



Thermal and Electrical Properties of Polyindole/ Magnetite Nanocomposites

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Abstract: A continuation work on the fabrication of polyindole (PIN)/ magnetite (Fe_3O_4) nanocomposites with respect to the effect of various concentrations of Fe_3O_4 nanoparticles on thermal and electrical conductivity behavior is presented. Thermal stability of the nanocomposites was determined by thermal gravimetric analysis (TGA). AC conductivity behavior was investigated in the frequency range of 100- 10^6 Hz at room temperature and the DC conductivity was studied in the temperature range 30-200°C. TGA results indicated that the thermal stability of the nanocomposite increased with increase in Fe_3O_4 percentage in the polyindole. AC conductivity was significantly increased with increase in Fe_3O_4 content (up to 10 weight percentage) and also with the increase in frequency. Dielectric constant and dielectric loss tangent values were increased with increase in content of nanoparticles up to 10 wt. %, and thereafter the value decreased with the further addition of nanoparticles. The observed enhancement in DC conductivity was attributed to the increase in number of conduction paths formed by the interfacial interaction between the polyindole chains and the nanoparticles. The enhancement in thermal and electrical conductivity with the addition of these properties suggests that the fabricated PIN/magnetite nanocomposites can be used as materials in sensors, actuators, etc.

Key Words: Polyindole, magnetite, nanocomposites, thermal properties, electrical conductivity

INTRODUCTION

Conducting polymers are important materials with applications in rechargeable batteries, sensors, electrochemical display devices, and microwave absorbing materials [1, 2]. Research in the field of these polymers has been aimed mainly at some suitable modification of existing polymers so that their performance can be improved. Conducting polymer based nanocomposites possess the advantages of both low dimensional systems (nanostructure filler) and organic conductors (conducting polymer). In recent years conducting polymer based composites containing inorganic oxides or salts of different metal nanoparticles have been of special interest due to their unique electromagnetic properties and their potential applications in several important technological fields [3, 4].

Nanometer sized iron oxide, in the crystalline form of magnetite (Fe_3O_4) and containing supermagnetic and

ferromagnetic properties, has received immense interest because of its numerous applications in various fields, e.g., magnetic recording media, giant magnetoresistive sensors, and photonic crystals [5,6]. Transition metal oxide nanomaterials, such as copper oxide, zinc oxide, and iron oxide, have special physico-chemical properties arising from the quantum size effect and high specific surface area, which can be different from their atomic or bulk counterparts. The large surface to volume ratio of the nanoparticles results in the formation of composites with unusual physical and chemical properties. Compared with organic polymer ferromagnets, conducting polymer-inorganic ferromagnetic composites are considered to be easier to prepare and easier to be put into use.

The majority of authors who have worked on the synthesis of conducting polymer/ Fe_3O_4 composites have reported that the conductivity increases with increasing the loading of fillers [7, 8]. A conducting polypyrrole-ferromagnet composite film has been prepared by means

of the technique of anodic oxidation [9]. However, because the quantity of the composite product was limited by the electrochemical method, it is still desirable to synthesize conducting polymer composites with both conducting and ferromagnetic behaviors by a chemical method that can produce larger quantities.

Hetero-aromatic organic molecules containing nitrogen and sulphur have very interesting properties. Among this class of polymers, polypyrrole and polythiophene have been studied extensively owing to their good conductivity and relative stability. Polyindole (PIN) is also an electroactive polymer which can be obtained from the electrochemical oxidation of indole or chemical oxidation using different oxidants [10]. However, only a limited number of investigations have been carried out on chemically synthesized PIN [11, 12]. PIN possesses high electrical conductivity; however, it has poor thermal stability and processability, and is insoluble, infusible, and brittle. In order to overcome these problems and obtain a useful magnetic polymer, we developed a simple, inexpensive, and environmentally friendly *in-situ* polymerization process to synthesize magnetite / polyindole nanocomposites and to analyze for the influence of magnetite nanoparticles in thermal, AC and DC conductivity.

EXPERIMENT

Materials and Methods

Indole (Sigma-Aldrich, India), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, ammonium persulfate (APS), sodium dodecylsulfate (SDS) and ethanol, from Merck, India, were used for the synthesis. Deionized water was used as a solvent for all solutions. Fe_3O_4 nanoparticles with a particle size of 32 nm were prepared by the chemical coprecipitation techniques as described previously [13].

Synthesis of Polyindole/ Fe_3O_4 Nanocomposites

PIN/ Fe_3O_4 nanocomposites were synthesized by *in-situ* polymerization of indole in aqueous solutions containing magnetite nano fluid using ammonium peroxodisulfate as oxidizing agent [14]. Fe_3O_4 nanoparticles (5, 10, 15, and 20 wt %) were mixed with SDS in distilled water and ultrasonicated for 10 minutes, followed by dispersing with the indole (0.5 M) and again ultrasonicated for a period of 20 minutes; ammonium peroxodisulfate was then gradually added into the stirred

Fe_3O_4 /indole solution at 10 °C. The polymerization was carried out at room temperature for 8 hours with constant mechanical stirring. The precipitated PIN/ Fe_3O_4 nanocomposites were filtered and rinsed with distilled water and ethanol. The synthesized polymer composites were vacuum dried at 50 °C for 24 hours. Polyindole was also synthesized via the same preparation without using the Fe_3O_4 and SDS.

Analytic Methods

Thermal stability of the polymer composites was investigated by a Perkin Elmer thermogravimetric analyzer with pure nitrogen gas at a heating rate of 20 °C/min. Electrical conductivity of the polymer materials was measured on pressed pellets (circular shape of 0.3 – 0.5 mm thick, 1.2 cm diameter) with the use of a hydraulic press by applying 3 metric ton pressure at room temperature. AC resistivity of the samples was measured with a Hewlett-Packard LCR Meter, fully automatic system in a frequency range 100–10⁶ Hz at room temperature. Dielectric constant or relative permittivity was calculated using the formula:

$$\epsilon_r = Cd / \epsilon_0 A$$

where d is the thickness of the sample, C the capacitance, A the area of cross section of the sample, and ϵ_0 is the permittivity of free space. ϵ_r is the relative permittivity of the material which is a dimensionless quantity. From these measurements, ϵ_r and $\tan\delta$ for the nanocomposites were determined. DC conductivities at different temperatures were measured using a standard four-probe method with a Keithley 2400 system digital electrometer.

RESULTS & DISCUSSION

Thermal Stability

The TGA thermograms of PIN and PIN/ Fe_3O_4 nanocomposites, determined with four different concentrations of nanoparticles, are displayed in Figure 1. All of the samples show three stages of mass loss. The initial mass losses (50 to 160 °C) were due to the volatilization of water and oligomers elimination. The second mass loss (200 to 350 °C) has been inferred to the decomposition of unreacted monomer and dopant

molecules from the polymer [15]. The final mass loss, from 415 to 680 °C, is attributed to the further decomposition of carbon containing residues. As shown in Figure 1 (curves b-d), the decomposition temperatures of the nanocomposites were higher than that of PIN and shifted towards higher temperatures as the mass percentage of Fe₃O₄ increased. This is attributed to the nanoparticles decreasing the rate of the degradation of the polymer and impacting the shape of the TGA curves. PIN showed 50 % mass loss at 800 °C, while the decomposition losses of the nanocomposite (10 wt %) were about 34 % at the same temperature. The improved thermal stability is apparently to a reasonable degree of scientific certainty due to the coordination interaction between Fe₃O₄ and polyindole chains.

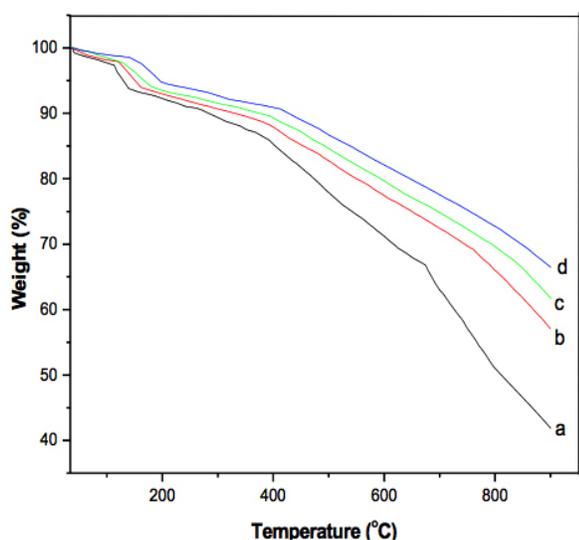


Fig 1. TGA curves of (a) PIN (b) 10 wt % Fe₃O₄/PIN (c) 15 wt % Fe₃O₄/PIN (d) 20 wt % Fe₃O₄/PIN.

AC Conductivity

The variation of AC conductivity of PIN and PIN with various concentration of Fe₃O₄ nanocomposite is presented as double logarithmic plots of σ_{AC} vs frequency in Figure 2. The AC conductivities of the composites were significantly higher than that of the virgin polymer. The pure, compressed, synthesized PIN was very light with poor linkages, resulting in relatively poor conductivity. The most important, and interesting, observation is that the conductivity was highest for 10 weight percent of Fe₃O₄ in the polymer composite. In the present study,

the composites were synthesized under identical conditions with the monomer indole first adsorbed on the surfaces of the Fe₃O₄ nanoparticle. Upon addition of oxidant, polymerization took place on the surface of each nanoparticle. The interaction of the metal nanoparticles and polyindole in the composite seems to strengthen the compactness of the original samples. This improves the link between the grains and the coupling through the grain boundaries becomes stronger which ultimately results in increased conductivity in the PIN/ Fe₃O₄ nanocomposites as compared to pristine PIN. The decrease in conductivity with increase in concentration (above 10 wt. %) of nanoparticle is due to the agglomeration of nanoparticles. Moreover, the composites with 20 wt. % sample exhibit a lower AC conductivity than 5 wt. % composite throughout the entire frequency range. The conductivity of nanocomposites depends on the polarity of polymer matrix, surface area, shape of nanoparticles, interfacial interaction between the polymer and nano-filler, and also the quality of conductive network formed [16]. Therefore, at higher concentration of nanoparticles, the interfacial interaction between the polymer and Fe₃O₄ is poor due to the greater number of metal oxide particles in the polymer matrix.

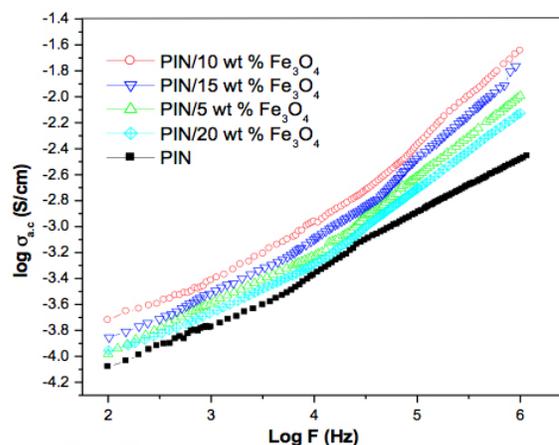


Fig 2. AC conductivity of polyindole with different concentrations of magnetite nanoparticles at various frequencies.

Dielectric Behavior

The variation of dielectric constant (ϵ_r) and dielectric loss tangent ($\tan \delta$) as a function of frequency ranging from 100 – 10⁶ Hz at room temperature are presented in Figures

3 and 4, respectively. The dielectric constant initially decreased rapidly with increase in frequency and then, at frequencies higher than 10^4 Hz, became nearly constant. The dielectric properties of materials are mainly analyzed in terms of their polarizabilities at a given frequency. The electron exchange between the Fe atoms of Fe_3O_4 and nitrogen atoms of PIN, results in local displacement of electrons in the direction of the applied field, which induces interfacial polarization. This type of polarization principally influences the low frequency ($10^2 - 10^4$ Hz) dielectric properties. As the frequency decreased, the time available for the drift of charge carriers increased and the observed value of dielectric constant became significantly higher than that of PIN.

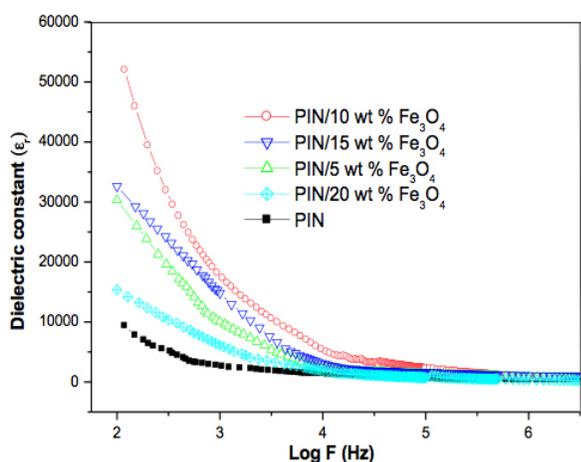


Fig 3. Frequency dependence of dielectric constant of PIN with various weight percentages of Fe_3O_4 nanoparticles.

The dielectric constant increased with the increase in concentration of nanoparticles up to a certain concentration (10 wt. %), but the magnitude of conductivity decreased with further addition of magnetite (i.e., 15 to 20 wt. %) (Figure 3). This can be explained on the basis of space charge polarization and reversal of the direction of polarization [17]. At higher loading of fillers, the particle-to-particle distance between the fillers was too short; therefore, the contribution to the dielectric constant by space charge polarization and rotation of the direction of polarization occurring mainly as the interface diminishes. As a result, the magnitude of the dielectric constant was lower at higher content of magnetite nanoparticles.

Figure 4 shows that the $\tan \delta$ also decreased steeply with increasing frequency. At highest frequency the $\tan \delta$

became constant. At lower frequencies the $\tan \delta$ values were higher for higher content of magnetite nanoparticles. This is due to the increased interaction between the nanoparticles and polymer chains leading to an ordered arrangement of the composites, which causes a space charge build up at the interfaces [18]. This accumulation of space charge leads to an increase in dielectric loss due to the movement of virtual charges that get trapped at the interface of a multi-component material with different conductivities. The dielectric loss tangent value of PIN was lower than the composites and among the composite, 10 wt. % of sample exhibited the higher dielectric values. The higher surface area of nanoparticles provide better particle to particle contact and this leads to a higher packing of chain inside the polymer composite. It was responsible for the higher tangent values. Further, the sudden decrease in dielectric constant above 10 wt. % of composite was due to the agglomeration of nanoparticles in the polymer chain. This reduces the segmental mobility and hence increases the rigidity of the chain. The improvement in electric properties suggests that the fabricated PIN/ Fe_3O_4 nanocomposite has potential application in the fields of nanotechnology, plus multifunctional material in various electronic industries.

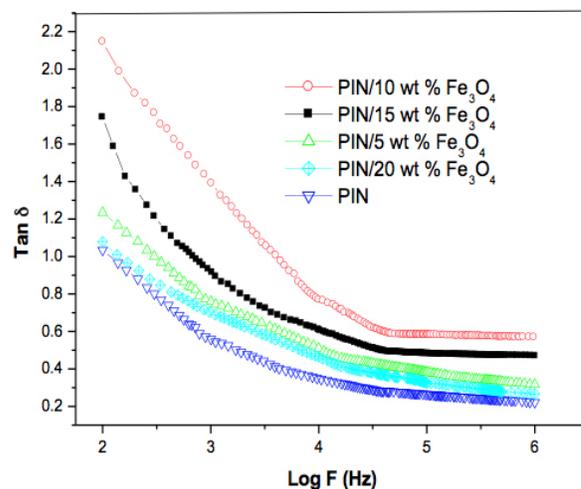


Fig 4. Dielectric loss tangent versus frequency plot for PIN and its nanocomposites.

Temperature Dependent DC Conductivity Studies

The temperature dependence of the electrical conductivity of PIN and four types PIN/ Fe_3O_4 composites at various temperatures from 30 °C to 200 °C are given in

Figure 5. Two ranges of near linear variations with applied voltage were obtained for the Fe_3O_4 nanoparticles incorporated PIN. In the case of the nanocomposites, the growing polymer chains were presumed uniformly adsorbed on the surface of the magnetite particles and, thereby, led to an arrangement of nanoparticles in the polymer matrix.

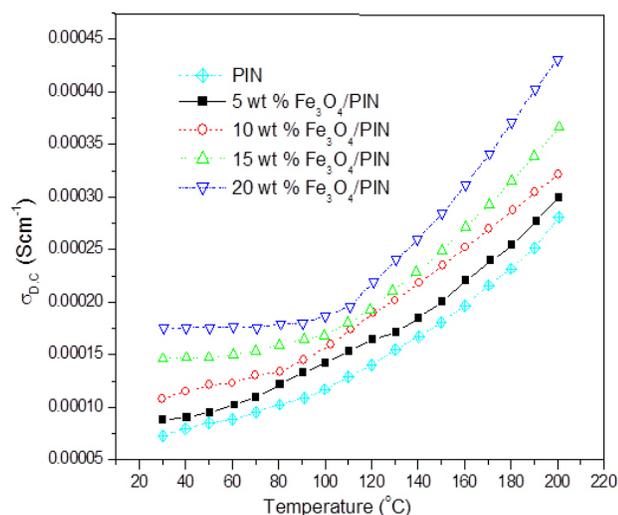


Fig 5. I-V characteristics of PIN and PIN magnetite nanocomposites at different temperatures.

From the figure, it can be noted that from 30 °C to 100 °C, the conductivity values did not show much variation (>10 wt. % of nanoparticles) and increased suddenly in the temperature range from 100 °C to 200 °C. At low temperature, the polymer can behave like a hard and glassy material. PIN has a glass transition temperature (T_g) of 128 °C and a melting temperature (T_m) of 273 °C. The higher conductivity of PIN/ Fe_3O_4 composite at higher temperatures is due to the phase transition of polymer composite from the glassy state to a rubbery region [11]. Moreover, it is important to mention here that the high value of DC conductivity above T_g is apparently attributed to the increase in the number of conduction paths created by the interaction between magnetite nanoparticles and the polymer chains.

CONCLUSIONS

Polyindole with different mass percentage of Fe_3O_4 (0, 5, 10, 15, and 20 wt. %) was prepared by an in situ polymerization method. TGA results indicated that the

PIN/ Fe_3O_4 composite had better thermal stability than that of PIN and the thermal stability of the composite increased with an increase in concentration of metal oxide nanoparticles. This might be due to the interaction between the electronegative nitrogen of PIN and the magnetite nanoparticles. AC electrical conductivity, dielectric constant, and dielectric loss factor of PIN/ Fe_3O_4 were studied as a function of frequency at different volume fractions of nanoparticles. The electrical properties of the composite increased with an increase in concentration of magnetite up to 10 wt.% and with further addition of nano-fillers, the conductivity was found to decrease. The higher value of conductivity of the composite was apparently due to the increased polymer filler interaction. The dielectric constant and loss factor increased with an increase in Fe_3O_4 weight percentage in the composite up to a certain concentration (10 wt. %) of filler. These properties (dielectric constant and loss factor) decreased with further addition of nanoparticles. The high values of the dielectric constant of the nanocomposite suggest a possible application of these materials in the field of actuators and sensors. DC conductivity of the polymer composites was higher than that of the PIN and the conductivity increased with an increase in mass percentage of magnetite nanoparticles.

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