacteria. The antibacterial activity of the samples treated with MWCNT was about 96.8% and 98% for *S. aureus* and *E. coli* bacteria, respectively. In other words, combining MWCNT with PA66 has improved the antibacterial activity of web. Moreover, samples showed better efficiency against *E. coli* in comparison with *S. aureus*. This can be explained by the difference in the thicknesses of the cell walls; *S. aureus* has a thicker cell wall.

Table 2. Electrical resistivity of samples

Sample	RAW	A	B	C	D
MWCNT%	0%	1%	2%	3%	4%
Electrical resistivity [Ω/square]	∞	24×10^{10}	68×10^6	89×10^3	5.9×10^3

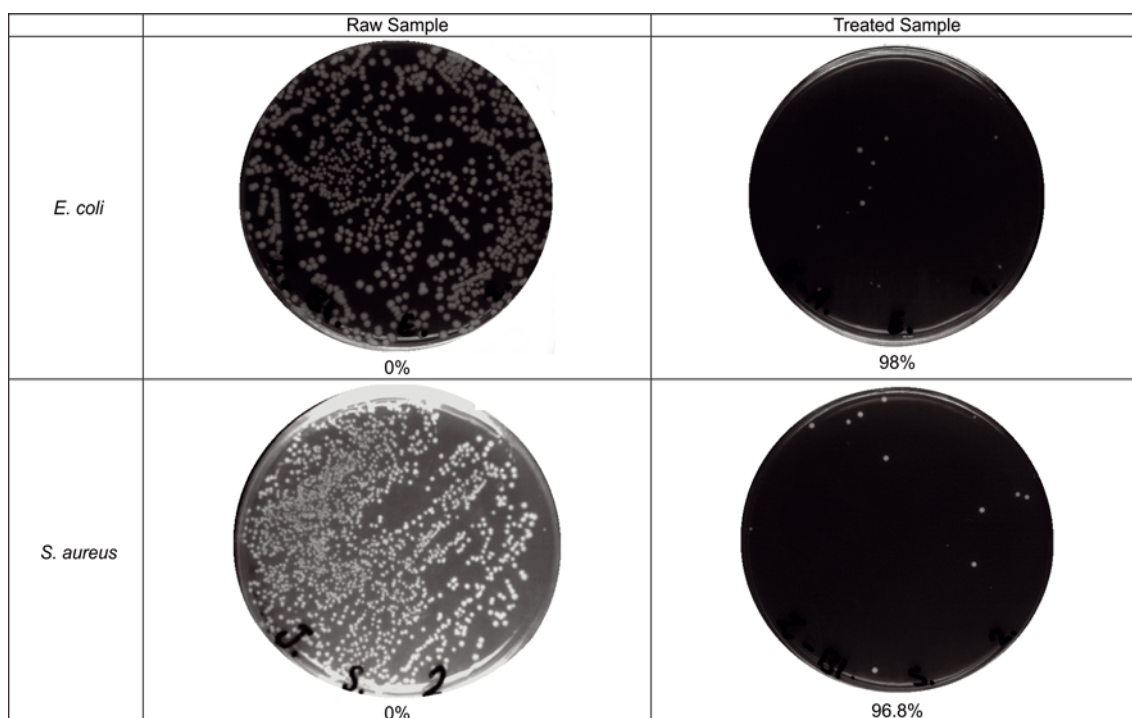


Figure 6. Antibacterial efficiency of raw and treated samples

CONCLUSION

In this study, MWCNT/PA66 nanocomposites were successfully fabricated by electrospinning method with multifunctional properties. Electrical conductivity, suitable antibacterial property and UV blocking activities were obtained. Through FTIR pattern, and FE-SEM images, the successful distribution of multi-walled carbon nanotube on the base of polyamide66 was verified. Moreover, the morphologies of electrospun nanofibers were illustrated without any beads. Fabrication of PA66 with MWCNT improved some properties of this nanocomposite such as antibacterial activity and UV blocking, which can help with prevention of various diseases.

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