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Fabrication of Homogeneous Multi-Walled Carbon Nanotube/ Poly (Vinyl Alcohol) Composite Nanofibers for Microwave Absorption Application

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Poly (vinyl alcohol) (PVA) / sodium dodecyl sulfate (SDS) / multi walled carbon nanotubes (MWCNT) camposite nanofibers with various MWCNT contents (up to 10 wt%) were fabricated by electrospinning process and their microwave absorption properties were evaluated by a vector network analyzer in the frequency range of 8 – 12 GHz (X-band) at room temperature. The uniform, stable dispersion and well oriented MWCNT within the PVA matrix were achieved through using SDS as dispersing agent. The SEM analysis of the nanofibers samples revealed that the deformation of the nanofibers increases with increasing MWCNT concentration. Very smooth surface of the composite electrospun nanofibers even for the nanofibers with concentration of 10 wt% MWCNT have been successfully prepared because of the high stability dispersion of MWCNT. It was observed that absorption microwave properties improved with increasing in the loading levels of MWCNT. Finally, the PVA/SDS/MWCNT composite nanofibers sample with the 10 wt% content of MWCNT has shown the reflection loss of 15 dB at the frequency of 8 GHz.

Keywords: Carbon nanotubes, Poly (Vinyl Alcohol), Nanofibers, Electrospinning, Microwave absorption.

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1. INTRODUCTION

Electromagnetic interference (EMI) as a novel kind of environmental pollution, which consists of any unwanted signals with frequencies ranging from the lower power frequencies to the microwave region, that emitted by electrical and electronic equipment [1]. Nowadays, this interference has been increased because of significant developments in electronic systems causing serious problems, such as disturbance of performance and malfunctions of these systems and even can affect the human body [2]. Therefore, EMI shielding materials are necessary because of health concerns and protecting electrical and electronic equipment when these equipments interfere with each other [3-4]. The amount of attenuation in the electromagnetic field by a shield is defined as shielding efficiency (SE). There are three mechanisms for control this electromagnetic pollution which is consisting of surface reflection, absorption and multiple reflections of the electromagnetic wave. Among them, absorption is best mechanism for shielding of the electromagnetic wave and using microwave absorption materials is great technique to prevent EMI [5].

In the past, typical metals such as copper or aluminum were the most common materials for EMI shielding, which had excellent shielding effectiveness [6]. High conductivity and dielectric constant of materials result in high shielding effectiveness. Some metals such as silver and copper have high conductivity and high dielectric constant leading to excellent shielding effectiveness [5, 7]. The main mechanism for the EMI shielding by metallic materials described by radiation reflects, therefore these materials cannot be used in applications where absorption is important like stealth technology. Furthermore, they have some disadvantages like high density especially in high loading of metal filler, easy corrosion and complex processing [8, 9].

Recently, carbonic materials have been also used in EMI shielding and microwave absorbing applications, as conductive fillers. Various carbonic microwave absorber media have been investigated, which includes carbon nanotubes (CNT), carbon fibers (CF), carbon nanofibers (CNF), and carbon black (CB). Among mentioned media, microwave absorption by CNT has been of great concern. CNT are classified in two general types, namely single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). MWCNT with their exceptional mechanical, electrical and thermal properties are reported to be excellent shielding materials for electromagnetic interference, because of their high conductivity and low density characteristics. The main mechanism described for shielding by the MWCNT is the radiation absorption, therefore MWCNT can be useful for applications where absorption is important [2, 6, 10].

Several experimental and theoretical studies, using different techniques, have been focused on microwave absorption on CF, CNF, and CB in composite structures with controversial results [11-14]. Currently, there are few studies in the literature regarding the use of MWCNTs in composite for improving their microwave absorption [15]. In the present study, the synthesis of novel poly (vinyl alcohol) (PVA) / MWCNT composite nanofibers by electrospinning process has been reported. The microwave absorption behaviors in these composite nanofibers have been investigated using vector network analyzer. Also the effect of MWCNT amounts on the

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absorption capacity of the composite nanofibers is also investigated.

2. EXPERIMENTAL

2.1 Materials

PVA powder (M_w = 72000 g/mol, 98% hydrolyzed) as a polymer was obtained from Merck and MWCNT (purity > 95%, diameter < 8 nm, Length: 30 μm) were supplied from Neutrino Company. Sodium dodecyl sulfate (SDS) was obtained from Sigma-Aldrich. The solvent used for dissolving PVA and PVA/SDS/MWCNT dispersion was distilled water. All reagents used were of analytical grade and were used as received without further purification.

2.2 Preparation of Electrosppining Solutions

Electrospping solutions were prepared in three steps (Fig. 1). First, the solution samples were prepared by dissolving 1 wt% SDS in distilled water using magnetic stirrer (corning hot plate stirrer PC-351) at 25°C for 1 hr. In the second step; different weights of MWCNT were dispersed in the SDS/H_2O solutions by

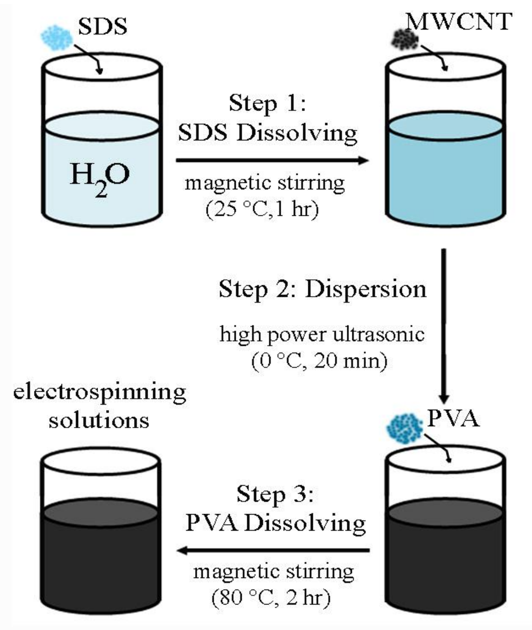


Fig. 1 – Illustration of the dispersion process steps.

Table 1. Concentrations of MWCNT, SDS, and PVA in the mixed solutions

Code.	Mass in 100ml H_2O			MWCNT mass ratio (wt %)
	PVA (mg)	SDS (mg)	MWCNT (mg)	
CNT-0	8000	920	0	0
CNT-2	8000	920	180	2
CNT-5	8000	920	450	5
CNT-10	8000	920	900	10

using a high power ultrasonic homogenizer (UP200, Germany) at 0 °C for 20 min. Finally, the electrospinning solutions were prepared by dissolving 8 wt% of PVA in sonicated solutions by using a magnetic stirrer at 80°C for 2 hr. The calculated MWCNTs concentrations in each composition of any sample are listed in Table 1.

2.3 Measurment and Characterization

The surface morphology of the nanofibers was examined by SEM (Philips, XL-30) at an accelerating voltage of 25 kV under magnification of 10000X, and the average fibers diameter was measured with the SEM images using Image J software (National Institute of Health, USA) from 100 fibers/sample. The microwave-absorbing properties of the composite nanofibers were investigated using HP Vector Network Analyzer (Model 8510ES) in the frequency range of 8-12 GHz at room temperature. All samples were cut into a rectangular shape (22.86 mm × 10.16 mm, thickness 1mm) to fit in rectangular wave-guide of X-band. The wave-guide fitted with the sample was backed by a metal layer for measurement of reflection loss.

3. RESULTS AND DISCUSSION

3.1 Optimized Dispersion of MWCNT

The difficulty in preparing well dispersed MWCNT composite solutions have been related to their high specific surface area and consequently, possessing very stronger van der Waals interactions. Generally, to improve the morphological properties of the fabricated films containing MWCNT, the dispersion condition is very significant. It is important that MWCNTs to be dispersed uniformly without breakage and aggregation. The SDS/MWCNT solution presented highly stable dispersion behavior without any precipitation at room temperature even after two months. The schematic mechanism of dispersion process has been presented in Fig. 2. SDS surfactant is a class of molecules exhibiting a strong tendency to adsorb at interfaces. This is characterized by the presence of both polar (hydrophilic) and nonpolar (hydrophobic) segments. The hydrophilic polar group in SDS dissolves well in water. On the other hand, the hydrophobic backbone in SDS interacts with the MWCNT. Finally, by following this route complete and efficient surface coating of MWCNT by SDS molecules preventing re-aggregation can be achieved.

3.2 Morphplogy of Composite Nanofibers

Fig. 3 display SEM photographs of the PVA/SDS/ MWCNT composite nanofibers. The surface of the CNT-0 and CNT-2 electrospun nanofibers is very smooth, as shown in Fig. 3a and 3b, respectively. Low surface roughness and unevenness in the CNT-5 sample was observed, while still good alignment in the sample structures can be seen (Fig. 3c). However, considerable aggregation and local irregularities were observed as the MWCNT content increased to 10 wt% (see the sample CNT-10 in Fig. 3d). However, considerable aggregation and local irregularities in nanofibers structure by incorporating low concentrations of MWCNT (1-2 wt%) have been also reported by other researchers [16].

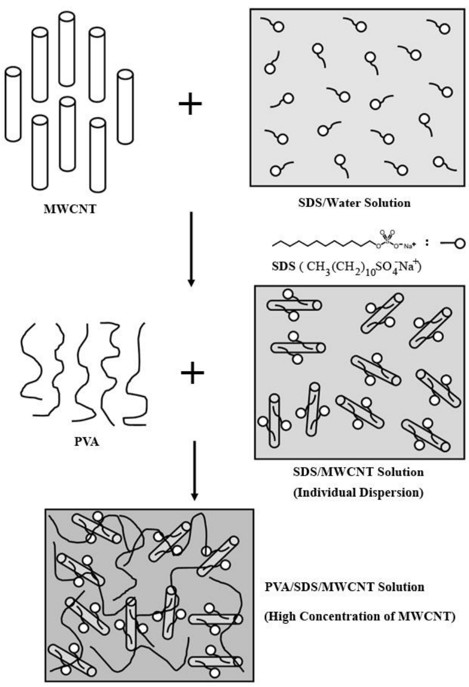
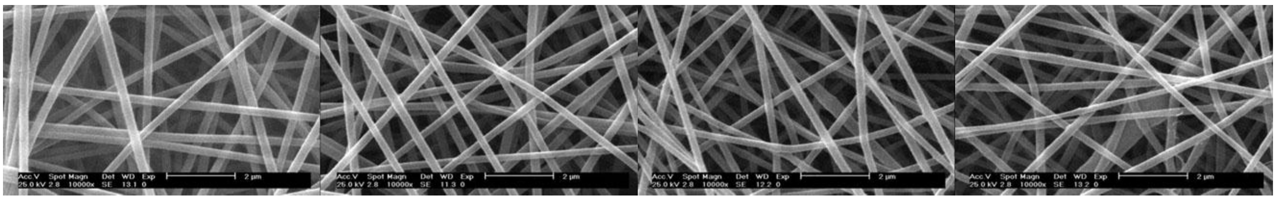


Fig. 2 – Schematic mechanism of dispersion process

The dispersion condition is a very important step in electrospinning process and plays a significant role in achieving the good morphological properties of the fabricated composite nanofibers containing MWCNT. The high stability dispersion of MWCNT leads to very smooth and soft surface of the composite electrospun nanofibers even for nanofibers with high concentrations of MWCNT (~10 wt%). The SDS/MWCNT solution presented high stable dispersion behavior without any precipitation at room temperature for one month. So, it is believed that good dispersion of MWCNT in the prepared solutions and their high stability performances even at high concentrations of MWCNT have loaded to smooth and soft surfaces in all samples.

Changes in the average diameter of the various nanofibers samples produced versus increasing the MWCNTs concentration is shown in Fig. 4. With increasing the concentration of MWCNTs in the solution from 0 to 5 wt%, the mean diameter of nanofibers decreased from 291 ± 22 nm for CNT-0 to 216 ± 20 nm for CNT-5. When MWCNTs concentration was increased to 10 wt% the average diameter increased to 224 ± 30 nm. The average nanofibers diameter for 10 wt% MWCNT sample was not significantly different from previous group ($P < 0.05$) but significantly different from all other groups. As described in the literature, decreasing polymer concentration cause reduction in the viscoelastic force versus the electrostatic force and when the viscoelastic force is lower than the electrostatic force, the average diameter of nanofibers decreased [17, 18].



a b c d

Fig. 3 – SEM photographs of electrospun composite nanofibers samples: (a) CNT-0, (b) CNT-2, (c) CNT-5, and (d) CNT-10

3.3 Electromagnetic Properties

The electromagnetic absorbing properties of the absorbers can be defined by the reflection loss [11-14]. The reflection loss (RL) is described as:

$$RL = 20\log\left|\frac{Z-1}{Z+1}\right|$$

while Z is the normalized impedance and is calculated as followed:

$$Z = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\frac{2\pi}{c}\sqrt{\mu_r\varepsilon_r}\,fd\right]$$

Where μ_r and ε_r are the complex relative permeability and permittivity, respectively, c is the velocity of electromagnetic wave in vacuum, f is the frequency and d is the thickness of the absorber [11].

The frequency dependencies of the microwave absorbing properties of the PVA/SDS/MWCNT nanofibers samples are shown in Fig. 5. For the CNT-0 sample, the maximum reflection loss has reached -6 dB at frequency of 11.5 GHz. For the CNT-2 sample, the maximum absorption peak has increased to -8 dB at the frequency of 11.5 GHz. With increasing of MWCNT concentration to 5 wt% for the CNT-5 sample, the maximum absorption peak did not changed, however the electromagnetic absorption properties have improved to 2 dB in the lower frequency range. However, for the CNT-10 sample with content of 10 wt% MWCNT, the absorption peak at the frequency of 11.5 GHz did not changed, but the reflection loss increased to -15 dB at the frequency of 8 GHz.

Compared to the result of electromagnetic absorption properties of this sample with other samples, generally, electromagnetic absorption properties have improved with increasing the content of MWCNT. As described in the literature [19, 20], by increasing the MWCNT content, the electrical conductivity is increased and this improvement in electrical properties can lead to increase in the conductive current and dielectric properties. On the other hand, the loss tangent (tanδ) is an important parameter in describing electromagnetic absorbing properties in such a way that electromagnetic absorbing properties can be improved with increasing the loss tangent value. With the increase in MWCNT

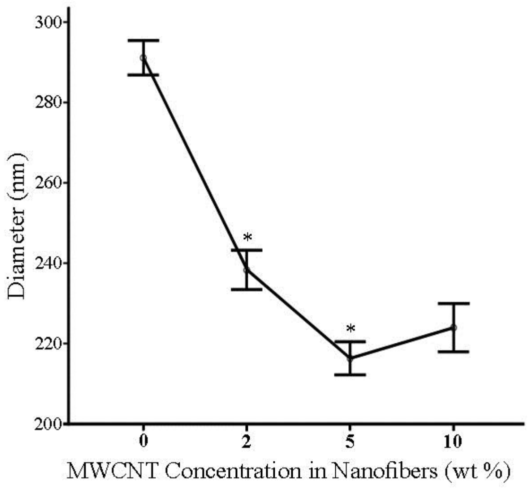


Fig. 4 – Error plot of composite nanofibers average diameter versus concentration of MWCNT. (*: $P < 0.05$, values are significantly different from the previous group compared)

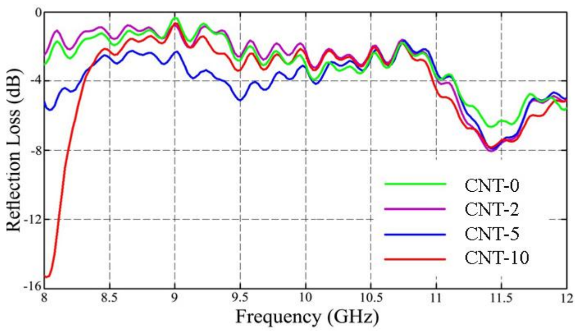


Fig. 5 – Reflection loss dependency on the frequency for the PVA/SDS/MWCNT nanofibers

content, the dielectric loss tangent becomes larger leading to increase in the absorption loss. However in this work the lowest reflectivity (-15 dB at 8 GHz) obtained by PVA/SDS/MWCNT composite nanofibers sample with corresponding thickness of 1 mm. Thus it can be concluded absorbing composite nanofibers with thin thickness, can lead to stronger absorption with lower cost.

4. CONCLUSION

In the present work, the composite solutions of PVA/SDS/MWCNT prepared under various MWCNT contents up to 10 wt% have been successfully fabricated to composite nanofibers made by electrospinning process. The MWCNT concentration varied from 0 to 10 wt%. With increasing the concentration of MWCNT in the solution from 0 to 5 wt%, the average nanofibers diameter decreased from 291 ± 22 nm to 216 ± 20 nm. When MWCNTs concentration was increased to 10 wt% the average diameter increased to 224 ± 30nm. The high stability dispersion of MWCNT leads to very smooth surface of the nanofibers even for the PVA/SDS/MWCNT composite nanofibers with the content of 10 wt% MWCNT. The maximum reflection loss have improved with increasing the content of MWCNT from -6 dB at the frequency of 11.5 GHz for the pure PVA/SDS nanofibers to -15 dB at the frequency of 8 GHz for PVA/SDS/MWCNT sample with the content of 10 wt% MWCNT.

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