

**Review Article**

Performance of Polyaniline Doped Carbon Nanotube Composite

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Abstract

Polyaniline (PANI) doped carbon nanotube (CNT) has been utilized to form conductive thermoplastic composites. The polyaniline/carbon nanotube (PANI/CNT) nanocomposites have been formulated using different methods such as electrochemical deposition, *in-situ* chemical polymerization, and number of other approaches. The structure and properties of these nanocomposites have been explored using range of structural and morphological techniques. In this article, mainly developments in PANI/CNT nanocomposites have been reviewed. The performance assessment of PANI/CNT nanocomposites has revealed various technical uses in electrode, electronic devices, batteries, and corrosion protection.

Keywords: Polyaniline, Carbon Nanotube, Nanocomposite, Batteries, Corrosion Protection

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1. Introduction

In current years, several studies have been conducted where nanoparticles have been integrated in polymer matrix for enhancement of thermal conductivity [1]. Carbon nanotube has generated enormous interest in most areas of science and engineering due to outstanding physical and chemical properties. For generation of high potential composites with improved characteristics, micro and nano-scale particles have been considered as filler material for polymers. Carbon nanotube (CNT) is one dimensional carbon material which may have aspect ratio greater than 1000, in comparison to other carbon materials such as diamond, graphite and fullerene. The combination of outstanding thermal, mechanical, and electronic properties has not been shown by any other nanomaterial. The polymer composite materials with reinforcement of at least one dimension in range of 1-100 nm is defined as nanocomposite. Most common fillers used for polymer reinforcement are carbon nanotube, layered silicate nanoclay, graphite, graphene, and grapheme oxide. The excellent electrical, mechanical, and thermal characteristics of CNT render them ultimate applicant as nanofiller in light weight polymer composite. Nanotube may strengthen polymer composites, so have become interesting structural materials not only in the weight-sensitive aerospace industry, but also in the armor, marine, civil engineering structures, automobile, railway, electronics, and sporting goods. All these industries demand high specific stiffness and specific strength [2]. By integration of carbon nanotube into variety of polymer matrices (such as polypropylene, polyamides, polyimides, epoxy and polyurethane, various nanocomposites have been generated [3]. The recent and future commercial employment of CNT has generated remarkable academic interest in polymer/CNT composite. [4, 5]. Nanotube-strengthened polyaniline (PANI)-based composites have become interesting structural materials not only in the weight-sensitive aerospace industry, but also in the armor, marine, civil engineering structures, automobile, railway, and sporting goods industries. Therefore, polyaniline/carbon nanotube composites have been the focus of this article.

2. Polyaniline: Structure and properties

Polyaniline (PANI) is ranked among most studied conducting polymers. Its electrical features, catalytic, optical, electrochemical, and surface features have been considered. PANI is usually synthesized from aniline monomer using oxidants. It has poor solubility in common solvents such as ethanol, methanol, and acetone. PANI nanostructure may have enhanced dispersibility in host matrices [6]. PANI is the most extensively studied conducting polymer due to low synthetic cost, superficial synthesis, and outstanding thermal and environmental stability. There are three main forms of PANI namely the fully oxidized (pernigraniline) state, fully reduce (leucoemeraldine), and the more conducting emeraldine base (half oxidized) (Fig. 1).

Emeraldine is most conductive form to produce emeraldine salt by doping. Polyaniline can be easily synthesized either electrochemically or chemically from acidic aqueous solutions. The chemical route has great importance because it is successful for the mass production of PANI. The most common synthesis route is the oxidative polymerization with ammonium peroxodisulfate as oxidant [7, 8]. Polyaniline is one of the most extensively studied conducting polymers due to strong bimolecular interaction, superficial synthesis, and electrochemical, electrical and optical features. It holds great potential in comparison to other conducting polymers due to outstanding tuneable conductivity by charge transfer doping and protonation [9]. Because of thermal stability and conducting behavior, it has been extensively employed in electrochromic devices, electrocatalysis, and biosensors [10].

Polyaniline also possess wide range of applications in supporting goods, aerospace, EMI shielding, electronics, radar absorbing material, and wind turbine blades.

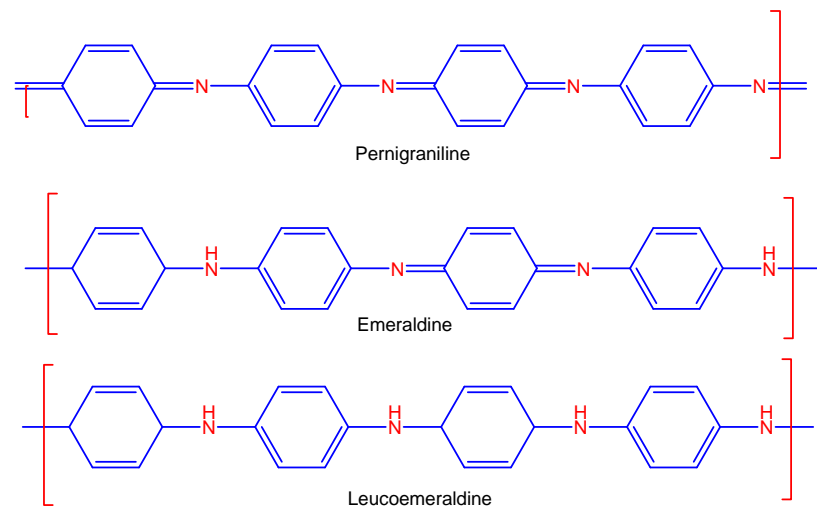


Fig. 1 Different oxidation states of PANI

3. Carbon naofiller

Filler is one of most important raw materials used in material science. The production of filler is known to be 50 million tons per year. They are generally employed in composite constituents to decrease the consumption of expensive binding material and to enhance physical features [11]. They can be of various shapes such as spherical particles, rod, disc flakes, etc. Generally, the particle size, geometry, functionalization, and chemical coating instigate various properties in filler materials. The integration of nanofiller in polymer matrix may considerably influence the properties of materials such as controlled rheological features, and enhanced thermal, optical, electrical, mechanical, and nonflammability properties [12-14]. Generally, nanofillers can be categorized as 1D nanofillers (nanofibers and nanotubes), 2D nanofillers (platelets, shell, laminates) and 0D or 3D nanofillers (silica, and beads) (Fig. 2).

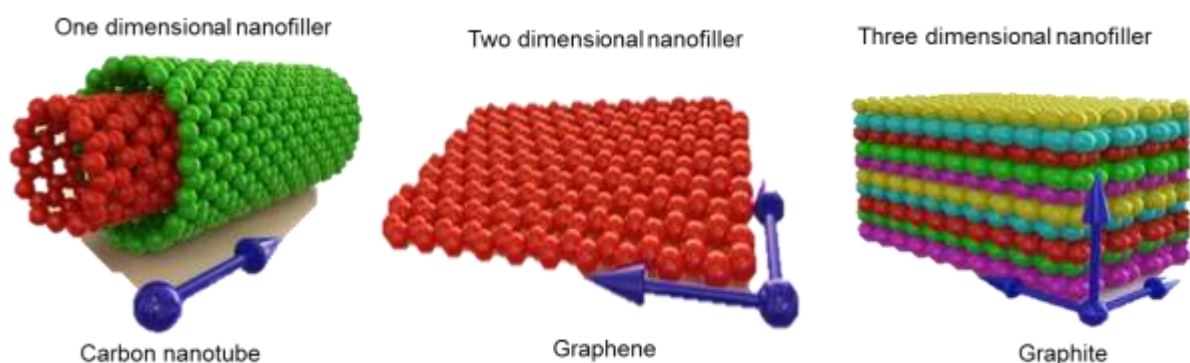


Fig. 2 Nano objects used as nanofiller

4. Carbon nanotube

Carbon nanotube is minute hollow cylinder with diameter ranging from 0.4-2.5 nm [15, 16]. An ideal single walled carbon nanotube (SWCNT) is formed by rolling a single graphene sheet, which is exclusively composed of carbon atoms. Principally, their length is unrestricted ranging from 10-100 μm . Most of specifically formed CNT are multi-walled carbon nanotube (MWCNT), which is comprised of more than two concentric cylinders of SWCNT. The diameter of MWCNT varies up to several hundred nanometers [17, 18]. Variation in CNT morphology may occur due to different synthesis methods used. Outstanding features of CNT offer potential for the fabrication of polymer composites with enhanced features such as strength, conductivity, elasticity, durability, and toughness [19]. Recent research has displayed the probability of utilizing CNT films in high flexible solar cells [20]. CNT is a very capable nanofiller material in composites having exceptional thermal, electrical, mechanical, and magnetic features. CNT strengthened polymer composites have fascinated much attraction due to better compatibility of polymer and nanofiller. Properties of polymer/CNT nanocomposite are also found better than the inorganic, ceramics, and metal reinforced composite. Therefore, CNT have been employed in numerous applications such as aerospace, radar absorbing material, electromagnetic interference shielding, sporting goods, fuel cells, wind turbine blades, automobiles, and electronics [21].

5. Polyaniline doped carbon nanotube composite

Enormous research on conjugated polymers such as polythiophene, polyaniline, polypyrrole, polyindole, polycarbazole, polyfluorene, poly(*p*-phenylene) and their substituted derivatives has gained interest due to applications in microelectronics, rechargeable batteries, sensors, electrochromic displays, photovoltaics, and light emitting devices [22, 23]. Among various conjugated polymers, PANI has gained special recognition due to good stability and interesting redox behavior. In past few years, various routes for the synthesis of nanostructured PANI in the form of dispersions, nanofibers, nanowires and nanotubules have been developed [24]. With the discovery of nano-sized materials, the main focus of nanoscience has been shifted from synthesis to applications [25]. In this context, there has been new surge for the development of conducting polymer/CNT nanocomposites. Studies revealed that certain discrete features of the conjugated polymer/CNT have been improved, so increasing the thermal stability and suitability for technological applications [26]. Over the last decade, polyaniline has been used as an electrode constituent in both aqueous and non-aqueous redox supercapacitors. For these applications it is desirable to prepare polyaniline with high surface area. High surface area generates high charge capability for double layer mechanism and efficient access of electrolyte to electrodes. Current studies revealed that besides enhancing the electrical and mechanical features of polymer, the polymer/CNT composite formation has been considered as significant tool for CNT integration in polymer based devices [27, 28]. Among these polymer/CNT composites several reports have focused on the combination of conducting polymers including poly(3-octylthiophene)/CNT or poly(*p*-phenylene vinylene) (PPV)/CNT for efficient photovoltaic cells. The poly(3,4-ethylene-dioxythiophene) (PEDOT)/CNT have been used for forming hole-conducting layers in organic light emitting diodes [29]. Thus, among numerous conducting polymers polyaniline has potential employment in the synthesis of polymer/CNT composites due to good processability, environmental stability, and reversible control of conductivity both by charge transfer doping and protonation [30]. In designing and fabrication of PANI/CNT composites, significant progress has been made with examples comprising PANI/multi-walled carbon nanotube composite with site selective interaction between MWCNT and quinoid ring of PANI. The

doped PANI/MWCNT composites with or without protonic acid has been synthesized by *in-situ* polymerization [31]. The preparation of coaxial nanowire of PANI/MWCNT has been carried out by electrochemical reaction and fabrication of PANI/single-wall carbon nanotube composites [32]. Acid functional nanotube (MWCNT-c) has also been used. Although, current studies revealed unique relationship between PANI and CNT (Fig. 3).

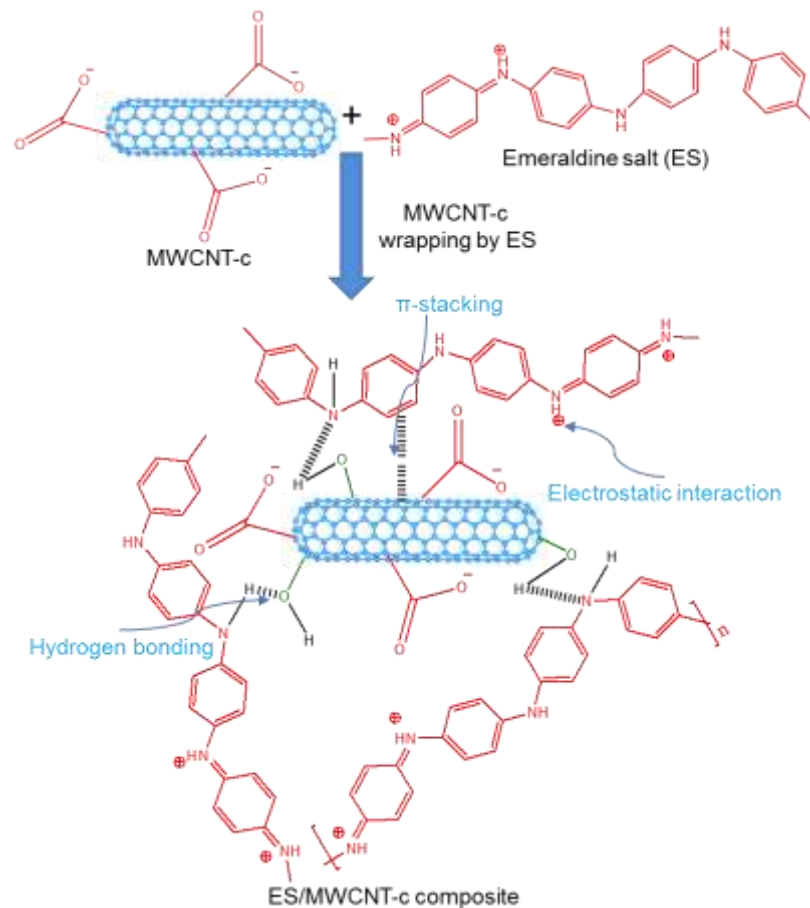


Fig. 3 Interactions responsible for Emeraldine salt/MWCNT-c composite formation

6. Applications of PANI/CNT nanocomposite

In polymeric systems, employment of inorganic and organic fillers has become a common research practice to form nanocomposite for aerospace constituents, sporting goods and automobiles. Several polymeric nanocomposites are commercially synthesized [33]. The alteration from microparticle to nanoparticle produces considerable changes in the physical features of final composite [34]. A nanostructured constituent may have significantly diverse features than the large dimensional material of same composition. There is inverse relation between material diameter and surface area per unit volume in the case of fiber and particle [35, 36]. Carbon nanofiller and organic matrix-based composites are progressively being employed in space craft and air craft industry because of remarkably high strength, modulus, light weight, good fatigue life, high stiffness, and excellent corrosion resistance (Fig. 4).

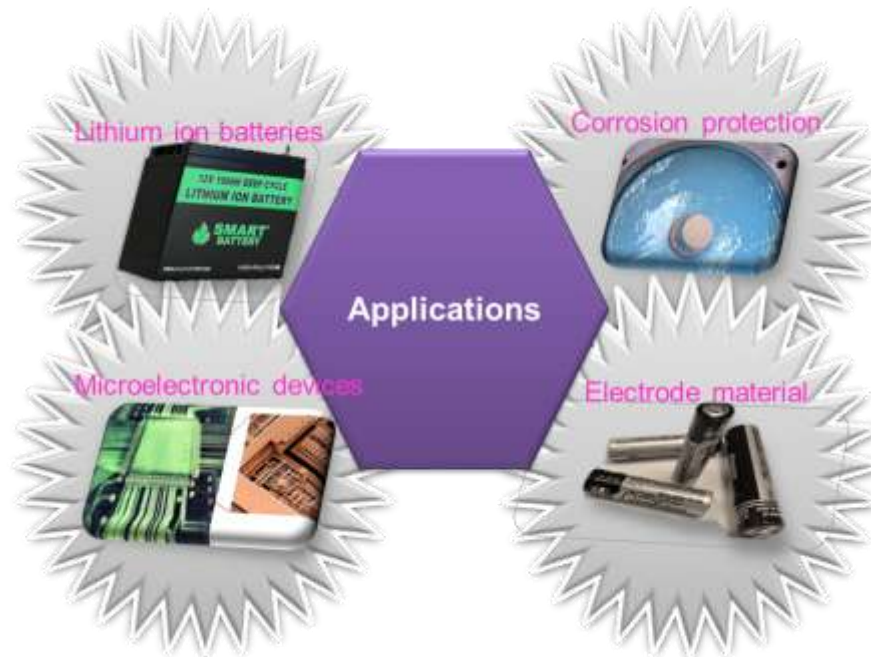


Fig. 4 Applications of PANI/CNT composite

6.1. Electrode material

For supercapacitor applications, high surface carbon, conducting polymers and noble metal oxides are chief families of electrode material being studied. Among them, conducting polymers have shown higher specific capacitance in comparison to that of carbon materials. Since they store charge through double layer and redox capacitive mechanism [37]. Porous carbon constituent may offer pseudo-capacitive behavior because of redox process undergone by adsorbed surface functionalities. However, the surface group contributions to total charge storage is not as significant as related to double layer charge. Since, PANI presents the significance of low cost in comparison to that of rhenium oxide, so they offer great interest as electrode material [38]. An extensive variety of conducting polymers such as polypyrrole, polyaniline, poly(ethylenedioxythiophene), polythiophene and its substituted parts have been studied for application of electrode materials. Polyaniline has been most efficiently investigated because of its low cost, ease of manufacture, high stability and conductivity [39, 40]. Over the last decades, reports have been published on the employment of polyaniline as electrode material in both non-aqueous and aqueous redox supercapacitors. For these applications, it is desirable to prepare polyaniline with high surface area. The taxonomy of supercapacitor materials is shown in Fig. 5.

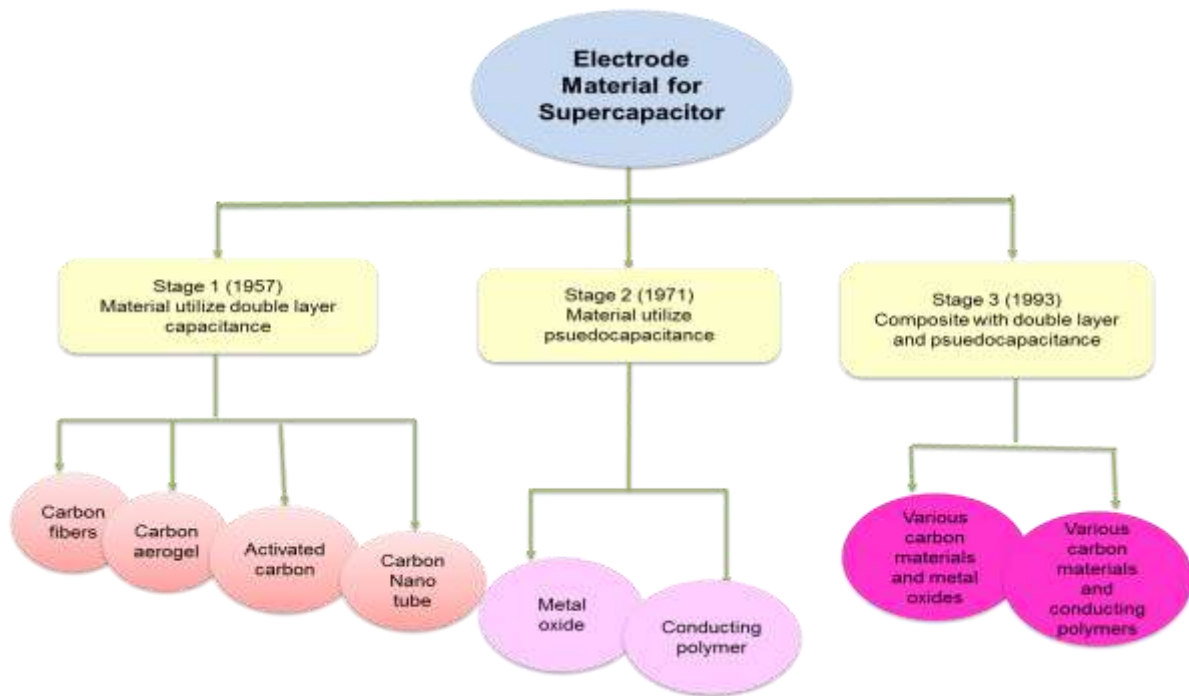


Fig. 5 Taxonomy of the supercapacitor materials.

High surface area produces high charge capability for efficient access of electrolyte to electrode in redox mechanism [41]. The preparation of PANI/CNT composites has fascinated great attention in current years due to integration of CNT in polyaniline. Thus, they can result in new composite materials with improved electronic features. For example, it has been studied that the PANI fibers comprising CNT has shown outstanding enhancement in conductivity and mechanical features. Multi-layer films of PANI/CNT have been synthesized through layer by layer route by Liu et. al. [42]. The CNT inside multi-layered film may expand the electrical conductivity of PANI to neutral electrolyte. Consequently, the improved conductivity of PANI/CNT composites may greatly be utilized for performance enhancement [43].

6.2. Corrosion coating

Polymer nanocomposites have fascinated great research and development interests because of their extensive applications in solar cells, batteries, sensors and anticorrosion coatings. Although, similar to other conducting polymers, PANI have poor mechanical stability due to typical shrinkage breaking and appearance of cracking in violent environment. This is often linked to volumetric changes of polymers during discharging and charging [44]. In addition, a huge concern is high porosity when PANI is utilized as coating material for corrosion protection at metal coating interface. For the enhancement of performance and functions, PANI has commonly been blended with other functional constituent for the formation of composites. By the combination of thin porous and free standing characteristics of CNT network and unique redox features of PANI, the PANI/CNT composites are expected to act as outstanding coating material for corrosion protection applications [45]. Currently, variety of routes has been reported for the construction of composites from combination of CNT and PANI. The target has been to gain enhanced synergetic influence with respect to initial constituents. Numerous contrasting theories have been proposed to describe the role of CNT in corrosion inhibition mechanism of polymer

coatings [46, 47]. Examples of anti-corrosion coatings based on PANI-modified organic polymers are shown in Table 1.

Table 1 Examples of anti-corrosion coatings based on PANI-modified organic polymers

Metal	Coating	Active agents
Steel	Epoxy	PANI-lignosulfonate
Steel	Epoxy	PANI and montmorillonite
Zinc	Polyvinylbutyral	PANI-Emeraldine salt of <i>p</i> -toluene sulphonic acid
Steel	Epoxy	PANI Fibers
Steel	Epoxy ester	Dodecylbenzenesulfonicacid polyaniline
AZ ₃₁	Sol-gel	PANI-emeraldine salt
Steel	Epoxy or polyamide	Aniline trimmers without and with SiO ₂

6.3. Microelectronic devices

In spite of substantial advances in organic electronic devices, they have been considered inferior in potential in comparison to that of inorganic devices. This can be partly ascribed to lack of proper knowledge of material features and the conduction mechanism in devices fabricated by these constituent [48]. Due to integration of conducting polymers in several applications in microelectronics, understanding of recent transport mechanism occurring in these materials becomes significant. PANI, in general, holds great potential because of excellent environmental and thermal stability relative to other polymers. It has been indicated by recent results that the nano-engineered conducting polymer composites with CNT may have considerably enhanced electronic and mechanical features in comparison to that of pure conducting polymer films. Moreover, CNT provide effective strengthening and enhanced thermal stability, thus making the composite more appropriate for microelectronic applications [49]. It has been suggested that nanotubes integrated into the polymer would act as nanometric heat sink considerably enhancing device break down characteristic. It was extensively believed that nano-engineered conducting polymer composites could provide high quality electronic constituent, while CNT with high aspect ratio and high conductivity would increase the mechanical, thermal, and electrical stability of nanocomposite [50]. Composites of PANI and SWCNT have been investigated for electronic device applications in metal/semiconductor contacts.

6.4. Li ion batteries

One of the main challenges to today's wireless and mobile society is to provide highly proficient, low cost and environmentally friendly energy storage media for powering even more diverse applications [52]. Among several energy and power technologies, rechargeable lithium ion batteries (LIB) are representative of chemical energy storage and conversion [53]. A common LIB comprises of negative electrode (graphite anode), a positive electrode (LiCoO₂ cathode), and a lithium ion conducting electrolyte. During the charging of cell, extraction of Li ions is carried out from cathode which move through electrolyte and are inserted into anode. Upon discharge, Li ions are released by anode and taken up again by cathode. Polyaniline has been widely studied for its use as battery material. This organic conductor has excellent redox reversibility and high environmental stability. PANI has been utilized as cathodic material in batteries with Li or Zn as anode [54]. The electrolyte usually comprises

of inorganic acids such as HCl, HClO₄ or H₂SO₄. There have been few reports available about the applications of PANI in polymer batteries. The employment of PANI anode and poly-1-naphthol cathode with methyl cyanide comprising perchloric acid and lithium percholate as electrolyte have been described with charge capacity of 150 mAh g⁻¹ [55].

7. Conclusion

In this article, polyaniline and CNT-based composites have been focused for various technical applications. The structure and properties of polyaniline have been conversed. The properties of polyaniline composite with carbon nanotube filler have also been discussed. It has been observed that significant enhancement in mechanical, thermal, and conductivity properties occurred by the addition of CNT nanofiller in polyaniline. The applications of PANI/CNT composite focusing on corrosion protection, electrode material, microelectronic devices, and lithium ion batteries have been discussed in detail. Consequently, these polyaniline/CNT composites have synergetic influence on properties to be employed in these applications.

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