Dielectric behavior of Polyaniline based Carbon Nanocomposite

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***Abstract*- Conducting polymers nanocomposite materials have emerged as a critical field of study in contemporary science and technology. Nanoparticles and nanocomposites composed of metals, polymers, carbon nanotubes, because of their optical, mechanical, dielectric, chemical, and magnetic properties, have been used in a huge number of applications. The current work agreements with the study of Dielectric properties of PANI/TiO_2, PANI/MWCNT and PANI/TiO_2/MWCNT carbon nanocomposites which are prepared by an "In-situ chemical oxidation polymerization of aniline" using ammonium peroxide sulfate (APS) as an oxidant. The dielectric constant value enhanced by 109.21% as observed for PANI/TiO_2 composite whereas in PANI/MWCNT composite this improvement observed 134.08%. Moreover, for PANI/TiO_2(8wt%) /MWCNT(8wt%) nanocomposites dielectric constant evaluated 157.49% improved with respect to polyaniline (PANI) specimen. The study finds that PANI/TiO_2/MWCNT specimens show superior structural and electrical characteristics, making them suitable for research and development in the area of energy storage devices and application.**

Keywords: Conducting Polymer, Nanocomposites, In-situ chemical oxidation polymerization, Dielectric properties.

1. INTRODUCTION

Nanomaterials possess unique physical properties on both the molecular and macroscales, opening up new avenues for physicochemical and biomedical study and application in a variety of fields of chemistry, genetics, and medicine. Commercially, energy storage systems are classified into mechanical (flywheel system for storing energy, compressed air energy storage systems, and hydroelectric energy storage systems), electromagnetic (capacitor, inductor, supercapacitor, and superconducting magnetic energy storage systems), chemical (biofuels, hydrogen, and liquid nitrogen), and biological energy storage systems [1–4]. The carbon atoms in conjugated polymers have alternating single and double bonds. Each bond incorporates a strong localised sigma bond that holds the polymer together, as well as a weaker localised π -bond. This unsaturated π -bonded polymers have low ionisation potentials and strong electron affinities, facilitating oxidation-reduction reactions. Thus, the electrical structure of conjugated polymers is radically distinct, with one vacant electron (the π -electron) in a single carbon atom due to chemical bonding. The overlapping of π -orbitals comprising consecutive atoms of carbon in the backbone of the polymer results in relocation of electrons along the polymer's backbone. This relocation of electrons creates a path for charge mobility around the polymer chain's backbone. Thus, the electrical composition of conducting polymers is defined as chain symmetry, i.e. the amount and type of atoms inside the repeat unit, resulting in semiconducting or even metallic properties for these polymers. Scientists are compelled to discover a way forward via a variety of methods, including the development of novel materials with superior energy conversion, storage, and use capabilities [5–7]. For example, electrochemical double-layer capacitors often referred to as supercapacitors, have piqued the interest of academics worldwide due to their potential use as energy storage devices [8].

Polymer nano-composites have received significant research and development attention due to their inclusive variety of applications in solar cells, energy storage devices, and sensors [9–10]. Particularly popular in recent years has been the creation of nanocomposites including conducting polymers and carbon allotropes, which has sparked significant attention due to the synergistic advantages that can be obtained by mixing these two kinds of materials. In conducting polymers (CPs), polyaniline (PANI) has long been the most popular choice owing to its water solubility and high conductivity, as well as its outstanding redox reversibility and environmental durability. Although PANI shows poor mechanical stability compared to other CPs, it is mostly due to the typical shrinking, breaking, and cracking that happens in a hostile environment as a result of volumetric changes in the polymer during the charging and discharging processes [11]. Many research projects are being carried out with the goal of developing materials with improved stability, high porosity characteristics, and good capacitive behaviour through the use of fillers in order to address the issue of PANI's poor stability. The majority of research focused on the optical characteristics of polymer-modified TiO_2 nanoparticles. High dielectric constant materials, such as capacitors and gate oxides, are very helpful in integrated electronic circuits. PANI doped with carbon allotropes has unique structural and electrochemical characteristics, as well as a high degree of stability, and therefore has enormous potential for use as filler materials in the electrode assignment of their PANI composites. In view of this, the present paper is related and dielectric study of specifically prepared PANI, PANI/TiO_2(8wt%), PANI/MWCNT(8wt%) and PANI/TiO_2 (8wt%) base matrix dispersed with MWCNT (8wt%) nanocomposites.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of Nanocomposites

The PANI, PANI/TiO_2 (wt%), PANI/MWCNT (8 wt%) and PANI/TiO_2/MWCNT nanocomposite materials were synthesised by in situ utilising "Ammonium peroxide sulphate (APS) [$(NH_4)_2S_2O_8$)] as an oxidant" in the presence of colloidal MWCNT (8wt%) and TiO_2 (8wt%) nanoparticles, respectively, at 0-5^{0}C in air [12-13].

2.2 Characterization of Nanocomposites

X-ray diffractometry (XRD, Bruker AXS D-8 Advance Diffractometer) was used to determine the phase and orientation of nanocomposites. Using an impedance analyzer, we investigated the dielectric characteristics of nanocomposites (Agilent 4294A precision).

3. RESULTS AND DISCUSSION

3.1 Structural characterization

The X-ray diffraction patterns corresponding to PANI, PANI/TiO_2 (8wt%), PANI/MWCNT (8wt%), and PANI/TiO_2(8wt%)/MWCNT(8wt%) nanocomposites are as shown in figure 1.

In figure 1 curve for pure PANI, shown the amorphous hump with no evidence of crystallinity of PANI, while exhibit two characteristic peaks for instance first sharp peak is observed at 25.25° which is due to combined effect of diffraction from anatase phase lattice plane of TiO_2 and graphite-like structure in multi wall of CNT [14]. Interestingly this composite also exhibits a second characteristic peak at 38.39° due to the presence of the dominant MWCNT crystalline phase [15]. Overall all of these specific samples become more crystalline, exhibit characteristic peaks of their doped constituents with slight shifting of respective diffraction angle.

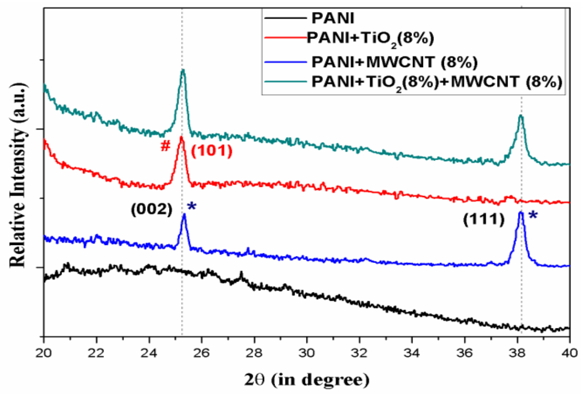

Fig. 1: XRD patterns of Pure PANI, PANI/TiO_2(8%), PANI/MWCNT(8%) and PANI/TiO_2(8%)/MWCNT(8%)

3.2. Dielectric properties

At room temperature, the relative dielectric constant and loss tangent profile curves of PANI, PANI/TiO_2(8wt%), PANI/MWCNT(8wt%) and PANI/TiO_2(8wt%)/MWCNT(8wt%) are as shown in figure 2 & 3, respectively. The Relative Dielectric constant profile curves for all the studied samples follows the "Debye-like relaxation mechanism" trends. At low frequency region dipole moments follow the applied field which causes higher values of dielectric constant but as we increase the frequency the field cannot induce the dipole moment which reduces the value of dielectric constant [16–18].

The value of dielectric constant of pure PANI specimen is evaluated 68.35. The structural analysis of respective TiO_2 and MWCNT filled PANI composite also reveals the formation of morphologically strengthen composite system formation therefore enhancement in dielectric properties of such composites is quite expecting. The dielectric constant value enhanced by 109.21% as observed for PANI/TiO_2 composite whereas in PANI/MWCNT composite this improvement observed 134.08%. Moreover, for PANI/TiO_2(8wt%)/MWCNT(8wt%) nanocomposites dielectric constant evaluated 157.49% improved with respect to pure PANI specimen. The evaluated values of Dielectric constant and loss tangent are as tabulated in Table 1 respectively. The loss tangent "tan δ" curves also follow the typical characteristic trend of base matrix PANI polymers as a decrease in "tan δ" values with increasing frequency in accordance with results reported in literature [16]. The higher dielectric constants along with higher loss tangent (dielectric losses) might originate from the increased conductivity, lowering the bandgap values as attributed in optical characterization due to dispersion of TiO_2 and MWCNT nanofillers that finally paved improved charge transport network in the relative PANI matrix.

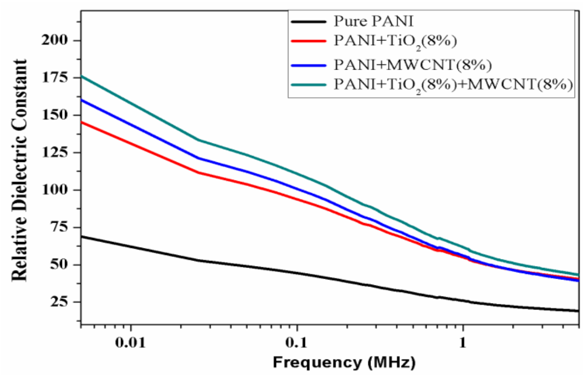

Fig. 2: Relative Dielectric constant Vs frequency of Pure PANI, PANI/TiO_2(8%), PANI/MWCNT(8%) and PANI/TiO_2(8%)/MWCNT(8%).

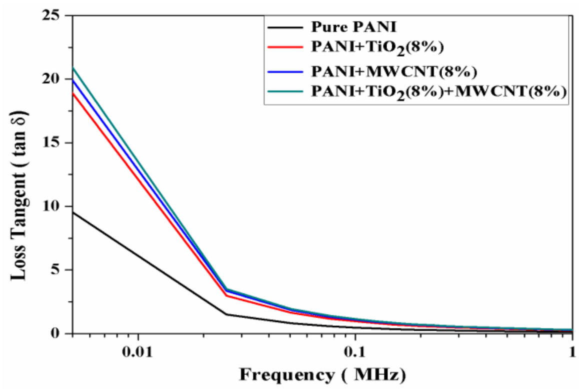

Fig. 3: Loss tangent Vs frequency of Pure PANI, PANI/TiO_2(8%), PANI/MWCNT(8%) and PANI/TiO_2(8%)/MWCNT(8%).

Table 1: Dielectric constant and loss tangent of pure PANI and PANI nanocomposites

S.No.	Nanocomposites	Dielectric Constant	Loss tangent
1	PANI	68.35	9.5
2	PANI/TiO_2(8%)	143	17.8
3	PANI/MWCNT(8%)	160	19.9
4	PANI/TiO_2/MWCNT(8%)	176	21.8

4. CONCLUSIONS

The study of structural, and dielectric study of specifically prepared PANI, PANI/TiO_2 (8wt%), PANI/MWCNT (8wt%), and PANI/TiO_2 (8wt%) base matrix dispersed with MWCNT (8wt%) nanocomposites reveals the following conclusions:

X-ray diffraction (XRD) study reveals that PANI/TiO_2(8wt%)/MWCNT(8wt%) composite exhibit dominant characteristic peaks due to TiO_2 and MWCNT crystalline phases along with slight shifting of some respective diffraction angles observed.

The PANI/TiO_2/MWCNT nanocomposites offer better dielectric constant and loss tangent values in comparison to other studied samples. The dielectric constant value enhanced by 109.21% as observed for PANI/TiO_2 composite whereas in PANI/MWCNT composite this improvement observed 134.08%. Moreover, for PANI/TiO_2(8wt%)/MWCNT(8wt%) nanocomposites dielectric constant evaluated 157.49% improved with respect to polyaniline (PANI) specimen. Finally, the study finds that PANI/TiO_2/MWCNT specimens show superior structural and electrical characteristics, making them suitable for research and development in the area of energy efficient supercapacitor design and application.

5. REFERENCES

[1] S. S. Siwal, Q. Zhang, N. Devi, and V. K. Thakur, “Carbon-based polymer nanocomposite for high-performance energy storage applications,” Polymers (Basel) (2020), 12, 3, 1–3.

[2] A. T. Smith, A. M. LaChance, S. Zeng, B. Liu, and L. Sun, “Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites,” Nano Mater. Sci. (2019), 1, 1, 31–47.

[3] R. Singh and R. B. Choudhary, “Optical absorbance and ohmic behavior of PANI and PANI/ZnO nanocomposites for solar cell application,” Optik (Stuttg). (2016), 127, 23, 11398–11405.

[4] J. Liu, X. Zhao, J. Zang, C. Cao, and Y. Feng, “Stretchable and High-Performance Supercapacitors with Crumpled Graphene Papers,” Sci. Rep. (2014), 4, 1, 1–7.

[5] Dorraji, MS Seyed, I. Ahadzadeh, and M. H. Rasoulifard. "Chitosan/polyaniline/MWCNT nanocomposite fibers as an electrode material for electrical double layer capacitors." International journal of hydrogen energy (2014), 39, 17, 9350-9355.

[6] Zhang, Yakun, Jianling Li, Feiyu Kang, Fei Gao, and Xindong Wang. "Fabrication and electrochemical characterization of two-dimensional ordered nanoporous manganese oxide for supercapacitor applications." international journal of hydrogen energy (2012), 37, 1, 860-866.

[7] Huang, Ke-Jing, Lan Wang, Yu-Jie Liu, Yan-Ming Liu, Hai-Bo Wang, Tian Gan, and Ling-Ling Wang. "Layered MoS2–graphene composites for supercapacitor applications with enhanced capacitive performance." International journal of hydrogen energy (2013), 38, 32, 14027-14034.

[8] Zhang, Yong, Hui Feng, Xingbing Wu, Lizhen Wang, Aiqin Zhang, Tongchi Xia, Huichao Dong, Xiaofeng Li, and Linsen Zhang. "Progress of electrochemical capacitor electrode materials: A review." International journal of hydrogen energy (2009), 34, 11, 4889-4899.

[9] Li, Wei, and Dojin Kim. "Polyaniline/multiwall carbon nanotube nanocomposite for detecting aromatic hydrocarbon vapors." Journal of materials science (2011), 46, 6, 1857-1861.

[10] Yin, Zhigang, Yunhai Ding, Qingdong Zheng, and Lunhui Guan. "CuO/polypyrrole core–shell nanocomposites as anode materials for lithium-ion batteries." Electrochemistry communications (2012), 20, 40-43.

[11] Kumar, A. Madhan, and Zuhair M. Gasem. "In situ electrochemical synthesis of polyaniline/f-MWCNT nanocomposite coatings on mild steel for corrosion protection in 3.5% NaCl solution." Progress in Organic Coatings (2015), 78, 387-394.

[12] S. G. Bachhav and D. R. Patil, “Synthesis and Characterization of Polyaniline-Multiwalled Carbon Nanotube Nanocomposites and Its Electrical Percolation Behavior,” Am. J. Mater. Sci. (2015), 5, 4, 90–95.

[13] Srivastava, Subodh, Sumit Kumar, V. N. Singh, M. Singh, and Y. K. Vijay. "Synthesis and characterization of TiO2 doped polyaniline composites for hydrogen gas sensing." International Journal of Hydrogen Energy (2011), 36, 10, 6343-6355.

[14] Z. F. Li, H. Zhang, Q. Liu, Y. Liu, L. Stanciu, and J. Xie, “Covalently-grafted polyaniline on graphene oxide sheets for high performance electrochemical supercapacitors,” Carbon N. Y. (2014), 71, 257–267.

[15] Li, Fang, JunJun Shi, and Xue Qin."Synthesis and supercapacitor characteristics of PANI/CNTs composites." Chinese science bulletin (2010), 55, 11, 1100-1106.

[16] Lu, Jiongxin, Kyoung-Sik Moon, Byung-Kook Kim, and C. P. Wong. "High dielectric constant polyaniline/epoxy composites via in situ polymerization for embedded capacitor applications." Polymer (2007), 48, 6, 1510-1516.

[17] Soares, Bluma G., Maria Elena Leyva, Guilherme MO Barra, and Dipak Khastgir. "Dielectric behavior of polyaniline

synthesized by different techniques." European Polymer Journal (2006), 42, 3, 676-686.

[18] Yan, X. Z., and T. Goodson. "High dielectric hyperbranched polyaniline materials." The Journal of Physical Chemistry B (2006), 110, 30, 14667-14672.