RESEARCH PAPER | Chemistry | Volume : 5 | Issue : 5 | May 2015 | ISSN - 2249-555X

Conformally Polyaniline Coated Multiwalled Carbon Nanotubes: Synthesis and Characterization

KEYWORDS

Sarika Mishra
1Department of Chemistry, Mahatma Gandhi ChitrakootGramoday University, Satna MP

Anoop Kumar S
2Department of Chemistry, SreeVidyadhi Raja N S S College, Theerthapadapuram.P.OVazhoor, Kottayam District, Kerala

Avanish Pratap Singh
3Department of Physics, Bhagini Nividita College, Najafgarh, New Delhi

A. C. Nigam
1Department of Chemistry, Mahatma Gandhi ChitrakootGramoday University, Satna MP

ABSTRACT *Conducting polymer composites are globally explored owing to their potential use in various applications such as organic light emitting diode, solar cells, corrosion protection and electromagnetic interference shielding. In this series, herein, we developed a strategy for conformal coating of polyaniline on multiwalled carbon nanotubes (MWCNTs) for their potential use in strategic areas. β–Naphthalenesulphonic acid (β–NSA) was used as surfactant and dopant which offers the conformal coating on MWCNTs. Polyaniline (PANI)– MWCNTs composites have been prepared by chemical oxidative polymerization route whose conductivity lies in the range 17.21–81.7 S/cm. The TEM analysis of composites reveals the presence of thick and uniform coating of PANI over surface of MWCNT. The SEM of PCNT25 also revealed the nonporous nature of coatings, which can be used for selective incorporation of other nanoparticles. Morphology of PC indicates the incorporation of MWCNT in PANI matrix. Such engineered conformally polymer coated MWCNTs could be a promising candidate for next generation building block material in various applications.*

A. INTRODUCTION

During the last two decades, lots of research has been devoted on the designing of polymeric composites for their potential use in various applications in many devices like optoelectronic devices[1], electronic charge dissipation[2] super capacitors & superconductors[3, 4], OLEDS[5], plastic solar cells[6]electromagnetic interference shielding[7-9]. Conducting polymers, such as polypyrrole, polyaniline, etc., consisted of conjugated electronic structures have received considerable attention in the field of material science due to a lot of promising technological applications[10-14]. Coatings on the surface of metals by polymeric materials have been widely used in industries for the protection of these materials against corrosion [15, 16].. The polymeric materials owing to their light weight, low cost, easy shaping, tunable conductivity can find applications in high tech devices[17]. Polymer composites with exotic corbon such as carbon particles, carbon fibers (CF), graphene, graphite , carbon nanotube (CNTs [18, 19]), carbon fiber [20]etc have been widely used for EMI shielding [12, 21, 22].Therefore, the lightweight polymer composites have gained much popularity and search of suitable lightweight materials with all functionality is the main focus areas among global research groups[23-26]. ICPs due their extended π-conjugated system have conductivity in semiconductor regime. Applications of ICPs and their composites (or blends) owing to the higher electrical conductivity of these polymers in doped states have been extensively studied by many researchers [27-29]. These materials unite high conductivity, low density & thereby light weight, corrosion resistance with exclusive shielding mechanism of absorption differing from the reflection one for metals and carbons[30] which is ideal for military applications.

Amongst all ICPs polyaniline (PANI) is recognized as an intractable polymer due to its environment stability and unique protonic conduction mechanism[31, 32]. Many research groups have presented the improved processability of PANI using different surfactant/dopant and mechanical properties by modifying the morphology (spherical/tubular) of the PANI. The protonation of PANI with organic sulphonic acids and macro molecules have been reported for the preparation of electrically conducting polymers with improved processability[33-35].

It is well established that MWCNTs independently as well as in composite form are potentially used in hi-tech applications [18, 36, 37]. Because of their unique structural properties, high aspect ratio and good mechanical strength carbon nanotubes have been investigated for many potential applications [38-40]. Particularly, their fascinating electrical and mechanical properties offer a new arena for the development of advanced engineering materials [41, 42]. The small diameter, high aspect ratio (with values typically higher than 1000:1 and reaching as high as 2,500,000:1) , high conductivity, and mechanical strength of CNT, make them an excellent option for creating conductive composites for high-performance composites at low filing [19, 23]. The mechanical properties of CNT have drawn intense interest in their potential for use as reinforcements in composite materials. As a result of these properties, CNT reinforcements are expected to produce significantly stronger and tougher composites than traditional reinforcing materials.

In this study, we attempt to design the uniform conformal coating of PANI on MWCNT surface by chemical synthesis. The obtained results of composite are focused on the conductivity, surface morphology and gross structural/microstructural analysis of MWCNT/PANI two phase systems. Moreover, the thermal stability of the composite system has been explored through thermogravimetric analysis. However, to the best of our knowledge, this type of con-

Volume : 5 | Issue : 5 | May 2015 | ISSN - 2249-555X

formal uniform polymer coating on MWCNT has not been thoroughly explored yet.

B. EXPERIMENTAL

The conformally PANI coated MWCNT (PCs) have been prepared by in-situ emulsion polymerization using β-NSA as anionic surfactant molecule which also acts as a dopant. Due to its amphiphilic and surfactant nature, β-NSA molecule (with hydrophilic SO_3H head and hydrophobic tail) easily forms micelles in aqueous solution. First MWCNTs were dispersed in β-NSA aqueous solution before polymerization. As a result, micelles containing MWCNT particles form in the reaction, these micelles have core-shell structure as shown in Figure 1 b. 0.1 M aniline monomer was added to above emulsion and homogenized for another 1-h. During this, aniline reacts with β-NSA to form aniline/β-NSA micelles which act as a soft template. Afterward the homogenized mixture was transferred to reactor, pre-cooled to 0°C. Polymerization was initiated by drop wise addition of ammonium peroxydisulfate (APS) and allowed continuous stirring at 0°C under. During this process the formed anilinium cations might be absorbed on the plane of these core-shell micelles. Furthermore, free aniline present in the solution might diffuse into the micelles to form aniline-filled micelles. Therefore, these micelles (with or without MWCNTs) act as soft templates for the formation of the tube like structure. The attached -SO_3H groups impart additional dopant property to β-NSA. As the polymerization advances, the micelles containing RF particles would become bigger spheres and take the shape of tubes/rods by elongation. Therefore, subsequent oxidation of aniline results radical cations which combine with another unit to form neutral dimer. Further oxidation of Dimer leads to the formation of a trimer, tetramer and finally the formation of polymer composites. Figure 1 discussed self-assembly process resulting in tube like structure of PANI and PCs composite [33, 34] and suggests that MWCNT particles should be situated inside the polymer tubes. Schematic representation of incorporation of MWCNT into PANI matrix is given in this scheme which suggests that MWCNT embedded in PANI tubes leads to the formation of PANI composites which has better electrical and magnetic properties. The presence of rGO containing iron oxide nano particles in polymer matrix has been confirmed by the XRD of the composites. The presence of MWCNT matrix has been confirmed by TEM.

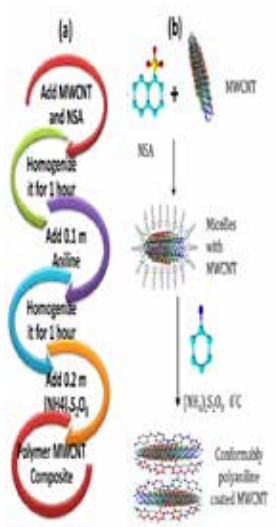


Figure 1. (a) Flow chart of the synthesis procedure of PANI composite and **(b)** Schematic representation of the PANI/MWCNT (PCs) composite

RESULT AND DISCUSSION

XRD Analysis

Figure 2 and 3 show the XRD patterns of pure MWCNT, PANI and PANI–MWCNT nanocomposites. The pure MWCNT (PC100) shows a sharp peak centered on 2value of 26° which corresponds to the (002) planes of MWCNT. The peaks around 43° are due to the (110) and (100) graphitic planes plus small amount of catalyst particle encapsulated inside the walls of the MWCNTs[43]. The characteristic peaks of the doped PANI (PCNT0) are observed around 2values of 15, 20, 25, 30° corresponding to (0 1 1), (0 2 0), (2 0 0) and (0 2 2) reflections of emeraldine salt form. The composites show the characteristic peaks of both PANI and MWCNT without any additional bands indicating absence of covalent interactions between the phases[7]. As the MWCNT content increases, the relative intensity of characteristic bands of PANI decreases whereas bands of MWCNT become more prominent. The slight shifting in the peak positions may be ascribed to charge transfer interactions between PANI and MWCNTs leading to variations in chain packing and configurations.

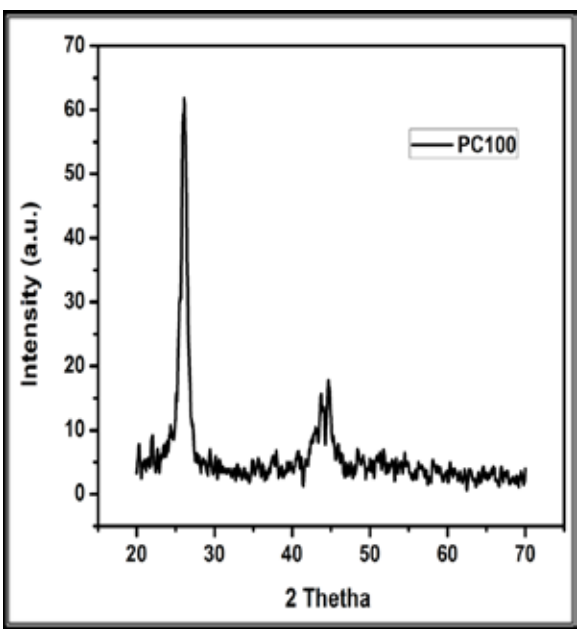
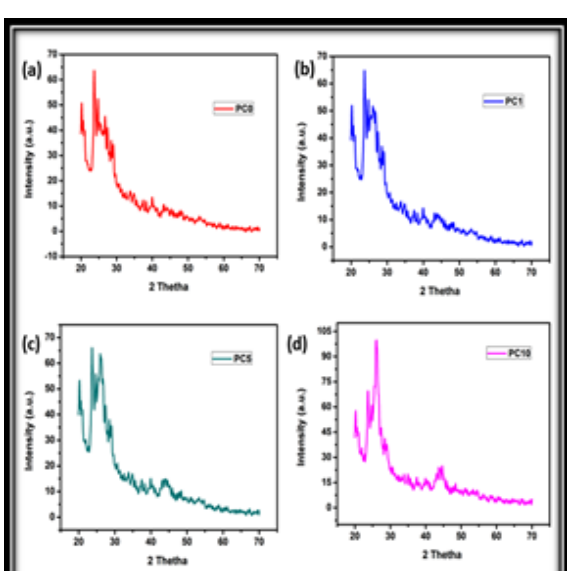


Figure 2.XRD pattern of pure MWCNT (PC100).



Volume : 5 | Issue : 5 | May 2015 | ISSN - 2249-555X

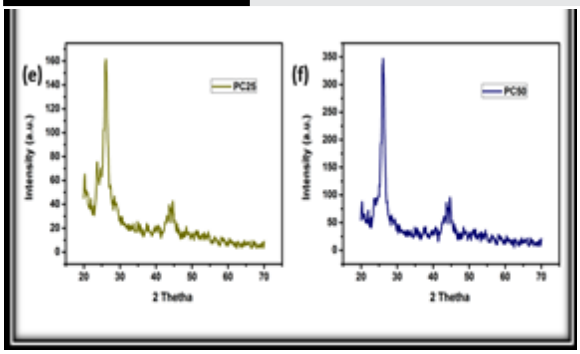


Figure 3. XRD pattern of PANI MWCNT composite containg different wt% of MWCNT in PANI matrix.

THERMOGRAVIMETRIC ANALYSIS

Figure 4 shows the thermo-gravimetric curves (TG) of pure MWCNT, PANI and their composites. The materials were heated from 25 to 900˚C under a constant heating rate of 10˚C/min and in the inert atmosphere of nitrogen gas (60 ml/min). The MWCNT has excellent thermal stability up to 900˚C and weight loss was only 1.5 %. The TGA curve of PCs indicated, first weight loss at 110˚C may be attributed to the loss of water and other volatiles species. The weight loss in the second step at about 280˚C involves the loss of phosphateions as well as onset of degradation of polyaniline backbone. The increasing MWCNT content slightly affects the decomposition temperature (DT) which increases from 280˚C (PANI) to 295˚C (PC). The third weight loss step between 300 to 800˚C can be ascribed to the complete degradation of dopant as well as polymeric backbone. The composites show little weight loss between the 800-900˚C and the residue remaining in this region gives an approximate estimate of filler content. Therefore, the final weight of MWCNT incorporated in polymer was found to 21 %. The results indicate that actually incorporated MWCNT fraction is less than the ratio of aniline: MWCNT taken in the initial reaction mass. The TGA data clarify that these composites are thermally stability up to 295˚C, which envisages them as a good candidate for melt blending with conventional thermoplastics like polyethylene, polypropylene, polystyrene etc.

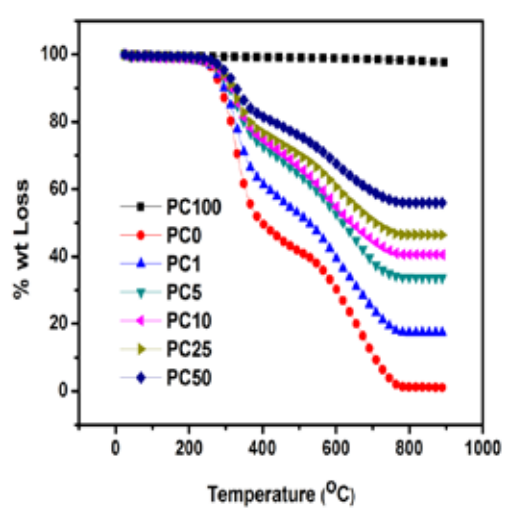


Figure 4. Thermal gravimetric analysis of PANI and its composite PC0, PC5, PC10, PC25 and PC50 having 0, 5, 10, 25 and 50 wt% MWCNT respectively.

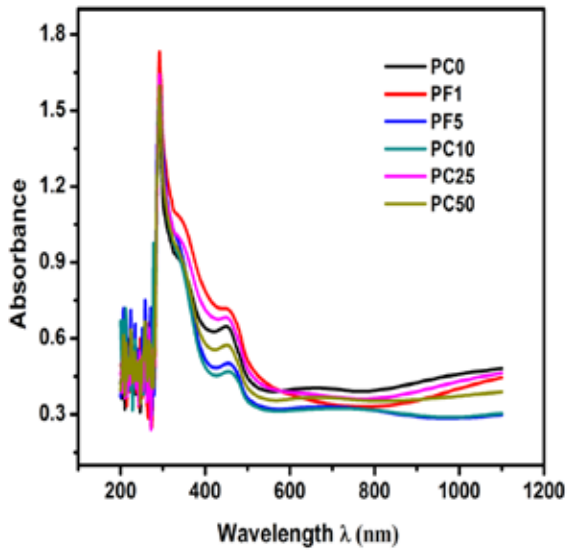


Figure 5.UV–Visible spectra PANI and its composite PC0, PC5, PC10, PC25 and PC50 having 0, 5, 10, 25 and 50 wt% MWCNT respectively.

ELECTRICAL CONDUCTIVITY

The room temperature current–voltage (I–V) characteristics were measured and resistance values were obtained from the slope of these plots. The electrical conductivities of the pellets can be calculated by considering the sample dimensions as:

$$R=\rho L/A \qquad (1)$$

where "L" is the length of the pellet, "R" is resistance and "A" is crosssectional area of the pellets normal to direction of current flow.

The conductivity (Figure 6) was found to exhibit continuous increase with the increase in the MWCNT content. The high conductivities of these composites are due to micrometer long MWCNTs as core and PANI coating as shell (see Fig. 8 SEM images).Measurement of electrical conductivity of terphenyl and quaterphenyl films revealed that organic nanocrystallites play interface nano trapping levels effectively interacting with phonon subsystems. These states may be principal for the achievement of conductivities varying in the large range of parameters. Introduction of MWCNT to PANI enhances the electrical properties by facilitating the charge transfer processes between the two components. Due to their highly conducting nature as well as high aspect ratio, the nanotubes can act as interconnecting bridge between the various conducting grains of the polyaniline, which are coated over individual MWCNTs. This increases the coherence or coupling between the chains and leads to enhancement of interchain transport. Further, the PANI–NSA coating is likely to facilitate the intertube charge transport by reducing the interfacial contact and tunneling resistances. This may be explained on the basis of cushioning effect of softer polyaniline coating over tubes which deforms easily during the pellet formation improving the surface contacts of coated tubes. This synergistic effect of two complementing phases (i.e. PANI and MWCNT) leads to conductivity of 81.7 Scm^{-1} in case of PCNT50, which is even better than bulk conductivity of either phase alone, i.e. control MWCNT (PC100, 102.4Scm^{-1}) or pure PANI (PC0, 17.21 S cm^{-1}). The lower

Volume : 5 | Issue : 5 | May 2015 | ISSN - 2249-555X

conductivity of bulk MWCNT pellet may be due to the fact that pressed pellets of uncoated MWCNTs contain highly entangled tubes (SEM Fig. 9) which even after pelletization represents poorly packed system. Therefore, the reduced intertubular charge transport was responsible for observed low bulk conductivities. The uniform coating of PANI reduces the disorder/voids in composites and improves intertubular charge transport leading to enhanced electrical properties.

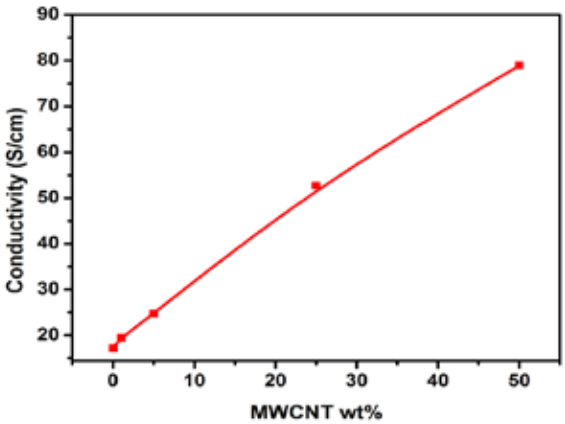


Figure 6. Variation of room temperature electrical conductivity of PANI–MWCNT nanocomposites with different loading levels of MWCNT

Surface Morphology And Microstructural Analysis-
Figure 7 shows the SEM micrograph of MWCNTs. The scanning electron micrographs of particles, PANI and PCs are shown in Figure 8 shows the SEM images of MWCNT, PANI and PANI–MWCNT nanocomposites. These micrographs show that PCNT0 (Figure 8a, b) exits as highly agglomerated globular particles whereas as grown MWCNTs (PCNT100) are entangled tubules (Figure 8) with diameter in the range of 10–60 nm and their lengths ranging in several microns. The small size of the nanotubes having high specific surface area provides large number of sorption sites to aniline monomer which can polymerize to form coating over the nanotubes. At very low concentration of MWCNTs, PANI coated tubes exist as globular agglomerates (Figure 8b). This may be attributed to the large proportion of bulk/solution polymerized PANI (existing in agglomerated form) as compared to aniline polymerized over MWCNT surface. However, with the increase in MWCNT content, there is systematic change in morphology from highly aggregated globules (Figure 9b) towards uniformly coated tubules (Figure 8e). Therefore, at certain critical concentration of MWCNT (in our case achieved in PCNT25) the polymerization takes place exclusively on surface of MWCNT with minimal bulk polymerization and agglomeration effects. TEM of pure MWCNT clearly shows that tubes are multiwalled with outer diameter in the range of 10–60 nm and their lengths ranging in several microns as observed in previous studies[44]. The TEM of the PANI composite (Figure 8 c-f) shows the presence of thick and uniform coating of PANI over surface of MWCNT. The SEM of PCNT25 also revealed the nanoporous nature of coatings, which can be used for selective incorporation of other nanoparticles MWCNT showed tubular morphology and PANI also showed tubular morphology. Morphology of PC indicates the incorporation of MWCNT in PANI matrix. SEM image of PSC revealed that the entrapment of MWCNT in the tubular space of PANI matrix during insitu polymerisation of polyaniline.

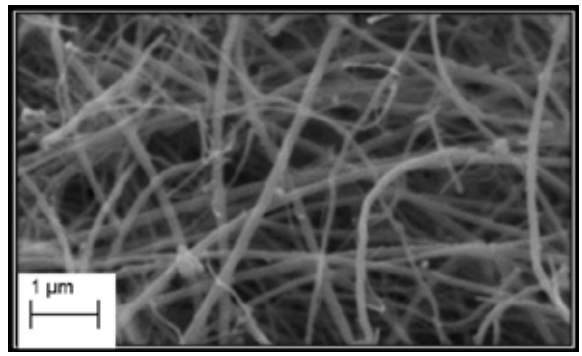


Figure 7.SEM micrographs of pristine multi walled carbon nano tube synthesised by CVD technique.

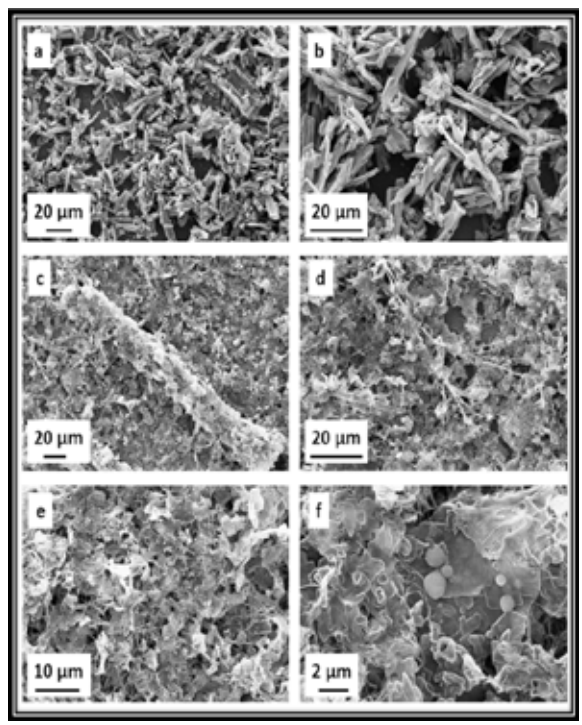


Figure 8.SEM micrographs powder sample of (a) and (b) showing PANI tubes, (c), (d), (e) & (f) PANI MWCNT composites.

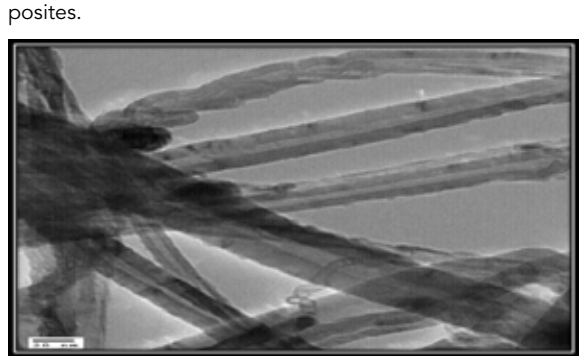


Figure 9.TEM image of MWCNT composite.

Volume : 5 | Issue : 5 | May 2015 | ISSN - 2249-555X

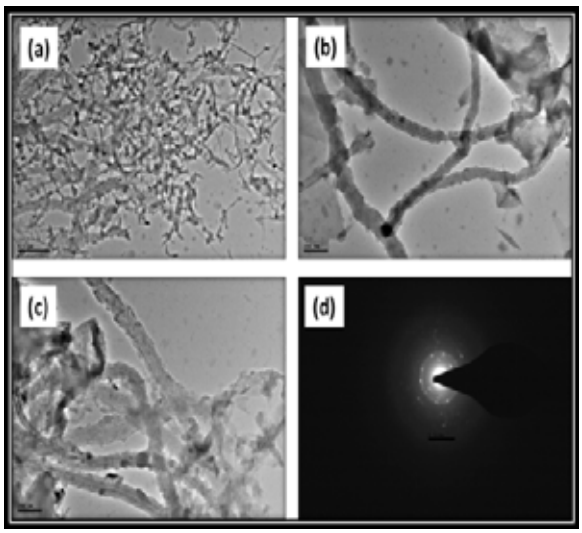


Figure 10.TEM image of PANI-MWCNT composite.

CONCLUSIONS

Highly conducting PANI–MWCNT composites were prepared by in situ polymerization. The XRD show systematic shifting in the positions of characteristic bands and peaks of PANI. This suggests significant interactions between the MWCNT and PANI. The SEM and TEM pictures show thick and uniform coating of PANI over surface of individual MWCNTs. Based on observed morphological features, we have suggested the probable formation mechanism of these composites. At very low concentration of MWCNTs, PANI coated tubes exist as globular agglomerates (PCNT5). However, at certain critical concentration of MWCNT (in PCNT25) the polymerization takes place exclusively on surface of MWCNT. The high electrical conductivity of 19.7 S cm^{-1} in PCNT25 (even better than bulk conductivity of control MWCNT pellet 19.1 S cm^{-1}) has been ascribed to the synergistic effect of two complementing phases (PANI and MWCNT). The TGA studies indicate that increasing amount of MWCNTs does not have any effect on the thermal decomposition temperature. The shielding measurements revealed that reflection loss increases slightly from−8.0 to−12.0 dB whereas absorption loss exhibits rapid enhancement from−18.5 to−28.0 dB with the increased CNT loading. The absorption dominated total shielding effectiveness in range of−27.5 to−39.2 dB indicates that these materials could be utilized effectively for the shielding purposes in the Ku-band (12.4–18.0 GHz). These PANI coated MWCNTs with large aspect ratio are also proposed as hybrid conductive fillers in various thermoplastic matrices for making structurally strong microwave shields

REFERENCE

[1] Dyer AL, Grenier CRG, Reynolds JR. A Poly(3,4-alkylenedioxythiophene) Electrochromic Variable Optical Attenuator with Near-Infrared Reflectivity Tuned Independently of the Visible Region. AdvFunct Mater. 2007;17(9):1480-6. | [2] Koul S, Chandra R, Dhawan SK. Conducting polyaniline composite for ESD and EMI at 101GHz. Polymer. 2000;41(26):9305-10. | [3] Yamamoto H, Oshima M, Hosaka T, Isa I. Solid electrolytic capacitors using an aluminum alloy electrode and conducting polymers. Synthetic Metals. 1999;104(1):33-8. | [4] Jérome D, Bechgaard K. Condensed-matter physics: superconducting plastic. Nature. 2001;410(6825):162-3. | [5] Fehse K, Schwartz G, Walzer K, Leo K. Combination of a polyaniline anode and doped charge transport layers for high-efficiency organic light emitting diodes. Journal of Applied Physics. 2007;101(12):124509-. | [6] Al-Ibrahim M, Ambacher O, Sensfuss S, Gobsch G. Effects of solvent and annealing on the improved performance of solar cells based on poly(3-hexylthiophene): Fullerene. ApplPhysLett. 2005;86(20):201120-. | [7] Singh AP, Mishra M, Sambyal P, Gupta BK, Singh BP, Chandra A, et al. Encapsulation of γ-Fe2O3 decorated reduced graphene oxide in polyaniline core-shell tubes as an exceptional tracker for electromagnetic environmental pollution. Journal of Materials Chemistry A. 2014;2(10):3581-93. | [8] Teotia S, Singh BP, Elizabeth I, Singh VN, Raman R, Singh AP, et al. Multifunctional, Robust, Light Weight, Free Standing MWCNT/ Phenolic Composite Paper as Anode for Lithium Ion Batteries and EMI Shielding Material. RSC Advances. 2014. | [9] Kumar R, Joon S, Singh AP, Singh B, Dhawan S. Self-Supported Lightweight Polyaniline Thin Sheets for Electromagnetic Interference Shielding with Improved Thermal and Mechanical Properties. American Journal of Polymer Science. 2015;5(1A):28-39. | [10] Kim H-R, Kim B-S, Kim I-S. Fabrication and EMI shielding effectiveness of Ag-decorated highly porous poly(vinyl alcohol)/Fe2O3 nanofibrous composites. Materials Chemistry and Physics. 2012;135(2–3):1024-9. | [11] Paligová M, Vilčáková J, Sáha P, Křesálek V, Stejskal J, Quadrat O. Electromagnetic shielding of epoxy resin composites containing carbon fibers coated with polyaniline base. Physica A: Statistical Mechanics and its Applications. 2004;335(3):421-9. | [12] Mishra M, Singh AP, Sambyal P, Teotia S, Dhawan SK. Facile synthesis of phenolic resin sheets consisting expanded graphite/γ-Fe2O3/SiO2 composite and its enhanced electromagnetic interference shielding properties. Indian Journal of Pure & Applied Physics. 2014;52:478-85. | [13] Rahaman M, Chaki TK, Khastgir D. Shielding with conductive polymer and carbon fiber composites. SPE Plast Res Online doi. 2011;10:1002. | [14] Sambyal P, Singh AP, Verma M, Farukh M, Singh BP, Dhawan SK. Tailored polyaniline/barium strontium titanate/expanded graphite multiphase composite for efficient radar absorption. RSC Advances. 2014;4(24):12614-24. | [15] Dhawan SK, Singh N, Rodrigues D. Electromagnetic shielding behavior of conducting polyaniline composites. SciTechnolAdv Mater. 2003;4:8. | [16] Barnes A, Despotakis A, Wright PV, Wong TCP, Chambers B, Anderson AP. Control of conductivity at microwave frequency in a poly(aniline hydrochloride) silver polymer electrolyte composite material. Electron Lett. 1996;32:358-9. | [17] Arranz-Andrés J, Pulido-González N, Fonseca C, Pérez E, Cerrada ML. Lightweight nanocomposites based on poly(vinylidene fluoride) and Al nanoparticles: Structural, thermal and mechanical characterization and EMI shielding capability. Materials Chemistry and Physics. 2013;142(2–3):469-78. | [18] Narayanan T, Sunny V, Shaijumon M, Ajayan P, Anantharaman M. Enhanced microwave absorption in nickel-filled multiwall carbon nanotubes in the S band. Electrochemical and Solid-State Letters. 2009;12(4):K21-K4. | [19] Singh AP, Gupta BK, Mishra M, Govind, Chandra A, Mathur RB, et al. Multiwalled carbon nanotube/cement composites with exceptional electromagnetic interference shielding properties. Carbon. 2013;56:86–96. | [20] chiou J-M, Zheng Q, . CDDL. Electromagnetic interference shielding by carbon fiber reinforced cement. Composites. 1989;20. | [21] Joo J, Epstein AJ. Electromagnetic radiation shielding by intrinsically conducting polymers.ApplPhysLett. 1994;65(18):2278-80. | [22] Yang Y, Gupta MC, Dudley KL, Lawrence RW. Conductive carbon nanofiber--polymer foam structures.Advanced materials. 2005;17(16):1999-2003. | [23] Che RC, Peng LM, Duan XF, Chen Q, Liang XL. Microwave Absorption Enhancement and Complex Permittivity and Permeability of Fe Encapsulated within Carbon Nanotubes. Advanced Materials. 2004;16(5):401-5. | [24] Dhawan SK, Singh N, Rodrigues D. Electromagnetic shielding behaviour of conducting polyaniline composites. SciTechnolAdv Mater. 2003;4(2):105-13. | [25] Hoang NH, Wojkiewicz JL, Miane JL, Biscarro RS. Lightweight electromagnetic shields using optimized polyaniline composites in the microwave band.Polymers for Advanced Technologies. 2007;18(4):257-62. | [26] Anoop Kumar S, Singh A, Saini P, Khatoon F, Dhawan SK. Synthesis, charge transport studies, and microwave shielding behavior of nanocomposites of polyaniline with Ti-doped γ-Fe2O3. J Mater Sci. 2012;47(5):2461-71. | [27] MÄ¤kelÄ¤ T, Pienimaa S, Taka T, Jussila S, Isotalo H. Thin polyaniline films in EMI shielding. Synthetic Metals. 1997;85(1-3):1335-6. | [28] Pomposo JA, RodrÄguez J, Grande H. Polypyrrole-based conducting hot melt adhesives for EMI shielding applications. Synthetic Metals. 1999;104(2):107-11. | [29] Wojkiewicz J, Fauveaux S, Miane JL. Dielectric behavior and shielding properties of polyaniline composites.ICSD01 Proceedings of the 20001 IEEE 7th International Conference on Solid Dielectrics (Cat No01CH37117). | [30] Cao J, Chung DDL. Coke powder as an admixture in cement for electromagnetic interference shielding.Carbon. 2003;41(12):2433-6. | [31] Ji X, Yao Y, Li J, Yan X, Huang F. A Supramolecular Cross-Linked Conjugated Polymer Network for Multiple Fluorescent Sensing. Journal of the American Chemical Society. 2013;135(1):74-7. | [32] Foster EL, De Leon ACC, Mangadlao J, Advincula R. Electropolymerized and polymer grafted superhydrophobic, superoleophilic, and hemi-wicking coatings. J Mater Chem. 2012;22(22):11025-. | [33] Cao Y, Smith P, Heeger AJ. Counter-ion induced processibility of conducting polyaniline. Synthetic Metals. 1993;57(1):3514-9. | [34] Adams PN, Laughlin PJ, Monkman AP. Synthesis of high molecular weight polyaniline at low temperatures. Synthetic metals. 1996;76(1):157-60. | [35] Singh AP, S. AK, Chandra A, Dhawan SK. Conduction mechanism in Polyaniline-flyash composite material for shielding against electromagnetic radiation in X-band & Ku band. Aip Advances. 2011;1(2):-. | [36] Kumar Srivastava R, Narayanan TN, Reena Mary AP, Anantharaman MR, Srivastava A, Vajtai R, et al. Ni filled flexible multi-walled carbon nanotube–polystyrene composite films as efficient microwave absorbers. Applied Physics Letters. 2011;99(11):113116--3. | [37] Singh AP, Garg P, Alam F, Singh K, Mathur RB, Tandon RP, et al. Phenolic resin-based composite sheets filled with mixtures of reduced graphene oxide, γ-Fe2O3 and carbon fibers for excellent electromagnetic interference shielding in the X-band. Carbon. 2012;50:3868–75. | [38] Dai H, Hafner JH, Rinzler AG, Colbert DT, Smalley RE. Nanotubes as nanoprobes in scanning probe microscopy. Nature. 1996;384:147-50. | [39] HeerWAd, Châtelain A, Ugarte D. A Carbon Nanotube Field-Emission Electron Source.Science. 1995;270:1179-80. | [40] Martel R, Schmidt T, Shea HR, Hertel T, Avouris P. Single- and multi-wall carbon nanotube field-effect transistors. ApplPhysLett. 1998;73:2447. | [41] Williams OA, Whitfield MD, Jackman RB, Foord JS, Butler JE, Nebel CE. Formation of shallow acceptor states in the surface region of thin film diamond. ApplPhysLett 2001;78:3460. | [42] Kleinsorge B, Ferrari AC, Robertson J, Milne WI. Influence of nitrogen and temperature on the deposition of tetrahedrally bonded amorphous carbon. J Appl Phys. 2000;88:1149. | [43] Tripathi P, Prakash Patel CR, Dixit A, Singh AP, Kumar P, Shaz MA, et al. High yield synthesis of electrolyte heating assisted electrochemically exfoliated graphene for electromagnetic interference shielding applications. RSC Advances. 2015;5(25):19074-81. | [44] Singh AP, Mishra M, Hashim DP, Narayanan T, Hahm MG, Kumar P, et al. Probing the engineered sandwich network of vertically aligned carbon nanotube–reduced graphene oxide composites for high performance electromagnetic interference shielding applications. Carbon 2015, p. 79-88. | |