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Polyaniline: tin oxide polymeric nanocomposite films. An electrical and dielectric study

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A conducting nanocomposite film of 60 nm nano-SnO_2-polyaniline (PANI) and polyvinyl alcohol (PVA) has been synthesized and analyzed in terms of AC conductivity and dielectric behavior. The conducting polymer nanocomposite of PANI/60 nm (SnO_2) and polyvinyl alcohol (PVA) has been prepared via in situ polymerization technique. The morphology of the nanocomposite film has been studied by SEM. The film has been characterized in terms of DC conductivity. The dielectric behavior and AC conductivity of the nanocomposite film have been investigated in the frequency range of 2 Hz to 90 KHz. The film has high dielectric constant which may be correlated with polarization. It has been observed that both dielectric loss and dielectric constant decrease with an increase in frequency.

Keywords: *nanocomposite; conducting polymer; AC conductivity; dielectric properties*

1. Introduction

Recent development in the nanotechnology has opened new possibilities in nanocomposite materials due to various options of developing novel material varieties and their tailoring for particular applications [1]. The nanocomposite materials have been developed from a mixture of organic and inorganic materials and hence, derived special properties from both the constituents. It has increased the interest of researchers to mix both the constituents for applications in electronics, optics, magnetism, biomedicine, etc. [2].

In the present work, we have taken organic constituent – conducting polymer polyaniline (PANI) and inorganic constituent – nanopowder of tin oxide (SnO_2). PANI has been used for different applications such as sensor electronic devices and electrical storage devices [3–5]. PANI is an environmentally stable polymer [6] and can be employed in industrial applications.

Polyaniline (PANI) nanostructures have shown high quality physicochemical properties and are considered as a material with a wide area of applications. The areas of applications of PANI nanostructures include electromagnetic interference (EMI) shielding, corrosion inhibition, chemical sensors, supercapacitors, etc. [7]. The PANI nanostructures have shown high capacitance but it has been reported that after some charging-discharging runs, the polymer backbone breaks. The poor strength and modest rigidity of PANI contributes to its reduced cycling stability. This limitation of PANI can be overcome by developing PANI nanocomposites. PANI nanocomposites comprising ZnO nanorods have been investigated for anticorrosive and antifouling properties by Mostafaei [8]. PANI/graphene nanocomposites have been investigated for electromagnetic interference shielding by Modak et al. [9]. Sen et al. [10] have reported multi-functionality of PANI nanocomposites at room temperature for sensing of a large number of combustible or toxic gases and pollutants. Multifunctionality of PANI nanocomposites has been studied by Patil et al. [11] for their superior capacitance. Different nano-metal oxides materials ZnO, TiO_2 and SnO_2 [12, 13] are being used to form nanocomposites for wide

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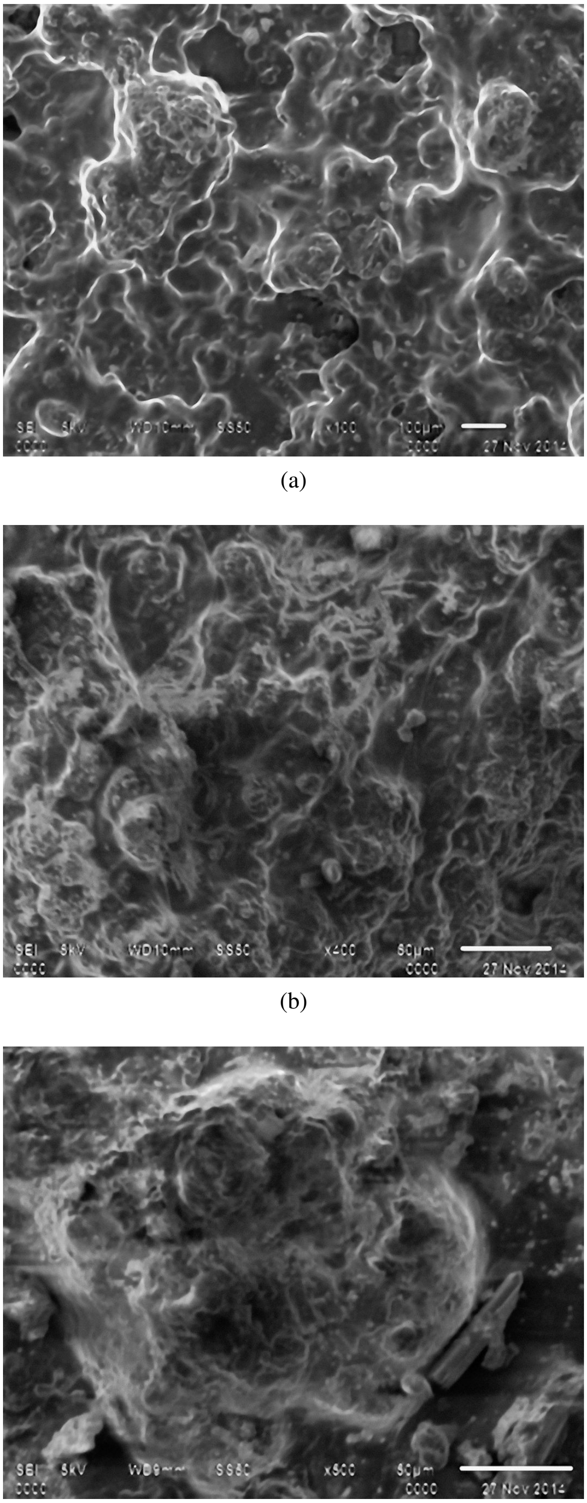
applications of PANI. SnO_2 is an n-type semiconducting material and is applied in battery electrodes, gas sensors, and electric storage devices [14, 15]. The nanomaterial composite size also affects the characteristics of nanocomposite material [16]. The conductivity of PANI is dependent upon the acid used: HCl, H_2SO_4 [17]; oxidant used: potassium dichromate ($K_2Cr_2O_7$), ammonium peroxidisulphate (APS) [18] and reaction medium pH [19]. To improve the processibility of PANI, numbers of stabilizers are also utilized for developing the composite film of PANI [20, 21].

The aim of this work is to tune the conductivity of PANI. For this purpose, the nanopowder of SnO_2/PANI has been mixed with varying loading by weight percentages. The nanocomposite films obtained have been then investigated in terms of dielectric constant and AC electrical conductivity.

2. Experimental

2.1. Materials

Nanopowder of SnO_2 (60 nm) (SRL, India), HCl (1 M), ammonium peroxodisulphate (APS), polyvinyl alcohol (PVA) and aniline (Merck, India) have been used for synthesis. All the chemicals were used as received from the companies without further purification.



(a)

(b)

(c)

Fig. 1. Morphology of (PANI-SnO_2)/PVA nanocomposite film (three images with increasing order of resolution showing the flower-type structures).

2.2. Synthesis of PANI-SnO_2 nanocomposite

In situ polymerization technique has been used for developing the nanocomposite of PANI-SnO_2 since the addition of nanoparticles increases the surface area [22] for polymerization process of aniline resulting in hybrid polymerization [14]. This technique has also shown to increase the yield of PANI [23]. 1 g nanopowder of SnO_2 has been dispersed in 1 M HCl for 3 h in a round bottom flask. 2 mL aniline has been then added into the flask and the solution has been stirred for 2 h. The temperature of the flask has been maintained between 0 °C and 5 °C during the synthesis process. A second solution of ammonium peroxodisulphate in the amount of 4.9984 g in 50 mL HCl has been prepared. This second solution has been poured into the round bottom flask. A green color of PANI has appeared. The solution was continuously stirred for 3 h to 4 h to complete the polymerization. The polymer was then filtered and washed with HCL and dried at room temperature for 4 days to 5 days.

2.3. Synthesis of nanocomposite film

To ease the processing, a nanocomposite film based on polyvinyl alcohol (PVA) has been developed. In a round bottom flask, 300 mL of distilled water at 80 °C to 90 °C have been taken and 1 g of PVA has been dissolved in it. After complete dissolving of PVA, the solution has been cooled to room temperature. The nanocomposite of PANI-SnO_2 has been loaded in different amounts ranging from 20 wt.% to 40 wt.% and dissolved in the PVA solution. The solution has been continuously stirred for 4 h to 5 h, then collected in polyethylene Petri dish and dried at room temperature for 4 days to 5 days.

2.4. Characterization

The scanning electron microscope (Model JEOL 6610 LV) has been used for studying structural morphology of the nanocomposite film. Keithley 6487 unit has been used for DC conductivity measurement and Wayne Kerr LCR meter (6500 B) has been used for the study of dielectric constant and AC conductivity of the nanocomposite films.

3. Results and discussion

In situ polymerization technique has been used for formation of nanocomposite of SnO_2 and polyaniline. Fig. 1 shows the morphology of the (PANI-SnO_2)/PVA nanocomposite film. Flower-type fibrous structure can be observed. Similar behavior has been discussed by Arora et al. [23] and Sun et al. [24]. In a vapor liquid system, Kim et al. [25] explained that nano- and microfibers could be developed between nano-SnO_2-PANI structures, hence the high content of polyaniline inside the structure of the composite material.

The micrographs of the film also show a net-like structure between the flower fibrous structure. This may be due to the distribution of PANI in the film shown at three resolutions (Fig. 1) lower to higher, respectively from fibrous to individual flower-type structure. Similar behavior has already been explained by Ray et al. [26] for ZrO_2/PANI composite. The FT-IR spectra have shown the presence of SnO_2 in PANI as reported by Swarup et al. [27]. Current-voltage characteristics have been used to obtain DC electrical conductivity of the nanocomposite films. I-V characteristics show a nonlinear behavior for the nanocomposite film. Dutta et al. [28] have also found the nonlinear electrical characteristics of PANI-SnO_2 composites. This nonlinear behavior might be due to the oxygen vacancies representing the barrier in conductivity but it helps in charge storage during the deposition of PANI [29–31]. The electrical conductivity behavior of the composite film has also been described by the percolation theory [32]; $\sigma_{DC} = p \cdot (n - n_q) \cdot r$, where σ_{DC} is the DC conductivity, p is a constant, n_q is percolation threshold, n is percolation, r is a parameter which depends on dimensions, i.e. one dimension, two dimensions, and three dimensions. The nanocomposite film has shown nonlinear behavior of DC conductivity (Fig. 2). It has been observed that on increasing loading of the nanocomposite (PANI/SnO_2) from 20 wt.% to 40 wt.% in PVA aqueous solution, the nonlinear behavior of DC conductivity increases. The correlation coefficient values for the nanocomposite films have also shown a decrease from 0.985 to 0.844 for 30 wt.% to 40 wt.% loading of the nanocomposite material (PANI/SnO_2) in PVA (Fig. 3).

The dielectric constant variation of the nanocomposite film with frequency in the range from 2 Hz to 90 kHz has been shown in Fig. 4a. The values of dielectric constant have been observed to decrease from 6×10^2 to 1×10^2 with an increase in frequency. This decrease in dielectric constant may be due to the presence of SnO_2 nanopowder. The dielectric behavior occurs in the nanocomposite film due to the space charge polarization and rotation direction polarization. In the nanocomposite film it is assumed that the space charge polarization

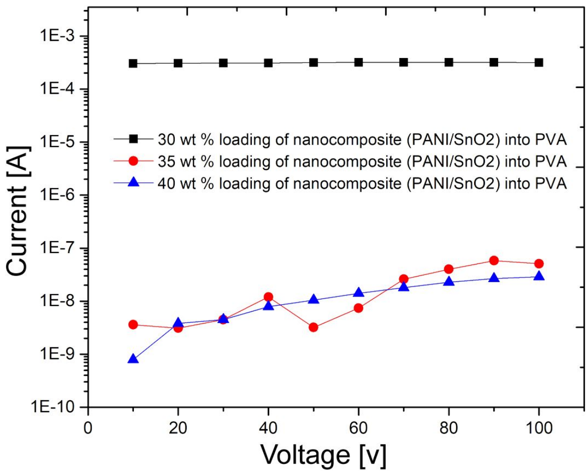


Fig. 2. DC characteristics of (PANI + SnO_2)/PVA nanocomposite film.

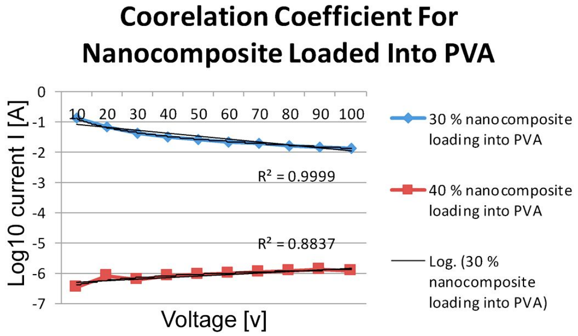


Fig. 3. Effect of wt.% loading on correlation coefficients of the nanocomposite film.

occurs due to the availability of p-type PANI and rotation direction polarization occurs from nano SnO_2. The same variation of dielectric behavior has also been discussed by Macappa et al. [33].

Fig. 4d shows the variation of AC conductivity with frequency from 2 Hz to 90 kHz for the nanocomposite film. In the high frequency region, the variation in the AC conductivity has been observed to be very small. This might be due to the agglomeration of nanocomposite material (PANI/SnO_2) in the aqueous PVA solution (flower-type structure as observed in Fig. 1). From Fig. 3 and Table 1, a good correlation has been observed between different composite materials. In the synthesized nanocomposite PANI/SnO_2 material, p-type PANI has encapsulated n-type SnO_2 and formed a p-n junction. A depletion layer between p-type material PANI and n-type material (TiO_2/PVA) which acts as dielectric has been apparent [34]. Furthermore, interlinking between nanocomposite PANI/SnO_2 material and PVA might be giving some amorphous structure which alters the conductivity. The conductivity has followed the power law above the critical frequency as observed from the method of least squares of linear regression. Fig. 4d shows that when the frequency increases, the conductivity increases. This may be due to the development of phonons between the crystallized nanocomposite (PANI/SnO_2) and PVA [35]. In double layer model, the frequency dependent variation of conductivity has been explained by Wagner et al. [36]. This model actually explains the inverse relation between frequency and current for dielectric response. Mostafaei et al. [38] and Su et al. [39] have presented also similar type of findings in their researches for pure PANI. Fig. 4b and Fig. 4c show the dielectric loss factor and tanδ versus frequency for the nanocomposite film. It has been observed that with an increase in frequency, the values of dielectric loss and tanδ decrease sharply and become constant at a certain frequency. The decrease in the tangent loss factor value with increasing frequency may explain the phenomenon of protonation discussed earlier [35]. At higher frequencies, the nanocomposite film exhibits almost zero dielectric loss which suggests that these nanocomposite films are lossless materials.

Table 1. Composite materials and their correlation coefficient

Composite material	Correlation coefficient	Literature
PANI/SnO_2	0.999	[40]
PANI/PVA	0.914	[41]
PANI/TiO_2	0.99998	[42]

The observed behavior of dielectric loss is in accordance with conductivity and dielectric constant results of the reported composites. It has been observed that for this nanocomposite material, the dielectric constant is stable at high frequency in comparison to the dielectric constant at low frequency. Similar behavior has been reported for PANI nanocomposites by Idrees et al. [43].

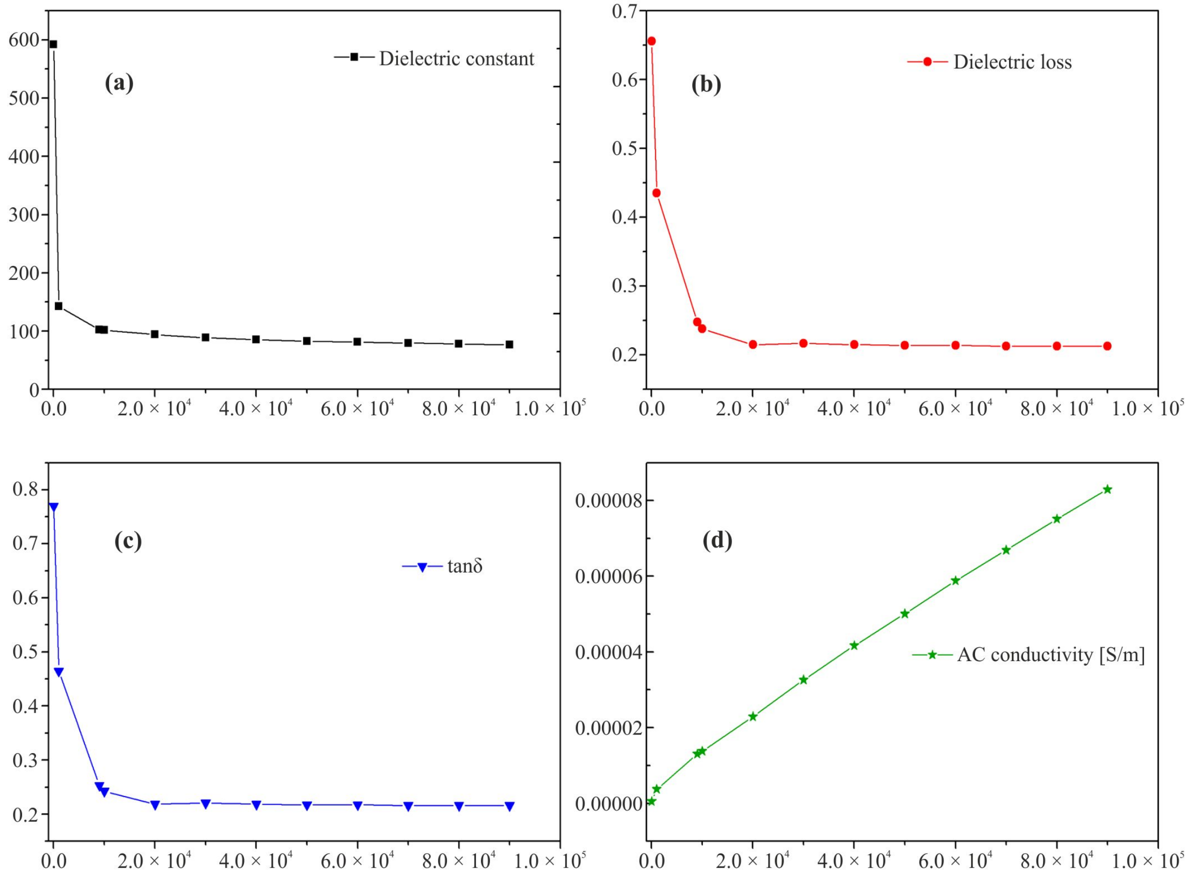


Fig. 4. Dielectric constant vs. frequency (a), dielectric loss vs. frequency (b), tanδ loss vs. frequency (c), AC conductivity vs. frequency (d) of PANI-SnO_2-PVA nanocomposite film.

The values of dielectric constant obtained in present study are larger than those for polyaniline-TiO_2 nanocomposite reported by Mo et al. [44].

4. Conclusions

In this paper, electrical properties of nanocomposite films have been discussed. The nanocomposite has been prepared from nanocomposite material nano-SnO_2 encapsulated with PANI, and PVA. Flower-type structures observed in the nanocomposite film may help in charge storage. The DC conductivity of the nanocomposite film has been found to change with the doping percentage of the material with PVA. It has also been discussed that the correlation coefficient is good for nano-SnO_2, PANI and PVA. The other electrical properties of the nanocomposite film: AC conductivity and dielectric properties have been found to change with frequency. When the frequency increased, the AC conductivity increased, whereas the dielectric constant decreased. The dielectric loss has also decreased with the increase in frequency. Hence, AC conductivity of the nanocomposite film follows the power law.

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