

Review of synthesis, Characterization, Mechanical and Electrical properties of CNTs/PANI nanocomposite

Md Zakir Hussain¹, Sabah Khan^{1,*}, Suborna Haque², Bhaskarjyoti Pathak²

¹Department of Mechanical Engineering, Jamia Millia Islamia, New Delhi, India

²Department of English, Goalpara Polytechnic, Goalpara, Assam, India

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Abstract

In recent years, attention has been made by researchers to fabricate carbon nano-tubes/Polyaniline (CNTs/PANI) nanocomposites due to its simple method of preparation, low cost, environmental friendly, excellent capacitive performance. The discovery of carbon nanotubes with unique electrical, thermal and mechanical properties has attracted researchers used as a filler material for applications in engineering discipline. This review gives a broad study on ongoing research effort on synthesis, characterization, mechanical and electrical properties of CNTs/PANI nanocomposites.

1. Introduction

In the last decade, nanoscience and nanotechnology have invited much interest of the researchers and industrial practitioners as enhancement in the property of the composite is observed when the atomic dimension of filler material reduces to nanometric scale.

Among the various conducting polymers, polyaniline (PANI) has received more attention due to its versatile conducting nature, processed by melt or solution process, environmentally and thermally stable, lightweight, inexpensive, mechanically flexible, low cost of processing, different colors, charges and conformations of the multiple oxidation states also make the material promising for applications such as actuators, supercapacitors, battery material, electrically conducting yarns, antistatic/anticorrosion coatings, electromagnetic shielding, flexible electrodes and hydrogen storage applications [1-7]. After the discovery of carbon nanotubes (CNTs) by Iijima et al. in 1991 [8], it has high mechanical, electronic properties and are attractive building block for the development of novel polyaniline based nanocomposite materials. The unresolved problems are not solved concerning the structures and properties of Polyaniline. The two major limitations of conducting polyaniline are an inability to process by conventional methods and its poor mechanical properties [9]. The Young's modulus of PANI hydrochloride and polyaniline base pellets are 0.9 ± 0.2 GPa and 1.3 ± 0.2 GPa respectively [10]. Improvement of polyaniline properties can be achieved either by forming composites of aniline with CNTs reinforcement or blends with commercially available polymers. The review of literatures focuses mainly on the preparation, characterization, mechanical and electrical properties of CNTs/PANI nanocomposites. In spite of extensive work has been done on electrical properties of CNTs/PANI, the information on its mechanical properties is missing in the literature. This review focuses mainly on the extensive literature related CNTs/PANI nanocomposites.

2. Review of CNTs/PANI nanocomposites

In the past few years, several techniques have been used to synthesize CNTs/PANI nanocomposites. Most of literatures indicate that the *in-situ* polymerization is most effective method lead to better dispersion of CNTs in CNTs/PANI nanocomposites. Ghatak et al. synthesized CNTs/PANI nanocomposites with the help of *in-situ* polymerization technique. Thermo gravimetric analysis showed that the composites had better thermal stability in comparison to pure PANI [11]. In situ polymerization also leads to better

dispersion of carbon nanotubes, enhancing field emission for displays and other devices. Shumaila Akram et al. synthesized MWCNT/PANI nanocomposites and found that in situ polymerization enhanced field emission properties in comparison to ex-situ polymerization process either combine with solid-state mixing or solution mixing [12]. The electrical, thermal, and mechanical properties of multiwalled carbon nano-tubes/polyaniline (MWCNTs/PANI) nanocomposites were depended with MWCNT content and the extent of their integration with PANI. These characteristics makes the material suitable for field emission devices such as video displays. Mahore et al. synthesized ternary nanocomposites by an *in situ* polymerization of aniline monomer in the presence of functionalized multi-walled carbon nanotubes using KMnO_4 as an oxidizing agent [13]. The well conducting properties of CNTs and their meso-porosity allow good charge propagation. The electrical conductivity of the PANI composite without MWCNTs was lower due to low solubility of PANI and porous structure. Use of MWCNTs as a filler material, it is possible to meet the need in new applications such as conducting coatings, spacecraft, conductive fabric.

Bachhav et al. successfully synthesized PANI-MWCNT nanocomposites by in situ oxidation polymerization of aniline monomer in the presence of MWCNTs [14]. Field emission scanning electron microscope (FESEM) images confirmed formation of PANI on the surface of MWCNTs. The enhancement in conductivity was observed with increasing MWCNTs weight percentage.

PANI, polyacrylonitrile and MWCNTs composite fibers has been fabricated using electrospinning method [15]. The low density of the nanofiber membranes with lots of pores, random distribution of MWCNTs, weak interaction between the nanofibers and small diameter of PANI/polyacrylonitrile/MWCNTs composite nanofibers decreases mechanical properties. The incorporation of MWCNTs reduced the diameter of the PANI/polyacrylonitrile/MWCNTs nanofibers under the same applied voltage and consequently the addition of the MWCNTs in the PANI solution enhanced the conductivity. Prerana Modak et al. synthesized Polyaniline/graphene nanocomposites using in-situ chemical oxidative polymerization [16]. The electrical conductivity of nanocomposites was found to be drastically increased as compared to that of pure PANI at room temperature. Byong-Wook Lee et al. demonstrated that the shapes of the MWCNTs-PANI nanocomposites changed by altering the reactant concentrations [17]. It was found that the electrical conductivity was strongly dependent on the shape and PANI content. Shin, Koo et al. synthesized PANI/MWCNTs nanocomposite by *in situ* chemical polymerization and the synthesized nanocomposite could be used as a sensing material for hydrogen gas at room temperature [18].

*Corresponding Author,

E-mail: khansabah629@gmail.com;

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Techniques are required to take advantage of mechanical properties of CNTs at nanometric scale to macroscopic scale. An improvement in mechanical properties of PANI/CNTs nanocomposites have been noticed in comparison to pristine CNTs sheet and prepared by in situ polymerization followed by hot pressing. The highest specific tensile strength observed on PANI/stretched CNT nanocomposite, which was achieved in a sample with ~42 wt% of PANI [19]. Tejendra K. Gupta et al. adapted a multiphase approach to enhance the electromagnetic interference shielding effectiveness of polyaniline based nanocomposites [20]. A bridge between PANI and MWCNTs plays a significant role for improving the properties of multiphase nanocomposites. The decrease in carrier mobility has a positive effect on the shore hardness value due to the strong interaction between the reinforcing constituent in multiphase nanocomposites and shore hardness increases from 56 to 91 at 10 wt% of MWCNTs. PANI/MWCNT-CdS nanocomposites with different content of CdS wt% has been synthesized by the chemical oxidative *in-situ* polymerization reaction [21]. XRD analysis revealed that the co-existence of MWCNT, CdS in PANI matrix. Parveen Saini et al. prepared high conducting polyaniline/MWCNT nanocomposites by in situ polymerization [22]. Due to synergistic effect between two phases, the electrical conductivity of MWCNT/PANI composite was higher than MWCNT or PANI. The absorption dominated total shielding effectiveness of these composites indicates the usefulness of these materials for microwave shielding. MWCNT-PANI nanocomposites were developed for the application in dye-sensitized solar cells by in situ chemical polymerization method [23]. FESEM surface morphology shows good distribution of CNT in PANI matrix. Tubular morphology of MWCNT-PANI nanocomposites was confirmed by TEM. The electrical conductivity may be taken as a function of length of the polymer, and the presence of active dopant present.

PANI has been used as effective materials for preparation of the chemical sensors. Functionalize MWCNTs/PANI nanocomposites were prepared by in situ chemical oxidation polymerization using ammonium persulfate as oxidant [24]. A dense network of functionalize MWCNTs and surface modification of MWCNTs could improve the dispersion of MWCNTs. The non-uniform coating of PANI layer on the MWCNTs surface may be due to the constrained chain growth and the adsorption effect of the MWCNTs surface. The nano-tubes were well embedded and tightly held to the PANI matrix, indicating the existence of strong interfacial bonding. The increased electrical conductivity of supercapacitors was attributed to effective utilization of surface area, the presence of CNTs, and uniform and aligned vertically PANI coating on graphene [25]. The structural stability of PANI in nanocomposite depends on efficient heat dissipation from the PANI coating around MWCNTs. Large contact area between MWCNTs and PANI, heterogeneous structure and high thermal conductivity of MWCNTs causes efficient heat dissipation. PANI nanocomposites can also be synthesized using an *in-situ* rapid mixing approach [26]. The nanocomposite consisted of MWCNTs uniformly coated with PANI in the state of emeraldine salt, with a well-defined core-shell heterogeneous structure. The presence of MWCNTs causes the occurrence of de-protonation process in PANI upon at lower temperature and significantly enhances the thermal stability of PANI. CNTs/PANI nanocomposite films prepared by filtration from dilute dispersions [27]. FESEM surface morphograph revealed that the structure of the nanocomposite was porous. Tensile tests were carried out on the free-standing films. Higher density could increase the number of physical cross links within the composite to improved mechanical properties.

CNTs/PANI nanocomposites synthesized via. in situ polymerization of aniline and CNT, treated by either acid treatment of CNTs suspension or by grafting functional groups to CNTs surface [28]. The enhanced electro-activity can be attributed to the acid treatment creating more functional groups on the CNTs. MWCNTs/PANI nanocomposite synthesized by an *in-situ* oxidative polymerization and the XRD data shows that the characteristic peaks for PANI at

15.3⁰, 20.4⁰ and 26.28⁰ at crystal planes of PANI (011), (020) and (200) respectively [29]. The electrical conductivity of PANI and PANI/CNTs varies with temperature. The thermal behaviour of PANI/CNTs nanocomposite and PANI/CNTs interaction may facilitate the charge transfer process between them and influence the charge transport properties.

Polyaniline with functionalized MWCNTs/PANI synthesized using *in situ* chemical oxidative method [30]. The higher thermal stability of the PANI/MWCNTs composite may be due to the stability of PANI and protective effect of PANI. Thermogravimetric analysis results shows that the thermal stability of CNTs/PANI composite was better than that of pure PANI [31]. CNTs functionalization methods make CNTs/PANI composites highly conductive. Single walled CNTs/ordered PANI synthesized through an in situ polymerization reaction [32]. The SWCNTs/PANI nanocomposites showed higher electrical conductivity due to the enhanced carrier mobility in the ordered structures of the PANI. A drop-casting technique was used to synthesize MWCNTs/PANI nanocomposite thin films for electrode applications. Uniform dispersed CNTs was observed on the surface of graphene and formed a nanoscale vermicular morphology of PANI films [33].

The emulsion polymerization method is a simple, effective, and inexpensive route for synthesizing functionalized MWCNTs/PANI nanocomposites and the method can be used for antistatic/anticorrosion coatings, hydrogen storage and EMI shielding applications. PANI-carboxylic acid functionalized MWCNTs were synthesized via emulsion polymerization using sodium dodecyl sulfate [34]. Uniform coating of PANI on the surface of the functionalized MWNTs was observed using FESEM. The FTIR spectra of the nanocomposites revealed that the PANI in the nanocomposites was richer in quinoid units than the pure PANI. The increase in the thermal conductivity of the nanocomposites was due to functionalized MWNTs, could serve as a conducting bridge by its network structure to link the PANI/sodium dodecyl sulfate complex and the charge transfer between the quinoid rings of the PANI and the carboxylic acid functionalized-MWCNTs.

The enhancement in conductivity of PANI/MWCNTs compared to neat PANI is due to the charge transfer effect from the quinoid rings of the PANI to the MWCNTs. The MWCNTs may serve as conducting bridges, connecting the PANI conducting domains [35].

3. Results and Discussions

Polyaniline is one of the conducting polymers that have potential in the near future advanced materials, due to its good processability, environmental friendly and electrical conductivity both by charge-transfer doping and protonation. The filler material CNTs are used in order to improve the interaction between the CNTs and PANI, which may lead to an increase in the electronic property. Helena Valentová et al. investigated the influence of preparation conditions of PANI pellets on mechanical and electrical properties of PANI [10]. It was found that a pressure of 300 MPa is needed to obtain a reliable value of conductivity, elastic modulus. Also, non-conducting polyaniline base has better mechanical properties compared with those of conducting polyaniline hydrochloride.

The electrical conductivity of the PANI composite without CNTs was lower due to poor solubility of PANI and porous structure of the nanocomposites. A bridge between PANI and CNTs also plays a significant role for improving the properties. Use of CNTs as a filler material, it is possible to meet the need in new applications such as conducting coatings, spacecraft, conductive fabric. A dense network of nanotubes functionalized CNTs and surface modification of CNTs could improve the dispersion of CNTs. The enhancement in conductivity of PANI/CNTs compared to neat PANI is due to the charge transfer effect from the quinoid rings of the PANI to the MWCNTs.

Table1. Properties of CNTs/PANI nanocomposites

Sl No	Author's	Sample	Properties	Ref.
1	Mahore et al.	Pure PANI 0.25% to 8% MWCNT/pure PANI	0.17 S/cm value 0.22 S/cm to 3.32 S/cm	[14]
2	Zhang et al.	0.2 wt% PANI/8 wt% PAN 0.2 wt% PANI/8 wt% PAN/3 wt% MWCNTs, 0.2 wt% PANI/8 wt% PAN/5 wt% MWCNTs, 0.2 wt% PANI/8 wt% PAN/7 wt% MWCNTs.	Electrical conductivity (S/m): 5.69×10^{-4} Modulus calculated: 0.137 GPa Electrical conductivity (S/m): 1.79 Modulus calculated: 0.04 GPa Electrical conductivity (S/m): 3.26 Modulus calculated: 0.036 GPa Electrical conductivity (S/m): 7.97 Modulus calculated: 0.030 GPa	[15]
3	Jae-Woo Kim et al.	42 wt% PANI/stretched CNT nanocomposite	Specific tensile strength: 484 MPa/(g/cm ³) Specific modulus: 17.1 GPa/(g/cm ³) DC-electrical conductivity: 621 S/cm	[19]
4	Parveen Saini et al.	PANI/MWCNT MWCNT PANI	Electrical conductivity: 19.7 S cm ⁻¹ Electrical conductivity: 19.1 S cm ⁻¹ Electrical conductivity: 2.0 S cm ⁻¹	[22]
5	Karim et al.	MWNT- PANI Pristine PANI PANI/functiona lized MWCNT	Electrical conductivity: 1.53 S/cm Electrical conductivity: 0.18 S/cm Nil	[23]
6	Blighe et al.	PANI-SWCNT	Young's modulus (GPa): 1.9 ± 0.7	[27]
7	S. B. Kondawar	PANI PANI- MWCNT	Electrical conductivity at 303K (S/cm): 0.504 Electrical conductivity at 303K (S/cm): 1.95	[29]
8	Han Jae seok	MWCNT/PANI film Pure PANI film	specific capacitance: ~134 F/g specific capacitance: ~120 F/g	[33]
9	T. Jeevana nda	PANI prepared in SDS emulsion PANI/1wt% carboxylic acid functionalized MWCNTs PANI/10wt% carboxylic acid functionalized MWCNTs	5.30×10^{-3} S cm ⁻¹ 2.0×10^{-2} S cm ⁻¹ 2.72×10^{-1} S cm ⁻¹	[34]

4. Conclusions

This review of different research paper has given us a brief description of the current literature related to the CNTs/PANI nanocomposites, their synthesis, characterization, electrical and mechanical properties and applications. However, the application of CNTs as a filler material in CNTs/PANI nanocomposites has not yet been fully explored which would demonstrate the need for work in this particular area. The nanocomposites can exhibit improved properties with respect to the pure PANI. The changes on electrical properties of PANI with addition of CNTs are due to high surface area, which increases the interaction between the CNTs and PANI, a bridge between PANI and MWCNTs which also plays a significant role in improving the properties of multi functional nanocomposites. The electrical conductivity of the PANI composite without MWCNTs was lower due to low solubility of PANI and porous structure. All the properties of CNTs/PANI nanocomposites depend on the method of CNTs/PANI synthesis, % CNTs content, functionalization of CNTs i.e. surface modification of CNTs.

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