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# Enhanced electromagnetic shielding behavior of multi-walled carbon nanotube entrenched poly (3,4-ethylenedioxythiophene) nanocomposites



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#### ARTICLE INFO

## Article history: Received 1 February 2015 Received in revised form 6 April 2015 Accepted 7 April 2015 Available online 16 April 2015

#### Kevwords:

- A. Carbon nanotubes
- A. Polymer-matrix composites (PMCs)
- D. Transmission electron microscopy (TEM)
- D. Raman spectroscopy
- EMI shielding

#### ABSTRACT

Exceptionally high electromagnetic shielding behavior shown by composites of poly (3,4-ethylene-dioxythiophene)/multi-walled carbon nanotube (PCNT) which showed maximum shielding attenuation of 58 dB in the Ku-band. The electron micrographs confirm the wrapping of poly (3,4-ethylenedioxthiophene) (PEDOT) over multiwalled carbon nanotubes (MWCNTs) resulting in strong interfacial, electronic and space charge polarizations. The EMI shielding results showed that shielding by PCNT composites are mainly due to shielding effectiveness by absorption rather than shielding attenuation by reflection. Complex permittivity and permeability of composites have been calculated using scattering parameters ( $S_{11}$  and  $S_{21}$ ) based on theoretical calculations given in the Nicolson–Ross–Weir method. The composites were further characterized by Raman spectroscopy, TGA, XRD, and FTIR.

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#### 1. Introduction

In this era of modern technologies, communications to remote areas usually involve electrical and electromagnetic technologies such as telephone, radio, microwave transmission, fiber optics and communication satellites. The electromagnetic fields produced by them progressively interfere with each other and is called electromagnetic interference (EMI) [1]. This interference results in the poor performance of electronic and electrical devices. The extensive use of these technologies has put this electromagnetic pollution to a level that was never attained before [2]. To diminish the effect of this problem an active material is required which can effectively block or shield electromagnetic waves. The EMI shielding can be achieved by attenuating the electromagnetic waves transmitted from an electrical circuit either by reflection of the wave or by absorption and dissipation of the radiation power inside the material [3]. Among the various materials used for EMI shielding, polymers coated by electroless method are commonly used for this purpose [4-7]. Further, extrinsically conducting polymer composites containing stainless steel fibers, carbon fibers and nickel coated carbon fibers as fillers are also used as EMI shielding enclosures [8-11]. To achieve shielding effectiveness (SE) for commercial applications, high loading of these fillers are required. However, this results in poor mechanical properties due to poor filler–matrix interactions [12].

Intrinsically conducting polymers (ICPs) possessing  $\pi$ -conjugated system has attracted the attention of material scientists because of their widespread applications like electrode material in rechargeable polymer batteries [13], antistatic coatings [14], electro chromic devices [15], organic light emitting diodes [16], EMI shielding [17], organic solar cells [18], and anti corrosive coatings [19]. Among various ICPs, PEDOT, a derivative of polythiophene has gained much attention because of its excellent environmental stability [20], optical transparency in its conducting form [21], low redox potential [22], good thermal stability [23], ease to synthesize [24] and ability to be doped either by n-type and p-type with moderately high conductivity [25]. PEDOT is considered as a promising material for optoelectronic organic devices [26] as it can be applied on flexible substrates and enables cost effective mass production of devices by roll to roll technique. Incorporation of electrically an electrically conducting filler to the polymer matrix could effectively increase the electrical conductivity of polymer [27-30]. Carbon nano tubes (CNTs) are known for their exceptional mechanical, electrical and thermal properties. These properties of CNTs have made them a potential candidate for high-tech applications. Apart from this, the high surface area, high aspect ratio, good conductivity and superior mechanical properties of CNTs made them promising filler for high-performance EMI shielding materials at low level of loading [31-35].

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Ohlan et al. studied the microwave absorption properties of PEDOT-barium ferrite nano composites with core shell morphology [36]. They showed absorption dominant rather than reflection. They observed that ferrite particles in the polymer matrix induce magnetic losses due to magnetic hysteresis and eddy current loss. Al-Saleh and Sundararaj demonstrated the EMI shielding mechanism of MWCNT/polypropylene composites determined experimentally and theoretically [3]. Wojkiewicz et al. investigated the EMI SE of polyaniline-polyurethane composites with different mass fractions of polyaniline in the X and Ku-band [37]. They found percolation threshold of 0.2% with a conductivity of 10<sup>4</sup> S/m of pani-PU composites. Moreover, EMI SE increases with pani loading in PU. Gupta and Choudhary fabricated light weight poly(trimethylene terephthalate)/MWCNT composites with varying loading of MWCNTs [38]. The EMI SE found was 36-42 dB at 10% loading of MWCNTs.

Since there is a lot of interest been made on the development of microwave absorbing materials which can find applications in military equipment, microwave darkroom, stealth technology of aircraft, radar cross reduction and antenna pattern shaping. The present study was carried out in Ku-band which lies in microwave region. An effort has been made to explore the effect of addition of MWCNTs in PEDOT matrix to shield the electromagnetic waves. PCNT composites with varying loading of MWCNTs (5.0, 10 and 15 wt%) were synthesized by in-situ emulsion polymerization. According to electromagnetic compatibility (EMC) regulations, a minimum of 30 dB of shielding effectiveness is required corresponding to a shielding of 99.9% of the incident radiation [39]. PEDOT polymer is extensively used for the solar cell and anti-static applications. Herein we report its EMI shielding potential in the Ku band frequency. To the best our knowledge, no studies have been done so far on the fabrication of PEDOT coated MWCNT composites for EMI shielding applications.

#### 2. Experimental

#### 2.1. Materials used

The monomer 3,4-ethylenedioxythiophene (EDOT) was purchased from TCI chemicals (India). Ammonium peroxydisulphate

(APS) was procured from Merck (India). Potassium bromide (used in FTIR measurements) and dodecyl benzene sulfonic acid (DBSA) was purchased from Acros organics (Belgium). Isopropyl alcohol was obtained from Qualigen (India). MWCNTs were synthesized in-house by chemical vapor deposition method (CVD) technique using toluene as carbon source and ferrocene as catalyst precursor [40]. The purity of as produced MWCNTs is >90%, whereas, the diameter ranges between 20 and 50 nm and length between 50 and 100 µm.

#### 2.2. Synthesis of PEDOT

Synthesis of PEDOT doped with DBSA was carried out using emulsion polymerization [41,42]. The DBSA functions both as a surfactant and dopant in the polymerization. In this method, 0.1 M of EDOT and 0.3 M of DBSA was homogenized in aqueous medium at room temperature for 60 min to form EDOT–DBSA micelles. The polymerization was initiated by the dropwise addition of oxidant, 0.1 M aqueous APS solution, at  $-2\,^{\circ}\text{C}$  with constant stirring for 8 h. A bluish green suspension containing precipitates of PEDOT was obtained thereafter. The resulting suspension was demulsified using isopropyl alcohol due to the formation of stable micro-emulsions of PEDOT, water and DBSA and then filtered in buchner funnel. The filtered precipitate so obtained was washed with distilled water and then dried at 60 °C in vacuum oven.

#### 2.3. Synthesis of MWCNTs incorporated PEDOT composites

The in-situ emulsion polymerization of EDOT was carried out in the presence of MWCNTs in aqueous medium as shown in Fig. 1. In a typical synthesis, 0.3 M DBSA (surfactant) was homogenized in water for an hour to form an aqueous emulsion. To this aqueous emulsion, calculated amount of MWCNTs was added (5.0, 10 and 15 wt%) and then homogenized by using the ART-Miccra D-8 (No.-10956) homogenizer at 12000 rpm for 2 h. The wt% of filler was taken with respect to the monomer (EDOT) weight. To this, 0.1 M of EDOT was added and stirred for 8 h to form an emulsion. The oxidant APS (0.1 M) was added drop-wise with vigorous stirring while keeping the temperature of the reactor at  $-2\,^{\circ}\text{C}$ . The bluish/black precipitate of polymer composite so obtained was

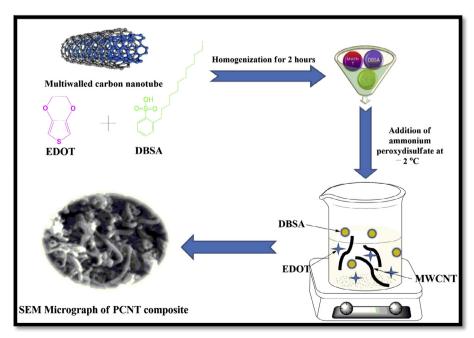


Fig. 1. In-situ synthesis of PCNT composite with SEM micrographs shows MWCNTs embedded PCNT composite.

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