Investigations on the influence of nano-ZnO in Thermal and Dielectric properties of Poly (o-toluidine)

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In the recent years, attention on developing nanocomposite with novel characteristics increases enormously mainly to meet various demands of application in different industries. Compositeof zinc oxide incorporated poly (o-toluidine) (POT) has been synthesised employing *in situ*-chemical oxidation method. The physical and electrical properties of synthesized samples were studied using X-ray diffraction (XRD), Thermal gravimetric analysis (TGA) and Dielectric analysis. The results of XRD ensured the elemental influence in the polymer nanocomposite samples. TGA analysis reveals that the residue mass (stability)of the material, even after 850°C, increases by increasing the concentration of zinc oxide in the POT. Increasing quantity of ZnO in POT helps to increase its dielectric constant and permittivity at the function of temperatures.

Keywords: Poly (o-toluidine) / n-ZnO,In situ-chemical oxidation method, TGA,Dielectric property.

1. Introduction

Development of polymer nanocomposites with incorporation of metal oxides increasing enormously in the recent years mainly to meet application demands in various fields. Polyaniline (PANI) is one of the prominent conducting polymers having exceptional electron conductivity due to its conjugated chemical bonds. Nanocomposite materials derived with the polymer as host material find applications in supercapacitors due to its high specific capacitance[1]. Poly (o-toluidine) (POT) is a derivate of PANI in which '--CH_3' is formed in the orth position of aromatic ring of the aniline monomer. POT retains its electrical conductivity nature as found in PANI can be easily synthesized in laboratories. These kinds of polymers find applications in sensors, photocatalytic, batteries, antimicrobial and anticorrosion [2-6].Zinc oxide is one of the metal oxides being a familiar transparent conducting oxide (TCO) with exceptional optical,electrical and thermal properties [7, 8].

Application of polymer nanocomposite as dielectric material also increases enormously mainly because of their unique characteristic features. In general, organic materials are of the least choice as dielectric material due to its lower dielectric responses and most of them not favour to induce the charge in the applied electric field. Inorganic materials like ceramic have exceptional dielectric property and found to be used as dielectric material in many cases. Polymer nanocomposite is the unique material composed with organic polymers with incorporation of inorganic additives. Its dielectric characteristics also found to be exceptional not observed earlier. Dielectric constant of these nanocomposites also can be tailor-made by incorporating polarisable components for copolymerisation and thereby enhance free volume in material structure. Estimated dielectric constant of most of the synthesised polymer nanocomposites is remarkably high and its role is most appreciable as capacitor in the novel energy storage devices. One of the research articles reporting the increase of dielectric constant of organic element polyaniline owing to the incorporation of inorganic component nickel oxide by virtue of ionic migrations in the composite material. Thus, incorporation of metal oxides into the polymeric network influenced enough to enhance its properties such as thermal, antimicrobial, etc. as reported in earlier observations [9, 10].

In the present work, polymer nanocomposite samples with incorporation of ZnO nanoparticles of different quantities such as 25, 50 and 75 Wt.% in poly (o-toluidine) host network has been synthesised employing *in situ* chemical oxidative polymerisation method. Synthesised three samples were tagged as PZnO25, PZnO50 and PZnO75 representing 'P' for host material 'ZnO' for incorporated metal oxide (nano zinc oxide) followed by its quantity of incorporations. Properties of the present samples have been observed using the tools such as XRD Thermogravimetric Analysis (TGA), Dielectric Analysisto explore the structural and crystalline characteristics, thermal responses and electrical property. It is also aimed to identify the suitability of present polymer nanocomposite samples to apply in capacitors since the proposed incorporation of metal oxides like zinc oxide has superior dielectric properties [11].

2. Experimental

2.1. Synthesis of Poly (Ortho - toluidine) (POT) and Pot/ZnO

In the present work, series of nanocomposite samples has been synthesised employing *in situ* chemical oxidative polymerisation method. Necessary chemicals were procured from Sigma Aldrich (99% purity) and MERK and used without any further purifications. The synthesis process, namely, *in situ* chemical oxidative polymerisation employed effectively in strong acidic medium. 1.2 mol L^{-1} of HCl is mixed with 3.6g of potassium dichromate and stirred for 1 hour simultaneously (o-toluidine) was mixed with nano zinc oxide with different weight perctange in seprate magnetic stirrer for 2 hours, both solutions were mixed together and grenish colour precipitate was observed and it was filtered and washed with warm water for several times. The obtained sample was kept in hot air oven for 12hrs and finally grinded.

3. Results and discussion

3.1. X-ray Diffraction (XRD)

X-ray diffraction study is a tool used to explore the structure of a material. In the present work, the prepared composite samples possessing ZnO quantity respectively 25, 50 and 75wt% in POT are named as PZnO25, PZnO50 and PZnO75 used to study its characteristic features. The observed XRD results of these three samples are shown in Fig.1.. The obtained XRD trace of PZnO25 reveals abroad characteristic peak in amorphous background around 20° can be attributed to the POT element and it is not obtained in PZnO50 and PZnO75 . There is a noisy and rearrangement of diffraction peaks could be found in PZnO50. It shows the structural reformation in the composite structure by virtue of ZnO additions. The quantity of ZnO starts to influence enough above 25 Wt.% of incorporations. The observed crystalline data ensured the hexagonal structure and using the crystalline data the other features like size are estimated by Scherrer equation and it is noted that PZnO25 has 20nm, PZnO50 has 12nm and PZnO75 has 7nm respectively. Observed diffraction peaks at the glancing angles 33.4°, 35.91°, 46.7°, 61.38°, and 66.35° Correspond to (002), (101), (102), (103) and (200) planes respectively. All these diffraction peaks are matched well with (JCPDS No. 89-1397,36-1451). In PZnO75 characteristic peaks at the glancing angles 27.29° and 40.37° due to increase in additive of zinc oxide reveals that the material has changed to crystalline nature.

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where, D is the crystallite size, k is the shape factor for the average crystallite (0.9), λ is the wavelength of the X-ray which is 1.54 Å for Cu target, β is the full width at half maxima of the crystalline peak in radians, θ is the angle between incident and reflected rays

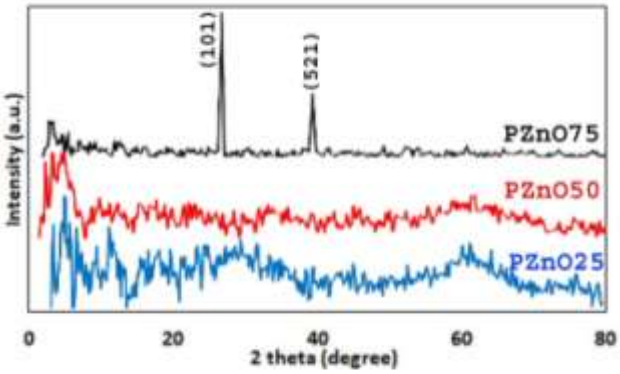

Fig.1. XRD of POT-n-ZnO

3.2. Thermogravimetric analysis (TGA)

The observed thermogravimetric analysis results are shown in Fig.2. This analysis explores the reaction of involved sample such as mass change, etc. against the application of thermal energy. Against the progressive increase of thermal energy, the changes occurred in the samplemass has been observed and recorded correspondingly at every thermal stage. It is clear from the observed TGA results (Fig.2) of polymer nanocomposites, that the rate of degradation is different in each stage of thermal scanning.As shown in Figure 3, the mass and volume of the sample decreases significantly. In this stage, the components including additive elements liberate from the structural bonding and thereby release exothermically. It has been observed that the thermal stability of composite samples rise abruptly with the concentration of ZnO, due to the influence of zinc oxide [12].In third stage, the entire polymeric network including dopant elements decomposes and the residue mass only withstand at the end. Mass changes at every stage of thermal analysis given in detail (Percentage wise) in Table 2. It has been seen that after 530°C, observed weight loss is the result of degradation of quinoid ring structure of polymer [12,13]. At the end of the TGA analysis t reveals that the thermal stability of composite increases with the additive quantity of incorporations. The samples with higher quantity of n-ZnO (PZnO75) records higher residue mass.

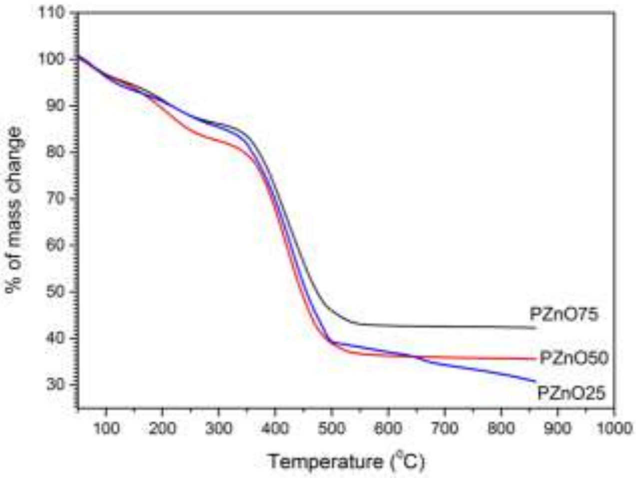

Fig.2. Thermal gravimetric analysis(TGA) curve of POT-n- ZnO

Table.1. Thermogravimetric analysis (TGA) of PZnO nanocomposites

Temperature (°C)	Weight loss (%)		
	PZnO25	**PZnO50**	**PZnO75**
144	7.16	6.7	6.25
264	15.27	15.11	14.8
327	17.8	17.65	16.5
532	22.2	28.19	37.6
Residue mass	**28.89%**	**34.76%**	**40.58%**

3.3. Dielectric analysis

In the present work, frequency dependence analysis helps to explore the interaction of metal oxide with the polymer compound. The charge carriers migrate and lead to large polarization against the applied external field that causes high dielectric constant [14]. The dielectric constant or relative permittivity is calculated by the equation 2.

$$\varepsilon_r = C \times D / \varepsilon_0 A \text{ ---------------------- } (2)$$

Where 'C' is the capacitance of the sample, D and A are the thickness and area of the sample, ε_0 dielectric permittivity of vacuum

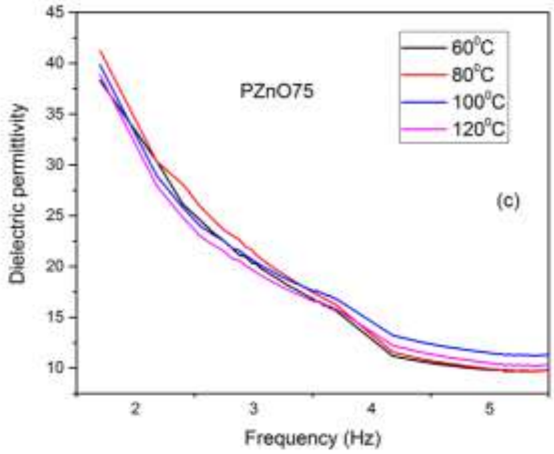

Fig.3 Shows dielectric permittivity with different temperature at different frequencies (POT doped with 75wt% of ZnO)

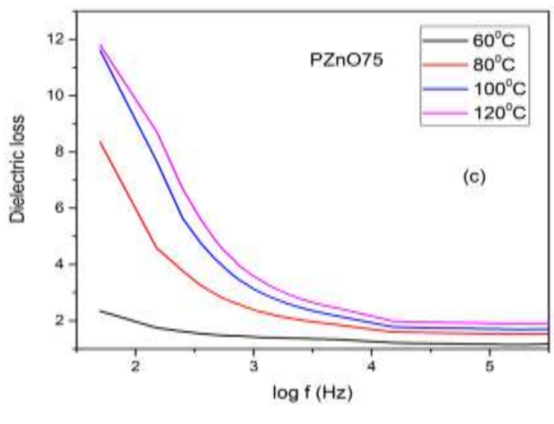

Fig.4 Shows dielectric loss with different temperature at different frequencies (POT doped with 75wt% of ZnO)

Nanomaterial has unique dielectric characteristics such as space charge polarization and rotation direction polarization [15]. More specifically, zinc oxide has high dielectric constant caused by the rotation direction polarization.dielectric loss in the sample at different temperature for the applied frequencies. Change in relative permittivity at the function of temperature reveals the dipole moment of molecules. Increase of ε_r is recording the free movement of charges at high temperature and it is expected to be fixed at the low temperature. In the sample with higher additive content (n-ZnO), permittivity ε_r increases and it shows that the incorporated n-ZnO content facilitates the charge migration in POT network and thereby increase the dipole moment. The raise in the loss tangent is due to the core – shell interfacial reaction at high temperature and increasing the quantity of dopant (n-ZnO). These results revelas that the prepared sample is suitable for different electronics application

4. Conclusion

Series of poly (o-toluidine) with incorporation of n-ZnO in different quantity has been synthesized by *in situ*-chemical oxidation method. Characteristic observation using XRD, , TGA and dielectric studies has been employed. Results of XRD reveal the improved crystalline orientation with hexagonal structure in POT sample by virtue of n-ZnO incorporation in high quantity (75 Wt. %). Estimated crystallite size increases with the addition of nano zinc oxide. TGA analysis explored the increase in thermal stability of polymer nanocomposite with increasing quantity of nano zinc oxide. PZnO75 has higherloss of dielectric conductivityand permittivity due to the large amount of oxygen vacancies. Incorporation of nano sized particles also influenced in enhancing dielectric properties.

References

[1] Zh. A. Boeva,V. G. Sergeyev, Polyaniline: Synthesis, Properties, and Application, Polymer Science series C, 56, (2014), 153-164.

[2] George, R.S.Andrade, Cristiane C, Nascimento, Zenon M . Lima, Erico Teixeira – Neto, Luiz .P. Costa, Iara F. Gimenez, Star shaped ZnO/Ag hybrid nanostructures for enhanced photocatalysis and antimicrobial activity, Applied surface science, 399 (2017) 573-582.

[3] A.M. Ismail , A.A.Menazea , HodaA.Kabary, A.E.El-Sherbiny, A.Samy,The influence of calcination temperature on structural and antimicrobial characteristics of zinc oxide nanoparticles synthesized by Sol–Gel method,Journal of Molecular Structure, 1196, (2019) 332-337.

[4] MeeriVisnapuu, MerilinRosenberg,EgleTruska, ErgoNõmmiste , AndrisŠutka , AnneKahru ,MihkelRähn , HeikiVija , KajaOrupõld , VambolaKisand , AngelaIvask , UVA-induced antimicrobial activity of ZnO/Ag nanocomposite covered surfaces,Colloids and Surfaces B: Biointerfaces , 169 (2018) 222-232.

[5] Milica M. Gvozdenovic, Braninir Z. Jugovic, Bojan M. Jokic, Enis S. Dzunuzovic, Braninimir N. Grgur, Electrochemical synthesis and characterization of poly(*o*-toluidine) as high energy storage material,Electrochimica Acta, 317 (2019) 746-752.

[6] XiaoyunBai, Guihua Chen, Kwok-Keung Shiu Electrochemical biosensor based on reduced graphene oxide modified electrode With Prussian blue and poly(toluidine blue O) coating, Electrochimica Acta, 89 (2013) 454– 460.

[7] Siti HuzaimahRibut , Che AzurahanimChe Abdullah , Mohd ZakiMohammad Yusoff, Investigations of structural and optical properties of zinc oxide thin films growth on various substrates, Results in Physics,13 (2019) 102146,

[8]A.Ismai, M.J.Abdullah, The structural and optical properties of ZnO thin films prepared at different RF sputtering power, Journal of King Saudi University – Science, 25 (2013) 209-215.

[9] Arunachalam Mahudeswaran, Devarajan Manoharan, Joseph Chandrasekaran, Janakiraman vivekanandan, Pachanoor Subbaian Vijayamamd, CSA doped Poly (aniline-co-o-toluidine) and Dispersed Zinc Oxide Nanoparticles: a Promising Material for Photovoltaics, Materials Research, 18 (2015) 482-488.

[10] Asif Ali Khan, ShakeebaShaheen,Thermal stability and electrical properties of conducting polymer based 'polymeric -inorganic' composites:Poly- o-anisidine and poly-o-toluidine Sn(IV) tungstate, Materials Research Bulletin 47 (2012) 4414–4419.

[11] Arup Choudhury, Carboxyl-functionalized MWCNT doped poly(o-toluidine) nanohybrids: Synthesis, characterization with AC electrical and dielectric properties, Synthetic Metals, 188 (2014) 13– 20.

[12] SalmaBilal, Shehna Farooq, Anwar-ul-HaqAliShah, RudolfHolze, Improved solubility,conductivity thermal stability and corrosion protection properties of poly(o-toluidine) synthesized via chemical polymerization, Synthetic Metals, 197 (2014) 144–153.

[13] Aisha Batool, Farah Kanwal, Muhammad Imran,Tahir Jamil, Saadat Anwar Siddiqi, Synthesis of polypyrrole/zinc oxide composites and study of their structural, thermal and electrical properties, 161 (2012) 2753-2758

[14] K. Jeyasubramanian, R.V. William, P. Thiruramanathan, G.S. Hikku, M. Vimal Kumar, B. Ashima, PandiyarasanVeluswamy, Hiroya Ikeda, Dielectric and magnetic properties of nanoporous nickel doped zinc oxide for spintronic applications, Journal of Magnetism and Magnetic Materials 485 (2019) 27–35.

[15] Amrut.S. Lanje, Satish J. Sharma, Raghumani S. Ningthoujam, J.S. Ahn, Ramchandra B. Pode, Low temperature dielectric studies of zinc oxide (ZnO) nanoparticles prepared by precipitation method, advanced powder technology, 24 (2013) 331-335.