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Dielectric and ac conductivity studies on Polyvinyl alcohol/Nickel Oxide Nano composites

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Abstract: Dielectric properties of Polyvinyl alcohol/Nickel oxide nanocomposite films have been studied in the present work. Nickel oxide nano powder is synthesized by Low Solution Heat Combustion method. The films were prepared by solution-casting technique. The prepared films have been characterized by X-ray diffraction (XRD) analysis. The XRD pattern of pure PVA shows a characteristic peak at 20° indicating its semicrystalline nature. The crystallite size of these nanoparticles is found to be ~44 nm. The dielectric permittivity, dielectric loss of PVA/NiO nanocomposites decreased with increase in frequency values.

Keywords: Polyvinyl alcohol, Nano Nickel oxide, X-ray diffraction, Dielectric parameters

1. Introduction

The polymer-nano composites in last few decades, have became the subject of worldwide research interest. Numerous research works, patent and funding are generated out of this field. To export the full potential of the technological applications of these materials, it is very important to endow them with good processibility, which has ultimately guided scientists towards using conventional polymers as one component of the composites, resulting in a special class of hybrid materials termed ‘polymeric nano composites’. Many investigations [26] regarding development of incorporation techniques of particles into the polymers matrices have been reported. The resulting composites have found successful applications in versatile fields e.g. battery cathodes [**1**], microelectronics [**2**], no linear optics [**3**], sensors [**4**] etc.

Nickel oxide NiO is an important transition metal oxide with cubic lattice structure. It has attracted increasing attention owing to potential use in a variety of applications such as: catalysis [5], battery cathodes [6], [7], gas sensors [8], electro chromic films [9] and magnetic materials [10], [11]. It can also be extensively used in dye sensitized photocathode’s [12]. It exhibits anodic electrochromism, excellent durability and electrochemical stability, large spin optical density and various manufacturing possibilities [13]. Also for low material cost as an ion storage material, NiO semiconductor becomes a motivating topic in the new area of research. Because of the volume effect, the quantum size effect, the surface effect and the macroscopic quantum tunnel effect, nanocrystalline NiO is expected to possess many improved properties than those of micrometer-sized NiO particles.

With advancements in all areas of industry and technology, the interest has been focused on nanoscale materials, which stems from the fact that new properties are required at this length scale and, equally important, that these properties change with their size and morphology. Thus, many methods have been attempted to prepare nano sized nickel oxide, including nanoparticles [14], nanorings [15], nanosheets, and nanoribbons [16]. However, there are only few biosensor applications. Li et al. developed a novel amperometric glucose sensor based on NiO hollow nanosphere [17]. The NiO is suitable for electrostatic immobilization of proteins having low ionization potential because the ionization potential of NiO is about 10.7 eV and the hollow-sphered NiO was good responsible for high loading of glucose oxidize and showed fast electron transfer with a sensitivity of 3.43 $\mu A\, mM^{-1}$ and a detection limit of 47 μM (S/N=3) [18]. Fluorescence based glucose sensors have appeared in the literature as an alternative way of continuous monitoring of glucose levels. These sensors are highly specific towards analytes but require built-in probes [19]. It has been reported that glucose is used as a reducing agent in preparation of metal nanoparticles [20]. So it could be assumed that glucose in blood serum would affect the optical properties of NiO nanoparticles when they are used in the organism. In the last decade the use of glucose biosensor was constructed by using metal nanoparticles [21], [22], [23] and metal-oxide including zinc oxide, copper oxides, manganese dioxide, titanium oxides, cerium oxide and silicon dioxide [24].

Many different research groups have investigated the structural, optical, thermal and electric properties of PVA containing different dopant. The previous investigations by different researchers have establishes the fact that PVA/NiO nanocomposites are scientifically challenging materials exhibiting a wide range of fascinating properties that can lead to a great variety of physical interests and technological applications. Although there exists a few brief reports on the investigations of PVA doped with NiO. Hence in the present investigation PVA nano metal oxide, Nickle oxide (CaO) matrix have been selected as novel dopant material. We, therefore, prompted in the present study to prepare NiO nano particles using combustion method and the PVA/NiO nano composites films using solution casting method. The prepared samples will be characterized using X-ray diffraction (XRD). Also AC conductivity studies are reported.

2. Materials

PVA of analytical grade is obtained in the powder form from nice chemicals pvt. Ltd. Cochin, with the average molecular weight of 1,25,000 g/mol (98% hydrolyzed) and it is used without further purification. Calcium nitrate $Ni(NO_3)_2$is purchased from molychem ltd. Mumbai and is used without furthers purification.Double filtered lemon juice is used as a fuel. Double distilled (DD) water is locally purchased and used for the preparation of reactant solutions.

2.1. Synthesis of nano nickle oxide

Low solution combustion (LSC) technique is employed for the preparation of nano nickel oxide. It is a wet-chemical method which does not require further calcinations and repeated heating. In this method of preparation, hydrated nickel oxide [NiO] is chosen as the metal precursor. The filtered lemon juice is used as a fuel. The stiochiometric ratio of nickel oxide and fuel were taken into crucible and well dissolved in double distilled water. The aqueous redox mixture was dispersed uniformly by stirring the mixture using a starrier for 5 min. than the resulting mixture was placed into a pre-heated muffle furnace maintained at (430±10)ºC. in the beginning, the solution was thermally dehydrated and ignited with the liberation of large amount of gases (N_2, O_2 etc.).the entire process took place within 8 min. The resultant powder occupied the entire volume of the reaction vessel. The combustion was self-propagating within a few minutes the reaction was completed and fluffy powder was obtained. After completion of the process, the product obtained was grinded well using mortar and pestle. The powder is voluminous, weakly agglomerated, foamy, nano in size and has a high surface area.

2.2. Preparation of PVA films

The pure PVA films were prepared by solution casting technique powdered PVA of about 2.5 g is dissolved in 50ml of double distilled water by stirring. The solution is then warmed up to 333k and thoroughly stirred, using a stirrer, for about I hour until the polymer became completely soluble. By removing the trapped air bubbles, the solution is poured onto leveled clean glass plate and left to dry at room temperature for about 48 hours. The dried film were peeled off from the glass plate and cut into suitable pieces for measurements**.**

2.3. Preparation of PVA/NiO nano composite films

Four PVA/ $NiNO_3$ nano composite films were also prepared by the solution casting method. First , the PVA stock solution is prepared by the above method and to this solution 2 wt% ,4 wt%,6 wt% and 8 wt% of $NiNO_3$ nano powder is mixed and stirred vigorously by using stirrer until transparent PVA/nanocomposite multi component dispersion is obtained.

Further, ultrasonication is done for complete dispersal of NiO in PVA solution. Than known volume of viscous PVA/NiO nano composite solution was poured onto a leveled clean glass plate and left to dry at room temperature for about 48 hours. The dried films were peeled off the glass and cut into suitable pieces.

3. Results and Discussion

3.1. X-Ray Diffraction Studies

Powder X-ray diffraction(XRD) is one of the primary techniques used by mineralogists and solid state chemists to examine the physic-chemical makeup of unknown materials.

Fig.1 shows X-ray diffraction pattern of pure PVA. The XRD pattern of pure PVA shows a characteristic peak for an orthorhombic lattice centered at 20° indicating its semi crystalline nature [25, 26]. The peaks have resulted from the part of crystallinity in PVA polymer molecules. This crystallinity is the result of strong intermolecular and intramolecular hydrogen bonding between the PVA molecular chain [27, 28].A broad peak was noticed at$2\theta\sim20°$ that can be assigned to the Vander Wall distance of 5A°.This peak may be attributed to the intermolecular distances between neighboring chains. A small hump was observed at $2\theta\sim42°$, corresponding to an approximately hexagonal ordering of the molecular chains [29]. The Ni nanoparticles have shown good crystallinity because of the existence of sharp peaks in the XRD pattern.

The average crystallite size is found to be ~19 nm. In the XRD pattern, different lines are attributed to the (110), (111), (211), and (220) and planes are in good agreement with the data of NiO powder file (JCPDS number 47-1049) which corresponds to the cubic crystalline structure with lattice constants a=b=c=4.1771 Å.

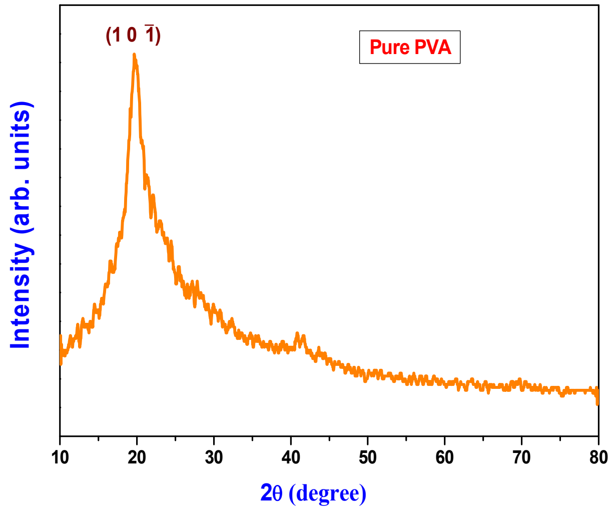

Figure 1 XRD pattern of pure PVA

Fig. 2 shows the X-ray diffraction pattern of PVA–NiO composite(2%wt. 8% wt.) and nano NiO. In the XRD pattern, different lines are attributed to the (111), (110), (211) and (220) planes; by comparing the XRD pattern ofthe composite and NiO, it is confirmed that NiO has retained its structure even though it is dispersed in PVAduring polymerization reaction.

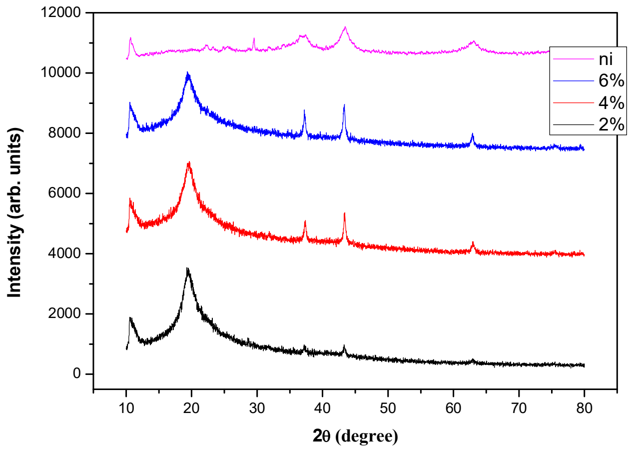

Figure 2 XRD pattern of PVA/NiO nanocomposite

3.2. ac Conductivity Measurements

The frequency dependent *ac* conductivity of prepared nanocomposite films is studied in the frequency range 100Hz to 1MHz at room temperature using LCR meter Newton Model PSM-1735. The *ac* conductivity of pure PVA at different frequencies is shown in Fig 3 at room temperature.

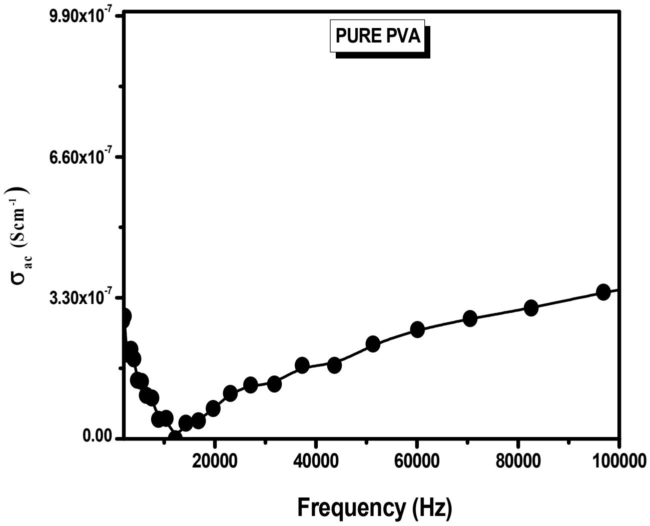

Figure 3 ac conductivityof pure PVA

At lower frequencies, the rise in conductivity is negligible. At higher frequency values, a sharp rise in the conductivity values is observed. In PVA, as the bond rotates with frequency, the existing flexible polar groups with polar bonds cause dielectric transition. Thus, there is a change in chemical composition of the polymer repeat unit due to formation of charge-transfer complexes within the PVA chains, which in turn makes the polymer chains more flexible and hence enhances *ac* electrical conductivity [30].

The *ac* conductivity of PVA-NiO nanocomposites at different frequencies is shown in Fig. 4 at room temperature.

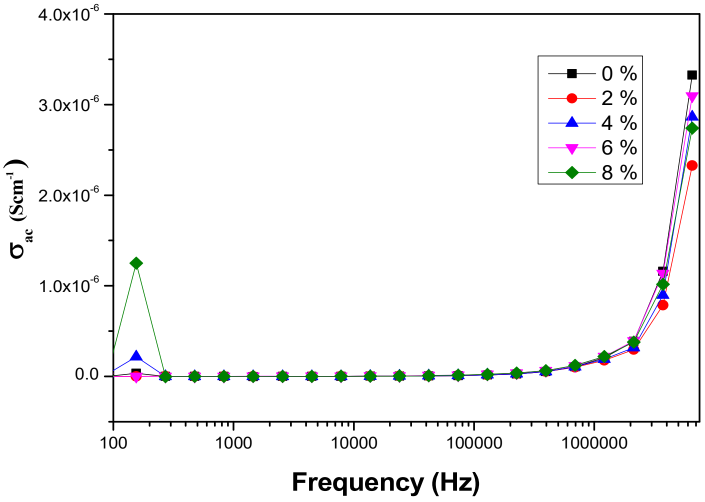

Figure 4 ac conductivity of PVA-NiO Nanocomposites

At lower frequencies, the rise in conductivity is negligible. In fact up to a frequency of 10^5 Hz, *ac* conductivity values were almost the same for all the nanocomposites. However, at higher frequency values, a sharp rise in the conductivity values is observed. This may be due to the electronic interaction processes taking place inside the composites as a result of which the composites became more relatively conductive. Also as the NiO concentration is increased, the inorganic filler molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier between two localized states and hence *ac* conductivity increases [31].

3.3. Dielectric Measurements

The various dielectric parameters *viz.* dielectric permittivity, dielectric loss, loss tangent were measured and their results are analysed in the following sections.

3.4. Dielectric Permittivity (ε′) Measurements

The dielectric permittivity (**ε′**) of PVA-NiO nanocomposites at different frequencies is shown in Fig. 5 at room temperature. The dielectric permittivity of PVA-NiO nanocomposites decreases with increase in frequency. This may be attributed to the tendency of dipoles present in the samples to orient themselves in the direction of the applied field.

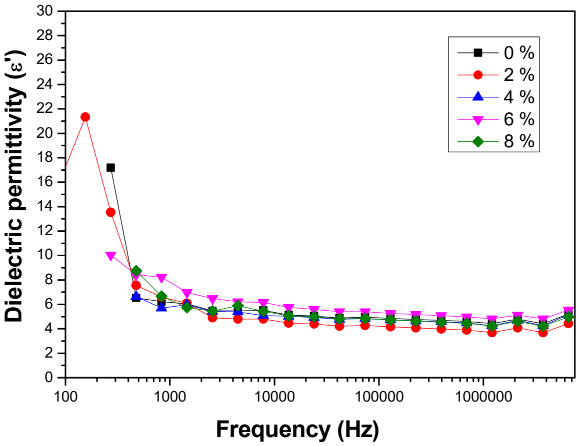

Figure 5 Dielectric permittivity of PVA/NiO

However, at higher frequency above 10^5 Hz, ε′ remains almost constant throughout the frequency region. This is because the bigger dipolar groups find it difficult to orient at higher frequencies. Electrical charges and dipoles respond to the electric field and reorient themselves under the field condition. On the other hand, the high value of ε′ at low frequency might be due to the electrode effect and interfacial effect of the sample [32]. The inherent permittivity in NiO nanoparticles also decreased with increasing frequencies of the applied field [33]. This combined decreasing effect of the permittivity for NiO nanoparticles resulted in a decrease in dielectric permittivity of PVA-NiO nanocomposites with increasing frequency of the applied field. Also, NiO doping in PVA matrix nearly decreases the value of ε′ with increasing NiO concentration.

3.5. Loss Tangent (Tanθ) Measurements

The behavior of loss tangent with respect to frequency follows the same trend as that of pure PVA at frequencies beyond 100 KHz. At higher frequencies, these nanocomposites exhibit almost zero dielectric loss which suggests that these composites are low-loss materials at frequencies beyond 1 MHz .The loss tangent spectrum show relaxation process for all PVA-NiO nanocomposites considered and as the content of NiO increases, the magnitude of the relaxation peak decreases [33] and the breadth increases [34]. The values of tanδ are found to be below 1, indicating that the dielectric phenomenon is predominant in these nanocomposites.

The loss tangent of PVA/NiO nanocomposites at different frequencies is shown in Fig. 6 at room temperature.

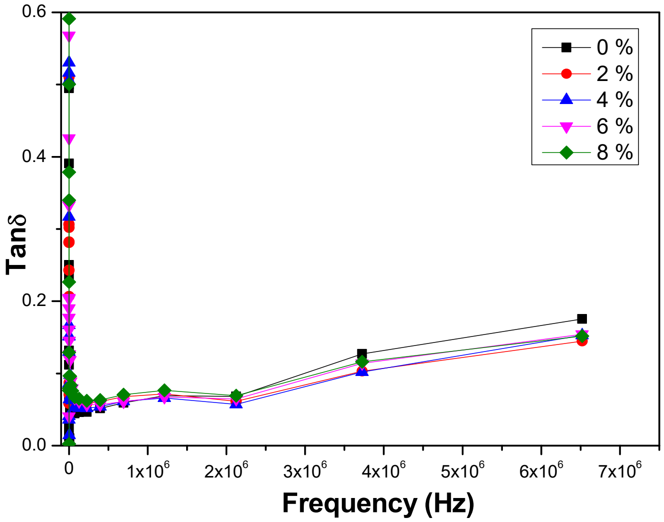

Figure 6 Loss Tangent of PVA/NiO nanocomposite

4. Summary and Conclusion

We have prepared Polyvinyl alcohol (PVA)-Nano Nickel oxide (NiO) composites of various weight percentages were synthesized by combustion method. The X-ray Diffraction analysis confirms the formation of PVA-Ni (0% to 8%) . Using Debye Scherre formula, the size of the Ni particles was calculated. The peaks at 2θ values of (36.562, 43.48, 62.04) degrees corresponds to (1 1 0), (1 1 1), (2 1 1) planes of Ni particles is observed. The intense peak at 20º is observed inpure PVA.

The various dielectric parameters *viz.* dielectric permittivity, dielectric loss, loss tangent were measured. At lower frequencies, the rise in conductivity is negligible. At higher frequency values, a sharp rise in the conductivity values is observed. At lower frequencies, the rise in conductivity is negligible. In fact up to a frequency of 10^5 Hz, *ac* conductivity values were almost the same for all the nanocomposites. However, at higher frequency values, a sharp rise in the conductivity values is observed. The dielectric permittivity of PVA-NiO nanocomposites decreases with increase in frequency. This may be attributed to the tendency of dipoles present in the samples to orient themselves in the direction of the applied field. However, at higher frequency above 10^5 Hz, ε' remains almost constant throughout the frequency region.

The behavior of loss tangent with respect to frequency follows the same trend as that of pure PVA at frequencies beyond 100 KHz. At higher frequencies, these nanocomposites exhibit almost zero dielectric loss which suggests that these composites are low-loss materials at frequencies beyond 1 MHz . The values of tanδ are found to be below 1, indicating that the dielectric phenomenon is predominant in these nanocomposites.

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