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Characterization and AC Conductivity of novel ZnO doped Polyvinyl Alcohol (PVA) Nano-composite films

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Abstract

AC conductivity of polyvinyl alcohol (PVA)-ZnO nano-composite films have been studied in the present work.ZnO nanoparticles have been synthesized using Low Solution Combustion method. The composites were prepared by solution-casting technique. The prepared PVA-ZnO composites have been characterized by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR), which confirmed the presence of ZnO in polyvinyl alcohol and the formation of the composites. AC conductivity of the PVA-ZnO nanocomposite films was found to be higher than that of the pure PVA above 10^5 *Hz. Maximum conductivity was observed in1 wt% of ZnO in polyvinyl alcohol and hence these composites may be useful in microwave absorption and electromagnetic-induction applications.*

Key words: Polyvinyl alcohol, Nano Zinc oxide, X-ray diffraction, AC conductivity.

Introduction

The doping of inorganic nanoparticles into the polymer matrix can provide high performance novel materials that find applications in many industrial and medical fields. Nanoscale fillers are different from conventional micron-size fillers due to their small size and corresponding increase in surface area. It is expected that the addition of nanoparticles into polymers would enhance the electrical properties of filled polymers [1].

Polyvinyl alcohol (PVA) is a potential material having a very high dielectric strength (>1000 kV/mm), good charge storage capacity and dopant-dependent electrical property. It is the largest water–soluble synthetic polar polymer produced in the world. Its water solubility allows the film production by solution casting process. These properties have paved way to the use of PVA in a wide range of applications such as medical, cosmetic, food, pharmaceutical and packaging industries.

Nano ZnO has received broad attention due to its distinguished performance in electronic, optic and photonic devices. Zinc Oxide is an n-type semiconductor that displays a hexagonal crystalline wurtzite structure with space group *P63 mc* [2]. The importance of ZnO is due to its unusual physical properties such as high conductance, chemical and thermal stability [3], wide and direct band gap (3.37 eV) [4] and a high excitation binding energy (60meV) [5].The ZnO nanostructures have great potentiality for being used in preparing solar cell, acoustic, electrical and optical devices, chemical sensors [6], catalysts, pigments, cosmetics, varistors and gas sensors [7].

Thus by combining the advantages of both PVA and ZnO, one can fabricate new hybrid materials with high dielectric permittivity, high breakdown voltages and energy storage density for applications in capacitors as electric energy storage devices [8].

In the present work, attempts have been made to synthesize the nano-zinc oxide particles by low solution heat combustion method and PVA-ZnO nano-composites by solution casting method. These polymer nanocomposites have been characterized by using various techniques such as X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The frequency dependent dielectric permittivity, dielectric loss, loss tangent, Q-factor, conductiviry was measured by employing LCR meter. (Newton Model PSM-1735)

EXPERIMENTAL

Materials

Polyvinyl alcohol of analytical grade was obtained in the powder form from Nice Chemicals Pvt.Ltd. Cochin, with the average molecular weight of 125,000 (98% hydrolyzed) Zinc Nitrate Hexhydrate of ARgrade was purchased from S.D.Fine Chem.Ltd. Mumbai.

Synthesis of Nano Zinc Oxide (ZnO)

Low Solution combustion (LSC) technique was employed for the preparation of nano- zinc oxide [9]. Hydrated Zinc Nitrate [Zn $(NO_3)_2$ $6H_2O$] is used for the synthesis of zinc oxide. The filtered lemon juice was used as a fuel [9].The stiochiometric ratio of zinc nitrate and fuel were taken into the cylindrical Petri dish of 300 ml and well dissolved in de-ionized water. The aqueous redox mixture was dispersed uniformly by stirring the mixture using a magnetic stirrer for 5 min. Then the resulting mixture was placed into a pre-heated muffle furnace maintained at (400 ± 10) °C. 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 and 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.

Synthesis of Polyvinyl Alcohol Film

The pure PVA films were prepared by solution casting technique [10]. Powdered PVA of about 2.5 g was dissolved in 50ml of double distilled water by stirring. The solution was then warmed up to 333 K and thoroughly stirred using a magnetic stirrer for about 1h until the polymer became completely soluble. By removing the trapped air bubbles, the solution was poured onto a leveled clean glass plate and left to dry at room tempertture for about 48 h. The dried films were peeled off from the glass plate and cut into suitable pieces for measurements [11].

Synthesis of PVA–ZnO nano-composite films

PVA-ZnO nano-composite films were also prepared again by the solution casting method. First, PVA stock solution was prepared by above method and to this solution 1.0 wt%, 2.0wt%, 3.0 wt% and 4.0 wt% of ZnO nano powder was mixed and stirred vigorously by using magnetic stirrer until transparent PVA–ZnO multicomponent dispersion was obtained. Further, ultrasonic-ation was done for complete dispersal of ZnO in PVA solution. Then known volume of viscous PVA–ZnO solution was poured onto a leveled clean glass plate and left to dry at room temperature for about 48 h. The dried films were peeled off from the glass plate and cut into suitable pieces for characterization.

Results And Discussion

X–Ray diffraction

In order to investigate the nature of the polymer composite films, X-ray diffraction studies were carried out using Philips X-ray diffractometer with Cu-Kα radiation. The XRD patterns of nano ZnO, pure PVA and PVA-ZnO nano-composite films are shown in Figure1.

The XRD spectra of nano ZnO shows characteristics diffraction peaks at an angles $2\theta = 31.71^0, 34.30^0, 47.51^0, 56.59^0, 62.79^0, 67.92^0, 68.98^0, 72.44^0$ and 76.73^0 are assigned to the scattering from (100), (0 0 2), (1 0 1), (1 0 2),(1 1 0),(1 0 3), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) planes respectively.

It was observed that all the diffraction peaks of Zn Oare in excellent accordance with hexagonalwurzite structure of ZnO with lattice const-ant a= b = 3.255A^{0}, c = 5.218 A^{0} consistent with the standard PDF database (JCPDS file No. 36-1451)[12].

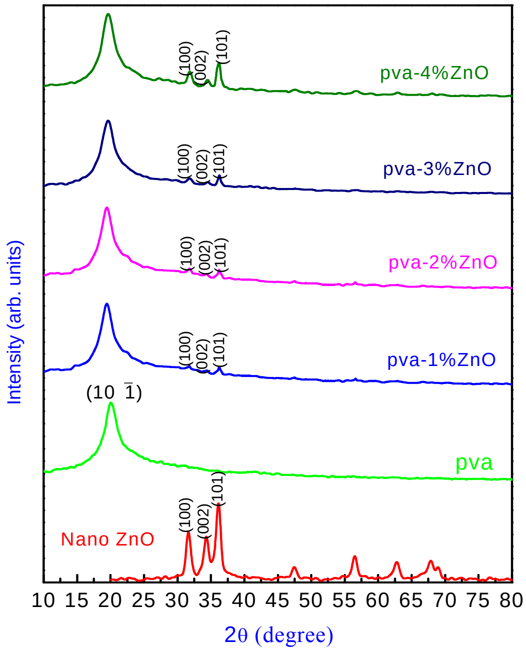

Figure 1: XRD pattern of nano ZnO, pure PVA, PVA-ZnO (1-4%) nano-composite.

The XRD pattern of pure PVA shows a characteristic peak for an orthorhombic lattice centered at 20° indicating its semi crystalline nature [13, 14]. On the incorporation of nano ZnO into PVA, the intensity of the peaks increases gradually, suggesting an increase in the degree of crystallinity of the composites. They observed that the intensity of XRD pattern increases with the addition of dopant. All the major diffraction peaks of ZnO are also present in the PVA-ZnO (1–4%) nanocomposites indicating the presence of PVA has no influence on crystallization performance of ZnO as well as confirms there is homogenous distribution of ZnO in PVA matrix.

FTIR Spectra

The chemical structural analysis of PVA-ZnO nanocomposites were carried out using Fourier Transform Infrared (FTIR) spectroscopy (Model: Perkin Elmer 1600) over the wave number range of 400–4000 cm^{-1} in KBr medium.FT-IR spectra of the PVA, PVA-ZnO nano-composites are shown in Figure2.

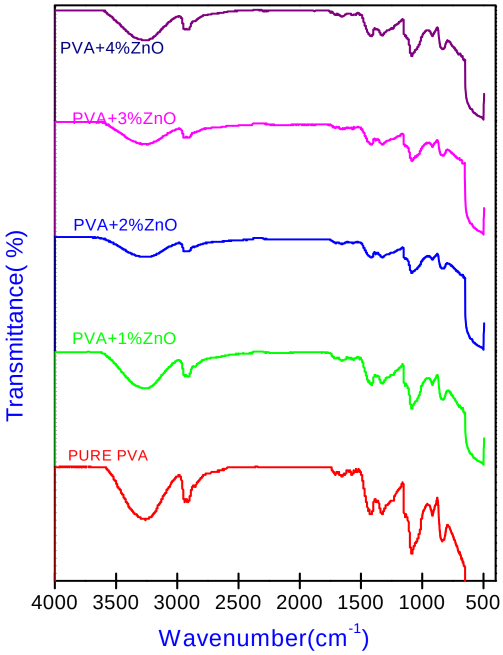

Figure 2: FTIR Spectra of PVA, PVA–ZnO (1–4%) nano-composites.

In the spectra pure PVA and all the composites showed a peak around 3290 cm^{-1}, is due to–OH group in the polymer backbone,2934 cm^{-1} and 2850 cm^{-1} are due to $-CH_2$ asymmetric and symmetric stretching respectively. The peak observed around 1326 cm^{-1} is due to $-CH_2$ stretching. Further-more; peaks observed around 500 cm^{-1} in the PVA-ZnO nanocomposites is due to Zn-O stretching[15], which is not observed in the pure PVA film. This suggests the presence of ZnO in the PVA matrix.

Dielectric Properties

The study of dielectric loss as a function of temperature and frequency is one of the most convenient and sensitive methods of investigating the polymer structure of a polymeric film. The polarization of a dielectric is contributed by the electronic, ionic, and dipolar polarization.

A sample of radius 0.65cm was taken and silver was deposited on both surfaces to ensure good contacts in electrical measurements. Silver coated samples were sandwiched between the two similar aluminum electrodes having a screw to avoid the parasite capacitance induced by the presence of air interstices at the interfaces between the sample and the electrodes. The whole assembly was placed in an isolated chamber.

The dielectric properties of PVA-ZnO nano-composites are studied as a function of frequency at room temperature. The values of dielectric constant and dielectric loss of samples were calculated using the following relations [16]:

$$\varepsilon' = \frac{C\,d}{\varepsilon_0 A} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} \qquad (1)$$

$$\varepsilon'' = \frac{\sigma_{ac}}{\varepsilon_0\, \omega} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} \qquad (2)$$

where d is thickness, A is the effective cross-sectional area of the sample, C is the capacitance of the sample and σ_{ac} is the electrical conductivity.

The loss tangent (tanδ) is determined using the equation,

$$\mathrm{Tan}\delta = \frac{\varepsilon''}{\varepsilon'} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} \qquad (3)$$

where δ is the phase angle between the electric field and the polarization of the dielectric.

The quality factor or Q-factor is the reciprocal of the loss tangent given by

$$Q = \frac{1}{Tan\delta} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} \qquad (4)$$

The variation of dielectric parameters with frequency for PVA-ZnO nano-composites are shown in Figure3 and Figure4 at temperature 300K. The variations of dielectric parameters with frequency can be explained in terms of the relaxation time; at low frequencies, the electric dipoles have sufficient time to align with the field before the field changes its direction; consequently the dielectric constant is high. At high frequencies, the dielectric constant decreases due to the shorter time available for the dipoles to align [17]. It is observed that PVA-1% ZnO leads to high tuneable dielectric properties of the composites.

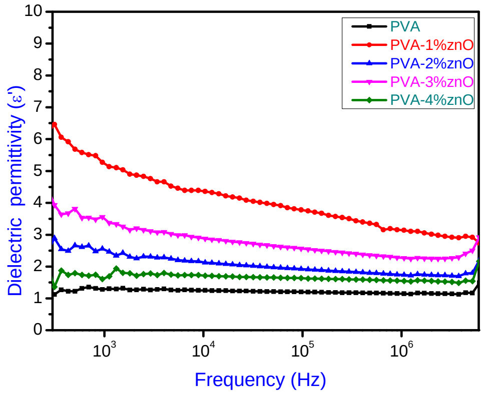

Figure3. Variation of dielectric permittivity for PVA-ZnO nano-composites at different frequencies.

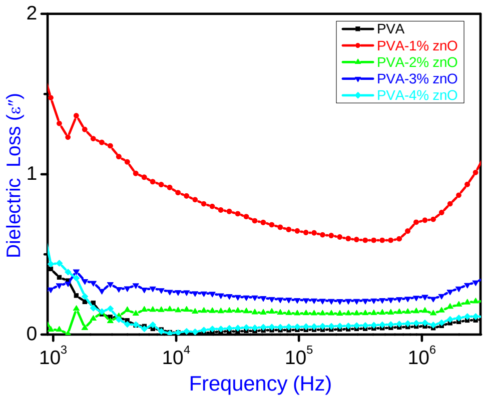

Figure 4.Variation of dielectric loss for PVA-ZnO nano-composites at different frequencies

The variation of loss tangent with frequency for PVA-ZnO nano-composites are shown in the Figure 5 at temperature 300K. The behavior of loss tangent with respect to frequency follows the same trend as that of pure PVA at frequencies beyond 10 KHz. At higher frequencies, these nano-composites exhibit almost zero dielectric loss which suggests that these composites are low- loss materials at frequencies beyond 1 MHz.

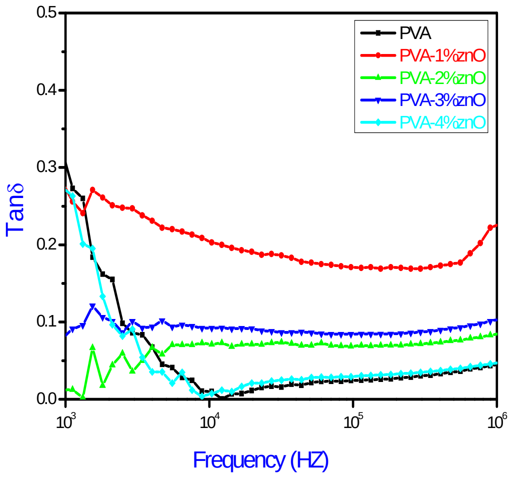

Figure 5.Variation of loss tangent for PVA-ZnO nano-composites at different frequencies.

The values of tanδ are found to be below 1, indicating that the dielectric phenomenon is predominant in all the nano-composites. Also from the plots it is clear that, the value of loss tangent for PVA-1%ZnO is more compared to other weight percentages of PVA-ZnO, which suggests higher electrical conductivity.

The variation of Q-factor with frequency for PVA-ZnO nano-composites are shown in the Fig.6 at temperature 300K. From the plot it is clear that, Q factor decreased for all nano composite as compated to pure PVA throughout the frequency range.

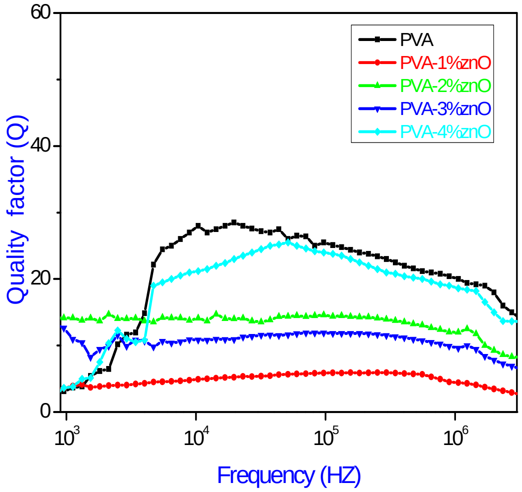

Figure 6. Quality factor of PVA-Zn nano-composites at different frequencies.

Also, for PVA-1%ZnO composite the value of Q is least compared to other weight percentages of PVA-ZnO, which suggests higher electrical conductivity. The dielectric constant and Q-factor are crucial quantities required in the design of devices. Thus these composites are useful in microwave absorption and electromagnetic-induction applications.

The variation of ac conductivity with frequency for PVA-ZnO nano-composites are shown in the Figure 7 at temperature 300K. It is observed that in all the cases, σ_{ac} remains constant up to 10^5 Hz. Among all the nano-composites, PVA-1%ZnO shows high conductivity due to interfacial polarization.

However, in case of PVA and other nanocomposites of different weight percentages, the conductivity value is low because of dipole polarization.This behavior of the nanocomposites may be due to the variation in the distribution of nano ZnO particles in PVA.

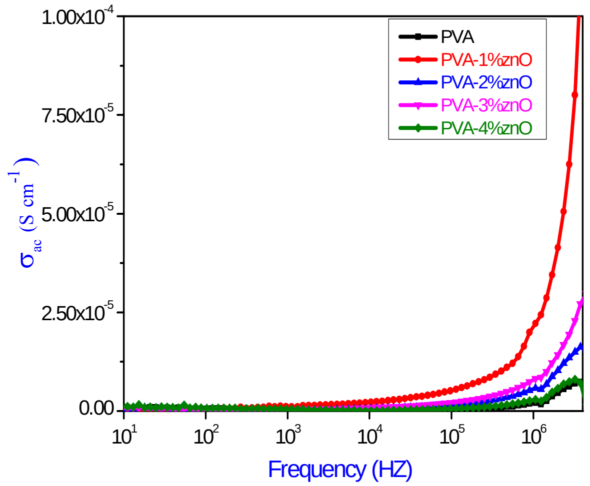

Figure7. Variation of ac conductivity of PVA-ZnO nano-composites at different frequencies.

Conclusions

Polyvinyl alcohol-Nano Zinc Oxide composites of various weight percentages were synthesized by solution casting method. Nano ZnO is synthesized by low solution combustion method. X-ray diffraction studies show the retention of ZnO in polymer matrix. FTIR Studies confirm the formation of PVA- ZnO composites. The values of tanδ are found to be below 1, indicating that the dielectric phenomenon is predominant in all the nano-composites. Maximum ac conductivity was observed in PVA-1%ZnO compared to other weight percentages.

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