Synthesis, UV-shielding and electromagnetic wave absorbing properties of polyvinylpyrrolidone-TiO₂/polyacrylonitrile-SiO₂ nanofibre nanocomposites

OMOLFAJR NAKHAEI^{1,2,*}, NASSER SHAHTAHMASSEBI^{1,2},
MAHMOOD REZAEI ROKNABADI¹ and MOHAMMAD BEHDANI¹

¹Department of Physics, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran

²Nano Research Center, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran

*Author for correspondence (fa.nakhaei1@mail.um.ac.ir, fajri.nakhaei@gmail.com)

MS received 11 November 2017; accepted 19 July 2018; published online 7 February 2019

Abstract. This paper reports electromagnetic interference (EMI) shielding effectiveness (SE) and UV-shielding performance of polyvinylpyrrolidone (PVP)-TiO₂/polyacrylonitrile (PAN)-SiO₂ nanofibre nanocomposites synthesized via the single nozzle co-electrospinning method. Herein, three samples with different average diameters were fabricated using 0.3, 0.4 and 0.5 ml h⁻¹ flow rates during the electrospinning process. Morphological characterization confirmed that a core-shell structure of nanofibre nanocomposites was formed successfully. The EMI SE of the as-prepared nanofibre nanocomposites was studied using a vector network analyser over the full X-band (8–12 GHz) frequency at room temperature. The experimental results demonstrate excellent microwave absorption properties for all samples. PVP-TiO₂/PAN-SiO₂ nanofibres with 596.67 nm average diameter show maximum total EMI (110 dB at about 9 GHz) and 98% UV-shielding performance.

Keywords. Nanocomposites; carbon nanofibres; polymers; electrospinning; electromagnetic shielding properties.

1. Introduction

In recent years, the need for advanced materials with multiple functions is increasing with the development in wireless communication devices and electronic equipment. Electromagnetic radiation has harmful effects on highly sensitive electronic equipment as well as the living environment for human beings. Now, electromagnetic shielding is an effective method resolving electromagnetic interference (EMI) and electromagnetic pollution. Therefore, great effort has been made for the development of high performance electromagnetic shielding material [1–4].

Metals have widely been used for EMI shielding applications, but recently, the use of metals for shielding applications is restricted because of poor mechanical flexibility, exceedingly high weight, propensity to corrosion and limited tuning of the shielding effectiveness (SE). Furthermore, metals could just reflect the microwaves resulting in secondary interference but conducting polymers and multifunctional nanofibre nanocomposites offer light weight, low cost and easy shaping materials for shielding applications [5–9]. Polymer nanocomposites have attracted a lot of interest in the last few decades due to cumulative demand for superior performance and technological importance in various industries including electronics, automobiles, military fields, aerospace, jet engines, energy storage devices and EMI shielding materials [10]. For high performance electromagnetic absorbing materials

excellent dielectric loss and magnetic loss are two important technical requirements. Currently, carbon materials and electrically conductive polymers containing dipole fillers are new and attractive alternative candidates for high performance EMI shielding applications [11,12].

Herein, among various nanocomposite materials, one-dimensional nanofibre nanocomposites are suitable for use as an appropriate electromagnetic shield. Nanofibres with their special structures are widely used for microwave absorption and EMI shielding applications [13–15]. In the current study, a single nozzle co-electrospinning method was utilized for synthesizing polyvinylpyrrolidone (PVP)-TiO₂/polyacrylonitrile (PAN)-SiO₂ nanofibre nanocomposites. First, a new structure of carbonic nanofibre nanocomposites containing TiO₂ and SiO₂ nanoparticles was fabricated. Then UV-shielding and EMI shielding performance of nanofibres with different average diameters are discussed.

2. Experimental

2.1 Materials

PVP (Mw = 130,000) and PAN (Mw = 150,000) polymers were purchased from Sigma Aldrich Co. and acetic acid (glacial) was procured from Merck Co. *N,N*-Dimethylformamide (DMF) was obtained from Scharlau Co. Furthermore,

TiO₂ nanoparticles with anatase phase and 10 nm average diameters were purchased from TECNAN Co.

2.2 Synthesis procedure

PAN and PVP polymers were dissolved separately in 10 ml DMF similar to our previous work [12]. 0.035 g TiO₂ (with anatase phase) and 0.6 g SiO₂ nanoparticles were dispersed in PVP and PAN solutions, respectively. Finally equal amounts of the above solutions were mixed together for the electrospinning process and used for fabricating three various samples designated as TS1, TS2 and TS3. It is notable that a simple syringe was used in the synthesis process and a core-shell structure was formed with phase-separated, mixed polymer composites. TS nanofibre nanocomposites were fabricated using an electrospinning device model (eSpinner NF CO-N/VI) from Asian Nanostructures Co. (ANSTCO, Iran) with drum linear and rotary speed of 220 mm h⁻¹ and 300 rpm, respectively. A 13 kV high voltage is applied between the metal needle and the ground drum. The distance between the needle tip and collector was kept at 13 cm and three different samples with changing the flow rate from one solution were fabricated. Figure 1 shows the synthesis process of TS core-shell nanofibres from the final polymeric solution.

Tunable diameter of nanofibres was obtained by changing electrospinning parameters including flow rates.

2.3 Designing fixture for EMI shielding measurements

After careful research and study on different methods of measuring microwave absorption and EMI shielding performance [14–17]. Copper fixture and Teflon pieces were designed and constructed to measure the *S* parameters of TS nanofibres. Also two waveguides were utilized for EMI measurements. Figure 2a and b illustrates the constructed fixture and EMI SE measurement set-up, respectively. Nanofibre nanocomposites

Figure 1. PVP–TiO₂/PAN–SiO₂ nanofibre nanocomposite production through the electrospinning approach.

(a)

(b)

Figure 2. Photographs of (a) copper fixture, Teflon pieces and (b) EMI SE measurement set-up.

were placed between two waveguides in the metal fixture during the measurement. For cancelling the effect of metal and Teflon pieces during measurement process thru-reflect-line (TRL) calibration is performed. For thru standard, a direct connection between two waveguides is performed. Reflect calibration is performed by measuring the reflection coefficient (*S*₁₁, *S*₂₂) in the state where metal plates are set at the end of each waveguide. For line standards, a short waveguide spacer (fabricated fixture) is selected. In order to investigate the effect of different average diameter of electrospun PVP–TiO₂/PAN–SiO₂ nanofibre nanocomposites on microwave absorption properties and shielding performance, three TS samples with about 500 μm thicknesses were selected. The EMI SE of TS nanofibres were measured in the frequency range of 8–12 GHz using the above mentioned method.

3. Results and discussion

3.1 Morphological characterization

Figure 3 illustrates X-ray diffraction (XRD) (Advanced Bruker model D8, using Cu Kα line $\lambda = 0.15406$ nm) pattern of TiO₂ nanoparticles and PVP–TiO₂/PAN–SiO₂ nanofibre

Figure 3. XRD pattern of (a) TiO₂ nanoparticles and (b) PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites.

nanocomposites. Figure 3a shows TiO₂ nanoparticles with anatase phase. In figure 3b all observed peaks can be categorized into two groups. The broad peak labelled with red colour, is attributed to hexagonal silicone oxide structure [18] and the rest of peaks (marked with blue colour) are attributed to tetragonal TiO₂ nanoparticles with anatase phase [19,20]. The standard XRD patterns indicate that the PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites were successfully achieved by the electrospinning method.

Scanning electron microscopy (SEM) (Leo 1450VP model) images of nanofibres that were fabricated with 0.3, 0.4 and 0.5 ml h⁻¹ flow rates are shown in figure 4a–c, respectively. SEM images show that uniform and smooth fibres without any beads with a core–shell structure were formed successfully. The core–shell structure of nanofibres usually is thicker

Figure 4. SEM images of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites that were synthesized with (a) 0.3, (b) 0.4 and (c) 0.5 ml h⁻¹ flow rates.

than 100 nm diameters [21–26]. As can be clearly seen in figure 4a–c, the average diameter of electrospun nanofibres increases with increasing flow rate. Three different flow rates

Table 1. Flow rates that were used in the synthesis process and average diameters of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites.

	TS1	TS2	TS3
Flow rate (ml h ⁻¹)	0.3	0.4	0.5
Diameters (nm)	596.67	800.71	820.14

(0.3, 0.4 and 0.5 ml h⁻¹) were utilized in the synthesis process and the average diameter of TS nanofibre nanocomposites is summarized in table 1.

For further morphological analysis, transmission electron microscopy (TEM) images were recorded. TEM (Leo 912AB model) images of the as-prepared samples are illustrated in figure 5. TEM images show a very thick core (PVP-TiO₂) with an ultrafine shell (PAN-SiO₂) formed a PVP-TiO₂/PAN-SiO₂ core-shell structure, successfully.

3.2 Optical characterization

3.2a UV-shielding activity of TS nanofibres: To study the UV-shielding ability of TS nanofibre nanocomposites, UV-Vis absorption spectra of all the samples were measured. Figure 6 shows UV-Vis transmittance spectra of TS samples. The transmittance spectra of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites illustrate all samples could shield nearly all UV and DUV radiation and the sample with 590 nm diameter shows maximum UV-shielding performance with about 2% UV transmittance. TS nanofibres can almost completely absorb UV rays <340 nm and thus can be directly applied as UV-shielding materials. Furthermore, transmittance spectra show that the main mechanism of shielding is by absorbing UV rays.

3.3 Microwave absorption and EMI shielding effectiveness

The electromagnetic SE of the as-prepared samples was studied using a two-port PNA Series Network Analyser over the X-band (8–12 GHz) frequency. All EMI shielding studies were measured by using a PNA Series Network Analyser (Agilent, E8363B model) at room temperature. SE in specific frequency range, is defined as the ratio of transmitted power (P_t) to incident power (P_i) of the electromagnetic wave and generally expressed in decibels (dB) as defined in equation (1) [8]:

$$SE_{\text{total}}(\text{dB}) = -10 \log(P_t/P_i) \quad (1)$$

The S parameters for all the samples with 500 μm average thicknesses were measured. S_{11} or (S_{22}) and S_{12} or (S_{21}) parameters, represent reflection and transmission coefficients, respectively and are obtained from the Network Analyser. Then, reflection shielding effectiveness (SE_R) and absorption shielding effectiveness (SE_A) were calculated

(a)

(b)

(c)

Figure 5. TEM images of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites that were synthesized with (a) 0.3, (b) 0.4 and (c) 0.5 ml h⁻¹ flow rates.

from S parameters using general formula as expressed in the work of Nasouri and Shoushtari [27]. The absorption and reflection SE of one-dimensional nanofibre nanocomposites as a function of frequency in the microwave range is illustrated in figure 7. As can be seen in figure 7, all samples show excellent microwave absorption properties (80–114 dB)

Figure 6. UV-Vis transmittance spectra of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites.

in comparison with other similar nanostructures [27–30]. Figure 7a–c shows the absorption and reflection SE reduces with increasing average diameter of core-shell nanofibres. TS1 sample with the 596.67 nm average diameter shows excellent absorption SE. The absorption SE of TS1 sample reaches the maximum value of 100 dB at 9 GHz and also maximum reflection loss value of –31 dB at about 10.2 GHz. All samples show nearly the same reflection loss because the reflection loss is due to the conductive components that are same for all the specimens. The conductivity of TS nanofibre nanocomposites is mainly due to the presence of PAN and PVP polymers. TS2 and TS3 with 800 and 820 nm average diameter, show maximum absorption SE value of 86 and 85 dB at 11.9 and 8.6 GHz, respectively.

Above figures show absorption is the dominant shielding mechanism. The conductivity of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites was calculated (6.28 S cm^{-1}) and compared with some similar nanocomposites, and the results are listed in table 2.

The conductivity of our samples is less than some other conductors because the dielectric nanoparticles (TiO₂ and SiO₂) play the main role in absorbing electromagnetic waves. Conductors and metals usually reflect electromagnetic waves because of their conductivity and their shielding is due to the reflection of electromagnetic waves.

The effect of average diameter of nanofibre nanocomposites on maximum absorption and reflection SE are shown in figure 8. As can be seen in figure 8, on increasing the flow rates in the electrospinning process the average diameter of the nanofibres increases. Increasing the diameters leads to a decrease in the absorption and reflection SE of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites. Figure 9 shows total SE of nanofibre nanocomposites calculated using equation (2):

$$SE_{\text{total}} (\text{dB}) = SE_A (\text{dB}) + SE_R (\text{dB}) \quad (2)$$

Figure 7. SE_A and SE_R of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites that were synthesized with (a) 0.3, (b) 0.4 and (c) 0.5 ml h⁻¹ flow rates.

Table 2. Electrical conductivity of some of nanostructures.

Authors	Composites	Conductivity (S cm^{-1})
Lyu [11]	PANI/ANF	300
Mondal [10]	Polyethylene–carbon nanofibre	10^{-5}
Verma [30]	MWCNTs	10^{-1}
This work	TS1 nanofibre	6.28

(a)

(b)

Figure 8. The effect of average diameter of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites on maximum (a) absorption and (b) reflection SE.

TS1 sample with about 590 nm average diameter reached a maximum total SE of 110 dB at about 9 GHz. The

conductivity of TS1 is 6.28 S cm^{-1} that facilitates appropriate SE. TS2 and TS3 samples show maximum total SE of 100 dB at 12 GHz and 98 dB at about 11 GHz. Results reveal all the samples show high SE but the TS1 sample with minimum diameter reaches the highest microwave absorption properties and reflection loss that are attributed to the special one-dimensional multilayer structure of the nanofibres and the effective dielectric loss due to SiO₂ and TiO₂ nanoparticles. Polymer matrices (PAN and PVP) with moderate conductivity cause nearly the same reflection SE (about -30 dB) for all samples.

Thinner TS nanofibres with a higher specific surface area show maximum SE among the as-prepared samples. This is mainly due to the fact that the solvent in the electrospinning process evaporates completely and the fibres are fully stretched [2]. So, in nanofibres with lower diameters, nanoparticles have the main role in microwave absorption electromagnetic waves.

Table 3 shows a comparison of EMI shielding performance of various nanocomposites. As can be seen in this table PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites show excellent absorption SE (110 dB) in comparison with other similar nanocomposites. Herein, the main mechanism of shielding is absorption and the shield should possess electric dipoles. Dipoles (SiO₂ and TiO₂ nanoparticles) can interact with transverse electric (E) and magnetic (H) vectors of the incident electromagnetic waves to introduce loss in the system [32]. Table 3 illustrates nanofibre nanocomposites show better SE than the other nanocomposites because of their fibrous structure and multiple scattering between nanofibres. Also, the fibrous structure could increase electromagnetic transmission path and improve reflection loss.

Considering above results, the new structure of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites indicates excellent potential for microwave absorption and high performance EMI shielding applications because of the combination of two kinds of materials (nanoparticles for absorption and conducting polymers for reflection microwaves). Also the fibrous structure of nanofibres causes multiple scattering and damping waves. Nanofibre nanocomposites with excellent electromagnetic wave absorption performance might find extensive applications in the military, electronics, governance of electromagnetic pollution, stealth (radar absorbing materials) and textile industry.

Figure 9. Total SE of PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites that were synthesized with (a) 0.3, (b) 0.4 and (c) 0.5 ml h⁻¹ flow rates.

Table 3. A comparison of EMI shielding performance of various nanocomposites.

Composites	SE _R (dB)	SE _A (dB)
TS1 nanofibres (this work)	30	108
Fe ₃ O ₄ /carbon nanofibre [8]	11	31
MWCNFs/PPC [30]	32.5	5
Fe ₃ O ₄ @SiO ₂ @ZnO [28]	—	25
Fe ₃ O ₄ @SiO ₂ [31]	—	23
Flexible graphite [33]	—	129

4. Conclusions

Considering the importance of electromagnetic shielding, novel PVP-TiO₂/PAN-SiO₂ nanofibre nanocomposites were synthesized through a simple single nozzle co-electrospinning process. Morphological characterization shows core-shell structures of nanofibre nanocomposites were formed successfully. Shielding studies exhibit excellent microwave absorption properties for TS nanofibre nanocomposites which makes them suitable for EMI shielding applications. A high level of shielding efficiency is acquired for composite nanofibres, compared with pristine carbon nanofibre. In addition, PAN and PVP polymers are introduced as appropriate polymers for synthesis of nanofibre nanocomposites with high shielding efficiency. For nearly all three carbon materials, shielding is dominated by absorption. Among various samples, TS1 with 569.67 nm average diameter indicates about 110 dB total SE at 9 GHz frequency and also 98% UV-prevention.

Acknowledgements

The authors truly appreciate Dr Mehdi Forouzanfar, Dr Javad Baseri and Dr Mojtaba Joodaki for their help in EMI shielding measurements performed at RF research Lab of the Department of Electrical Engineering at Ferdowsi University of Mashhad.

References

- [1] Jianzhong W 2017 *Rare Met. Mater. Eng.* **46** 73
- [2] Kim H, Kim B and Kim I 2012 *Mater. Chem. Phys.* **135** 1024
- [3] Zhou H, Zhuang J, Yan Q and Liu Q 2012 *Mater. Lett.* **85** 117
- [4] Thomassin J M, Jérôme C, Pardoën T, Bailly C and Huynen I 2013 *Mater. Sci. Eng. R* **74** 211
- [5] Kim D H, Kim Y and Kim J W 2016 *Mater. Des.* **89** 703
- [6] Chung D D L 2000 *J. Mater. Eng. Perform.* **9** 350
- [7] Saini P and Choudhary V 2013 *J. Nanopart. Res.* **15** 1415
- [8] Bayat M, Yang H, Ko F and Michelson D 2014 *Polymer* **55** 936

- [9] Kong L, Yin X, Zhang Y *et al* 2013 *J. Phys. Chem. C* **117** 19701
- [10] Mondal S, Nayak L, Rahaman M *et al* 2016 *Composites, Part B* **109** 155
- [11] Lyu J, Zhao X, Hou X, Zhang Y, Li T and Yan Y 2017 *Compos. Sci. Technol.* **149** 159
- [12] Nakhaei O, Shahtahmassebi N, Rezaee Roknabadi M and Behdani M 2016 *Appl. Phys. A* **122** 537
- [13] Wang L, Huang Y, Sun X *et al* 2014 *Nanoscale* **63** 157
- [14] Esfahani A, Katbab A, Dehkhoda P *et al* 2012 *Compos. Sci. Technol.* **72** 382
- [15] Cao M, Yang J, Song W *et al* 2012 *ACS Appl. Mater. Interfaces* **4** 6949
- [16] Wen B, Cao M, Hou Z *et al* 2013 *Carbon N Y* **65** 124
- [17] Shyr W and Shie J W 2012 *J. Magn. Magn. Mater.* **324** 4127
- [18] Zhidong H, Limin D, Ze W and Xianyou Z 2006 *J. Rare Earths* **24** 75
- [19] Bayal N and Jeevanandam P 2014 *Ceram. Int.* **40** 15463
- [20] Cheng Y, Huang W, Zhang Y *et al* 2010 *CrystEngComm* **12** 2256
- [21] Wang L, Huang R, Zhou B, Zhang Y and Dong Y 2016 *Mater. Lett.* **176** 38
- [22] Ara M, Naderi H, Mobasheri A, Rajabi M, Malekfar R and Koushki E 2013 *Phys. E Low Dimens. Syst. Nanostruct.* **48** 124
- [23] Yarin A L 2011 *Polym. Adv. Technol.* **22** 310
- [24] Konno M, Kishi Y, Tanaka M and Kawakami H 2014 *Polym. J.* **46** 792
- [25] Zhang J F, Yang D Z, Xu F, Zhang Z P, Yin R X and Nie J 2009 *Macromolecules* **42** 5278
- [26] Kayaci F, Vempati S, Ozgit Akgun C, Donmez I, Biyikli N and Uyar T 2015 *Appl. Catal. B Environ.* **176** 646
- [27] Nasouri K and Shoushtari A 2017 *Compos. Sci. Technol.* **145** 46
- [28] Wang Y, Sun D, Liu G and Jiang W 2015 *Adv. Powder Technol.* **26** 1537
- [29] Liu P, Qing H, Hou H, Wang Y and Zhang Y 2016 *Mater. Des.* **92** 823
- [30] Verma P, Saini P and Choudhary V 2015 *JMADE* **88** 269
- [31] Zheng J, Yu Z, Ji G, Lin X, Lv H and Du Y 2014 *J. Alloys Compd.* **602** 8
- [32] Hong C, Yang K, Oh S, Ahn J, Cho B and Nah C 2008 *Polym. Int.* **57** 1357
- [33] Hong X and Chung D D L 2017 *Carbon* **111** 529