FLEXIBLE, ELECTROSPUN POLYACRYLONITRILE BASED CARBON NANOFIBER COMPOSITES FOR ELECTROMAGNETIC INTERFERENCE SHIELDING

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by

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ABSTRACT

The rapid advancement of wireless communication technology, 5-G technology, and the miniaturisation of electronic equipment, and complexity of inbuilt circuitry cause electromagnetic interference (EMI) or EM pollution. EMI can affect human health, disturb the regular functioning of electronic equipment and it can also completely damage the electronic equipment. The demand for EMI shielding materials is rapidly increasing as the EM pollution and EMI become more complex. As a result, high-performance EMI shielding materials are required to protect human health and protect the electronic equipment employed in domestic, civil, or military applications. Metals and metal alloys were previously used to protect against EMI. However, metals are restricted in applications in EMI shielding due to their heavy weight, low corrosion resistance, and the emerging demands for flexible and miniaturised equipment. Thus, flexible, lightweight, water proof, and high-performance EMI shielding materials are on great demand.

Polymer composites have emerged as a superior option for EMI shielding materials due to their lightweight nature, corrosion resistance, and ease of manufacture. Polymer composites are promising EMI shielding materials because they can be tailored to meet commercial requirements while eliminating the majority of the disadvantages associated with conventional materials. But mostly, polymers are insulators and hence difficult to acquire EMI shielding properties. Hence, polymer composites which are made conductive by the addition of fillers are being explored for EMI shielding applications. However, composites require high loading of fillers which may cause poor dispersibility of fillers into the polymer matrix, poor interfacial polarization, and poor 3-D interconnected conductive network and may result in inferior EMI shielding properties than expected.

This thesis reports preparation of flexible and hydrophobic EMI shielding materials with synergistic effects of conductive CNF, fillers, and PDMS as polymer matrix. Polyacrylonitrile nanofiber is used as the precursor for carbon nanofibers (CNFs). Electrospinning which is a simple and versatile method for preparation of nanofibers is used in this study to produce 1-D nanostructure fibers with a large surface area, high porosity, and good interconnectivity, which could serve as an effective platform for the absorption and multiple internal reflection of EM waves inside shielding materials. Heat treatment of the electrospun polyacrylonitrile (PAN) nanofiber yielded carbon nanofibers (CNFs). The

carbonization of electrospun PAN fiber formed strong 3-D interconnected electrical conductive with good EMI shielding properties. Two approaches were adopted to enhance the EMI shielding property of CNF. In the first strategy, CNF was subjected to simple post treatment like coating with a conducting polymer while in the second strategy, CNF incorporated with various fillers were explored.

In the first approach, (chapter 4) CNF was coated with poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) with the assistance of polyvinylpyrrolidone (PVP). The material exhibited high EMI SE of 44 dB in the frequency range of 8-26.5 GHz with a thickness of 0.06 mm due to the synergetic effect of CNF matrix, PEDOT: PSS, and PVP. It also exhibited a SSE_t of 5678 dB cm^2 g^{-1} with low loading of PEDOT:PSS-PVP.

The second approach is to incorporate fillers into the CNF and distribute the fillers thoroughly and uniformly on individual fibres to improve EMI shielding. The incorporation of fillers into CNF first extends the 3-D interconnected electrical conductive network, then improves the electrical conductivity of CNF, it also forms hetero-interfaces that enhance interfacial polarization, and finally forms strong dipole polarization in the presence of EM waves. All of these parameters improved the EMI shielding properties of the fillers-incorporated CNF.

Chapter 5 concerns Tellurium nanoparticles (Te NPs) incorporated CNF (**Te-CNF**) for EMI shielding. Tellurium is a metalloid with a narrow band gap which belongs to chalcogen family and incorporation of Te-NPs in CNF may alter the electronic properties to improve 3-D conductive network. Te NPs also can introduce polarization sites and hetero interfaces in CNF. The Te-CNF exhibited an average EMI SE and SSE_t of 37.1 dB and 9280 dB cm^2 g^{-1} respectively, at a thickness of 0.08 mm and a density of 0.499 g cm^{-1} and possessed a high electrical conductivity of 0.68 S cm^{-1}.

Chapter 6 presents work on Nb_2O_5 NPs incorporated CNF (**Nb_2O_5-CNF**) for EMI shielding applications in wide frequency range (8.2 GHz – 26.5 GHz). Nb_2O_5 is a semiconductor, and their electrical conductivity can be enhanced by addition of carbonaceous materials. Uniform distribution of Nb_2O_5 NPs in 1-D N-doped CNF may increase dielectric loss and sites for polarization loss, interfacial polarization, and multiple internal reflections. The EMI SE of the resulting Nb_2O_5-CNF was improved from 57 dB to 67 dB as the loading of Nb_2O_5 NPs increased from 33 wt.% to 50 wt.%. The thickness of the material was 0.08 mm and more than 80 percent of SE_T was contributed by SE_A. Nb_2O_5-CNF exhibited high SSE_t value of 3295 dB cm^2 g^{-1} with 33 wt% loading of Nb_2O_5 NPs in CNFs. The excellent EMI shielding performance of Nb_2O_5-CNF can be attributed to their high electrical conductivity due to the formation of conductive paths with CNF and Nb_2O_5, as well as interfacial and dipole polarization due to the presence of Nb_2O_5.

Chapter 7 concerns with preparation of perovskite metal oxide ($La_{0.85}Sr_{0.15}CoO_3$) (LSCO) NPs by sol-gel method followed by calcination at 900 ºC and incorporation of the prepared LSCO NPs into CNFs through electrospinning, followed by heat treatment. As the loading of LSCO NPs in CNFs increases from 10 wt% to 25 wt%, the EMI SE increases from 34 dB to 45 dB with a thickness of 0.08 mm. LSCO-CNFs exhibited high SSE_t value of 7672 dB cm^2 g^{-1} with 25 wt% loading of LSCO NPs in CNFs. The LSCO-CNFs exhibited high EMI shielding properties because of their high electrical conductivity leading to the formation of conductive paths with CNFs, interfacial polarization as well as dipole polarization due to the multicomponent heterogeneous interfaces and the dielectric loss due to the defects produced by Sr doping in $LaCoO_3$.

The effect of alignment of CNF and alignment of $BaTiO_3$ NPs CNF on EMI shielding properties are presented in chapter 8. The alignment of $BaTiO_3$ NPs enhanced their piezoelectric, ferroelectric, and dielectric properties. The aligned $BaTiO_3$-CNF exhibited a higher EMI SE of 81 dB compared to the non-aligned $BaTiO_3$-CNF (61 dB). The high EMI SE value is due to high dielectric properties of $BaTiO_3$ NPs and formation of 3-D electrically conductive network of CNF. The alignment of CNF enhanced the electrical conductivity along the fiber axis. The synergistic effect of $BaTiO_3$ NPs and CNF was improved the EMI shielding performance.

Chapter 9 concerns with carbonic filler namely carbon black super P (CBSP) incorporated into CNF (**CBSP@CNF**). Herein, CBSP covered the surface of the individual fibers and also was incorporated inside the fibers. Due to this, CBSP@CNF possessed high electrical conductivity of 2.5 S cm^{-1} and exhibited excellent EMI shielding property. With a thickness of 0.06 mm and a density of 0.63 g cm^{-3}, CBSP@CNFs showed high EMI SE over a wide frequency range (8.2-26.5 GHz). The highest and average values of EMI SE in the range were 55 dB and 50 dB respectively. The CBSP@CNFs with 9 wt% and 16.6 wt% loading of CBSP exhibited 24,837 and 14741 dB cm^2 g^{-1} of SSE_t, respectively, which is remarkably higher than the most reported EMI shielding materials.

CNF is fragile and brittle in nature. So, in this study, polydimethylsiloxane (PDMS), which is a common flexible substrate has been used to improve the flexibility of CNF. Ease of handling of CNF as well as fillers incorporated CNF could be improved by making flexible PDMS composites of CNF. The PDMS composites of the CNFs discussed above exhibited similar EMI shielding behavior in the frequency range 8.2 – 26.5 GHz.

Carbon nanofibers (CNFs) coated with conducting polymers and incorporated with suitable fillers and their PDMS composites can open up new possibilities towards large scale production of lightweight, flexible, water proof, and easy-to-integrate materials to shield workspaces, surroundings, and complex electronic circuits against unwanted EM radiations.