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Effect of different oxidants on polyaniline/single walled carbon nanotubes composites synthesized via ultrasonically initiated in-situ chemical polymerization

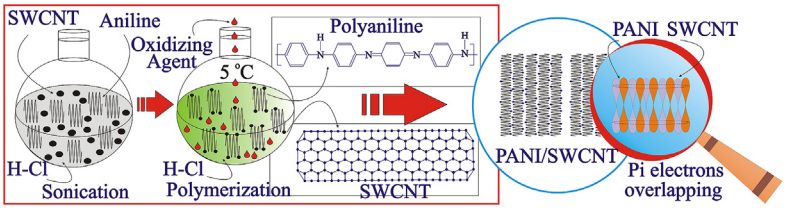
Nafisa Gull [a, *], Shahzad Maqsood Khan [a, **], Atif Islam [a], Saba Zia [a], Muhammad Shafiq [a], Aneela Sabir [a], Muhammad Azeem Munawar [a], Muhammad Taqi Zahid Butt [b], Tahir Jamil [a]

[a] Department of Polymer Engineering and Technology, University of the Punjab, Lahore, 54590, Pakistan
[b] College of Engineering and Emerging Technologies, University of the Punjab, Lahore, 54590, Pakistan

HIGHLIGHTS

- Ultrasonically initiated in-situ chemical polymerization protocol was devised for synthesis of PANI/SWCNT composites.
- SEM micrographs of PANI/SWCNT-1 showed uniform dispersed structure.
- Better thermal stability and conductivity was evidenced for H_2O_2 based PANI/SWCNT composite.
- π−π interaction between PANI and SWCNT is confirmed by FTIR and UV −Vis spectroscopy.

GRAPHICAL ABSTRACT



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ABSTRACT

This study is aimed at investigating the effect of different oxidants on properties of polyaniline/single walled carbon nanotubes (PANI/SWCNT) composites and scrutinizing a suitable oxidant to improve the properties of composites. PANI/SWCNT composites were fabricated via ultrasonically initiated in-situ chemical polymerization technique using four different oxidants; hydrogen peroxide (H_2O_2), ammonium peroxidisulphate ($(NH_4)_2S_2O_8$), potassium dichromate ($K_2Cr_2O_7$) and potassium iodate (KIO_3). Percent yield (97%), molecular weight (45532 g mol^{-1}) and electrical conductivity (0.835 S cm^{-1}) were found maximum for composite prepared in the presence of H_2O_2. Structural confirmation of PANI and charge transfer complex formation between PANI and SWCNT were confirmed by fourier transform infrared spectroscopy, UV−visible spectroscopy and X-ray diffraction spectroscopy. Thermogravimetric analysis verified that the PANI/SWCNT composite synthesized using H_2O_2 had maximum thermal stability with least thermal degradation (~28%). Minimal thermal transitions of the composite were also observed for same composite by differential scanning calorimetry. Scanning electron microscopic images of PANI/SWCNT composites revealed that SWCNT were properly dispersed in PANI matrix when H_2O_2 was used. Above results provide the valuable suggestion that; H_2O_2 is a promising oxidant to enhance structural, thermal, electrical and microscopic properties of composites.

* Corresponding author.
** Corresponding author.
E-mail addresses: gullchemist@gmail.com (N. Gull), shahzadkhan81@hotmail.com (S.M. Khan).

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1. Introduction

Carbon nanotubes (CNT), discovered by Iijima in 1991 [1], have received considerable attention due to their exotic properties like novel structure, outstanding electrical conductivity, high chemical stability, large surface area and high aspect ratio [2,3]. These properties make them valuable for potential applications in nano-electronics and biomedical field [4–6]. Despite the tempting properties of single walled carbon nanotubes (SWCNT), their low solubility in most of the organic solvents causes the homogeneous dispersion of SWCNT in the polymer matrix very difficult and limits their applications. Dispersion of SWCNT into matrix can be improved by either mixing in a conical twin-screw extruder, functionalization of SWCNT or through ultrasonication [7,8].

Polyaniline (PANI) is one of the most intensively studied conducting polymers because of its facile synthesis, strong biomolecular interactions and exciting electrical, electrochemical and optical properties [9,10]. It holds great promise than other conducting polymers due to its unique tuneable conductivity either by protonation or charge-transfer doping. Due to its conducting behavior and thermal stability, it has been widely used in electrocatalysis, electrochromic devices and biosensors [11–13]. Though, PANI has several advantages like high polymerization yield, good redox reversibility, high thermal and environmental stability yet it shows its conductivity only in acidic media at pH < 3 in Emeraldine salt state [14,15]. Chemistry of PANI is generally more complicated than other conducting polymers, owing to its dependency on different oxidation states which are pernigraniline base (fully oxidized form), emeraldine base (50% oxidized form) and leucoemeraldine base (fully reduced form) shown in Fig. 1 [16].

PANI reacts with SWCNT and form a composite with improved properties than either of the individual constituents [17]. Charge transfer reaction between PANI and SWCNT is facilitated due to overlapping of π-electrons between the graphitic structure of SWCNT and aromatic ring of PANI [18]. The molecular interaction between PANI and SWCNT is shown in Fig. 2.

In addition, SWCNT provide good reinforcement and enhanced thermal stability to PANI thus make them more appropriate for microelectronic applications such as biosensors, supercapacitors, metal-semiconductor devices and actuators [19]. However, it is crucial to tailor the properties and structures of composites in several applications by tuning the interfacial structure, thermal stability and morphology of PANI and SWCNT [13].

In-situ chemical polymerization method for fabrication of PANI/SWCNT composites is widely used due to its economical feasibility, high efficiency and robust strategy for mass production [20]. In this method, several oxidants can be used such as: $K_2Cr_2O_7$, $(NH_4)_2S_2O_8$, KIO_3, NH_4VO_3, etc. [21,22]. Oxidant plays an important role in chemical polymerization strategy of PANI based composites, particularly on redox state, degree of polymerization, degree of protonation, structural features and electrical, thermal and morphological properties [23].

In this work, we used a facile approach for the synthesis of PANI/SWCNT composites via ultrasonically initiated in-situ chemical polymerization using different oxidants and then systematically studied the physical, structural, thermal, electrical and morphological properties of these composites. Ultrasonication was carried out to reduce the entanglement and agglomeration of SWCNT in aqueous solution, so that in-situ polymerization of PANI/SWCNT can proceed with considerably small concentration of oxidant.

2. Experimental details

2.1. Materials

Aniline (purchased from Riedel deHaën, USA) was double distilled before treatment. SWCNT (acquired from CNME, International CO. Ltd.) with mean diameter 1.2 nm and length 50 μm were used in this study. Hydrochloric acid (37%), (obtained from Labscan Asia co. Ltd., Thailand) was used as doping agent. Methanol (obtained from Riedel deHaën, USA) was used for washing the final product. $(NH_4)_2S_2O_8$, H_2O_2, $K_2Cr_2O_7$ and KIO_3 (purchased from Merck, Germany) were used as oxidants for polymerization. Deionised water was used for the preparation of all solutions.

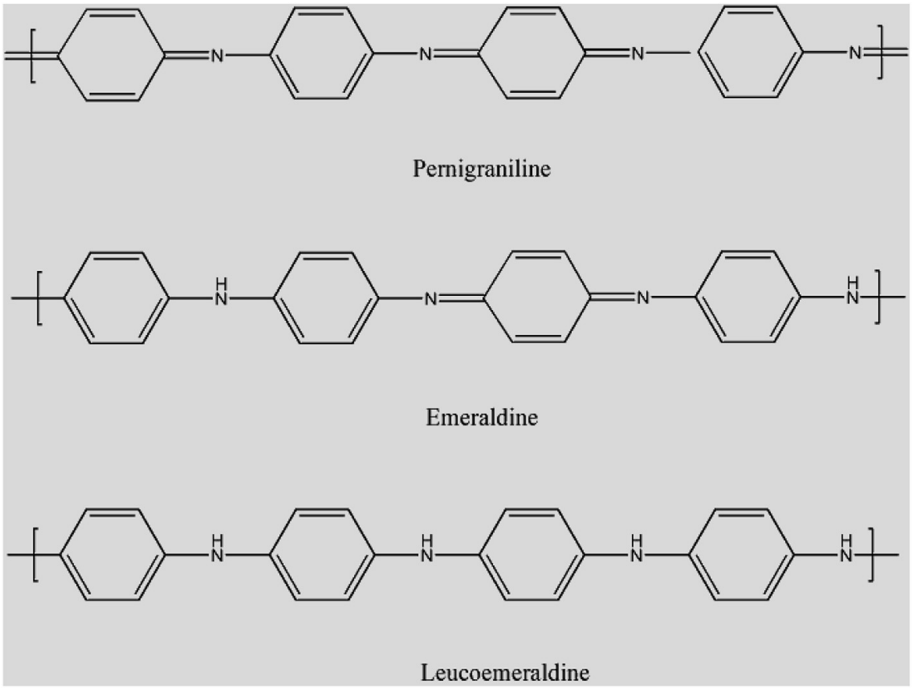

Fig. 1. Different oxidation states of PANI.