



EXPLORING THE COMPLEX DIELECTRIC PROPERTIES OF ONE POT CHEMICALLY ENGINEERED CONDUCTING POLYINDOLE

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ABSTRACT

This research article reported the real and imaginary part of dielectric constants of conducting polyindole (PIn) as-synthesized through chemical oxidative polymerization method in aqueous solution. The surface morphology of as-synthesized optimized sample was analyzed through Field Effect Scanning Electron Microscopy (FE-SEM) technique. An attempt has been made to explore the effect of frequencies on real and imaginary part of dielectric constants by using ac impedance analyzer in the frequency and temperature ranges 20 Hz-1 MHz and 303-393 K respectively. The decrease in dielectric constant with frequency is attributed to polar nature of the material.

Keywords: Chemical polymerization, Polyindole, FE-SEM, Dielectric constant

1. Introduction

Conducting polymers is the newly growing field of advanced materials science due to their promising technological applications in wide areas. A conducting polymer has a conjugated structure between sigma bond and π -bond along the polymer main chain. This material has promising ability to conduct electricity and generates charge carriers through a doping process as electrons or holes can be delocalized along the polymer chain (Swager, 2017, Wadatkar and Waghuley 2012). A hole is a positive charge where an electron is absent too naive. When a hole is filled by an electron which jumps from a neighboring atom, a new hole is created and so on, this allowing the charge to move a long distance. In the doped state, the charge compensation between a

conductive polymer and a dopant or counter ion is formed by the electrostatic force. The material presents many extraordinary properties over the conventional polymer because it is capable of variations in mass, color, and conductivity by doping/de-doping process (Phasuksom and Sirivat, 2016).

Polyindole (PIn) is one of conducting polymers containing the benzene ring linked with the pyrrolic ring. Although PIn contains the heterocyclic of nitrogen atom like polypyrrole (PPy) and polyaniline (PAni), its electrical conductivity is less by two orders of magnitude than those of the two polymers (Rajasudha, Rajeswari, Lavanya, Saraswathi, Annapoorani and Mehra, 2005). However, the outstanding properties of PIn are excellent thermal stability, high redox activity, and stability as well as slow degradation rate (Trung and Huyen, 2009, Abthagir, Dhanalakshmi and Saraswathi 1998). Consequently, PIn and its derivatives have been of interest for using in various applications such as battery (Zhijiang and Guang, 2010), sensor (Pandey, 1988), corrosion protection (Tuken, Yazici and Erbil, 2005), and drug delivery (Gupta, Chauhan and Prakash, 2010).

The electropolymerized conducting polymers made from carboxylic acid substituted indole at positions -5 and -6 are found processable in aqueous medium and are compatible with suitable additives/precursors for fabricating polymer modified electrodes (PMEs) (Pandey, Chauhan and Singh, 2012). The chemical method for formation of PIn and c-MWCNT hybrid materials through in-situ and interfacial polymerization routes, and studied the junction properties of composites using nano-contact, in configuration of Al/Composite/Pt nano probe (Joshi, Singh and Prakash, 2012). The

electrochemical synthesis of PIn upon anodic oxidation of indole in dichloromethane containing tetrabutylammonium perchlorate and described a secondary battery using polyindole as active material in aqueous neutral electrolyte (Pandey and Prakash, 1998). The chemical synthesis of nanosized (Au) and PIn composite via in-situ polymerization of indole by using metal salt chloro-auric acid as an oxidant, in a microemulsion system (Joshi and Prakash, 2011). The complex optical properties of conducting PIn as-synthesized by chemical oxidation polymerization process in aqueous solution at room temperature (Wadatkar and Waghuley, 2015). A new approach of synthesizing PIn via chemical oxidative polymerization in presence of poly (vinyl acetate) using CuCl_2 as an oxidant and methanol as solvent is reported and studied the dc electrical conductivity of as-synthesized polymeric materials. The aim of this research was to enhance the poor processability by synthesizing a composite material with high processable polymer matrix for potential application in various areas (Bhagat and Dhokane, 2014). In case of strong acid dopants (like, H_2SO_4 , HClO_4 , HCl and HNO_3), perchloric acid (HClO_4) could produce higher electrical conductivity of PDPI when compared with that H_2SO_4 and HNO_3 since the strong acid promoted more holes in the polymer backbone resulting in more charge carriers available and hence consequently enhances electrical conductivity of the as-synthesized polymeric samples (Permpool and Sirivat, 2014).

In the present work, we carried out the polymerization of indole using anhydrous FeCl_3 as an oxidizing agent to prepare conducting polyindole via the chemical oxidative polymerization route. The optimized sample was characterized by FE-SEM technique. The effect of frequency on real and imaginary part of dielectric constants at different temperature were explore for as-synthesized conducting PIn samples.

2. Experimental

Indole monomers, anhydrous iron (III) chloride (FeCl_3), and hydrogen peroxide (H_2O_2) from SD Fine Chemicals (AR-grade) were employed in the current study. The indole monomer was used as received for synthesis of PIn without further purification. The sample was

synthesized at room temperature (303 K) by mixing indole with FeCl_3 in deionised water. H_2O_2 was used to enhance the rate of reaction and conjointly yield (Wadatkar and Waghuley, 2018). During this approach, different samples of PIn were synthesized by chemical oxidative polymerization technique by varying the stoichiometric ratios of indole and FeCl_3 as 70:30, 60:40, 50:50, 40:60 and 30:70 Wt. %. To examine the effect of frequency on the real and imaginary part of dielectric constant, the samples were made in the form of pellets, polished and conducting silver paste was deposited on both sides. The area of the pellet was taken to be an area exposed to the electrode surface. The effect of frequency on the real and imaginary part of dielectric constant of the samples were obtained over a temperature range from 303-393 K.

3. Results and discussion

The morphology and structural features of the material report from FE-SEM (JEOL JSM-6360) technique. The surface morphology of optimized PIn powder sample with stoichiometric ratio of indole and FeCl_3 as (40:60) Wt. % was analyzed by FE-SEM and the micrograph is depicted in Figure 1 (A). The FE-SEM micrograph reveals a macro-granular structure formed by the aggregation of small globular structures. The nature of particles has irregular in structure which reflects definite amorphous morphology. The micrograph depicts the presence of aggregation up to some extent as well as an agglomeration of particles (Gupta, Singh, Melvin and Prakash, 2014).

The complex dielectric constant of a system is represented as

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1)$$

where ϵ' is the real part of dielectric constant (dielectric permittivity) and ϵ'' is the imaginary part of dielectric constant (dielectric loss).

Figure 1 (B) displays the frequency dependence plots of real part of dielectric constant ϵ' for PIn with different stoichiometric ratios of indole and FeCl_3 as 70:30, 60:40, 50:50, 40:60 and 30:70 Wt. %. at different temperature. From the plot, it is clear that at a particular temperature the value of real dielectric constant (ϵ') decreases sharply with increase in frequency that is the contribution from charge carriers towards the dielectric constant decreases with

increase in frequency and attains a constant limiting value, which is not related to the hopping dynamics of mobile ions and may be due to the effect of rapid polarization process occurring in the samples. The high value of ϵ' in low-frequency region is a bulk phenomenon, which may be due to the presence of metallic or blocking electrodes which do not permit the mobile ions to transfer into the external circuit that is charge accumulation at the electrode-sample interface, as a result mobile ions pile up near the electrodes and give a large bulk polarization in the materials. In the high frequency region, at low temperatures, the well-known non-Debye behavior is observed. The observed frequency dependence of ϵ' for other compositions shows similar nature (Dutta, Sinha, Jena and Adak, 2008, Dutta, Biswas and De, 2002).

The variation of frequency dependence real part of dielectric constant (ϵ') with temperature is different for nonpolar and polar polymers. In general, for non-polar polymers, the ϵ' increases with temperature. The behaviour of the ϵ' in the present investigations is typical of polar dielectric, where dipole orientation is facilitated by the increased temperature resulting in increased real part of dielectric constant.

Figure 1 (C) shows the frequency dependence plots of imaginary part of dielectric constant (ϵ'') at various temperatures for PIn with different stoichiometric ratios of indole and FeCl₃ as 70:30, 60:40, 50:50, 40:60 and 30:70 Wt. %. In this figure it is observed that the loss factor ϵ'' exhibit the loss peak in the high frequency region. This behaviour indicates that the polarization of the samples obeys the Debye model (Fal, Cholewa, Gizowska, Witek and Zyla, 2017).

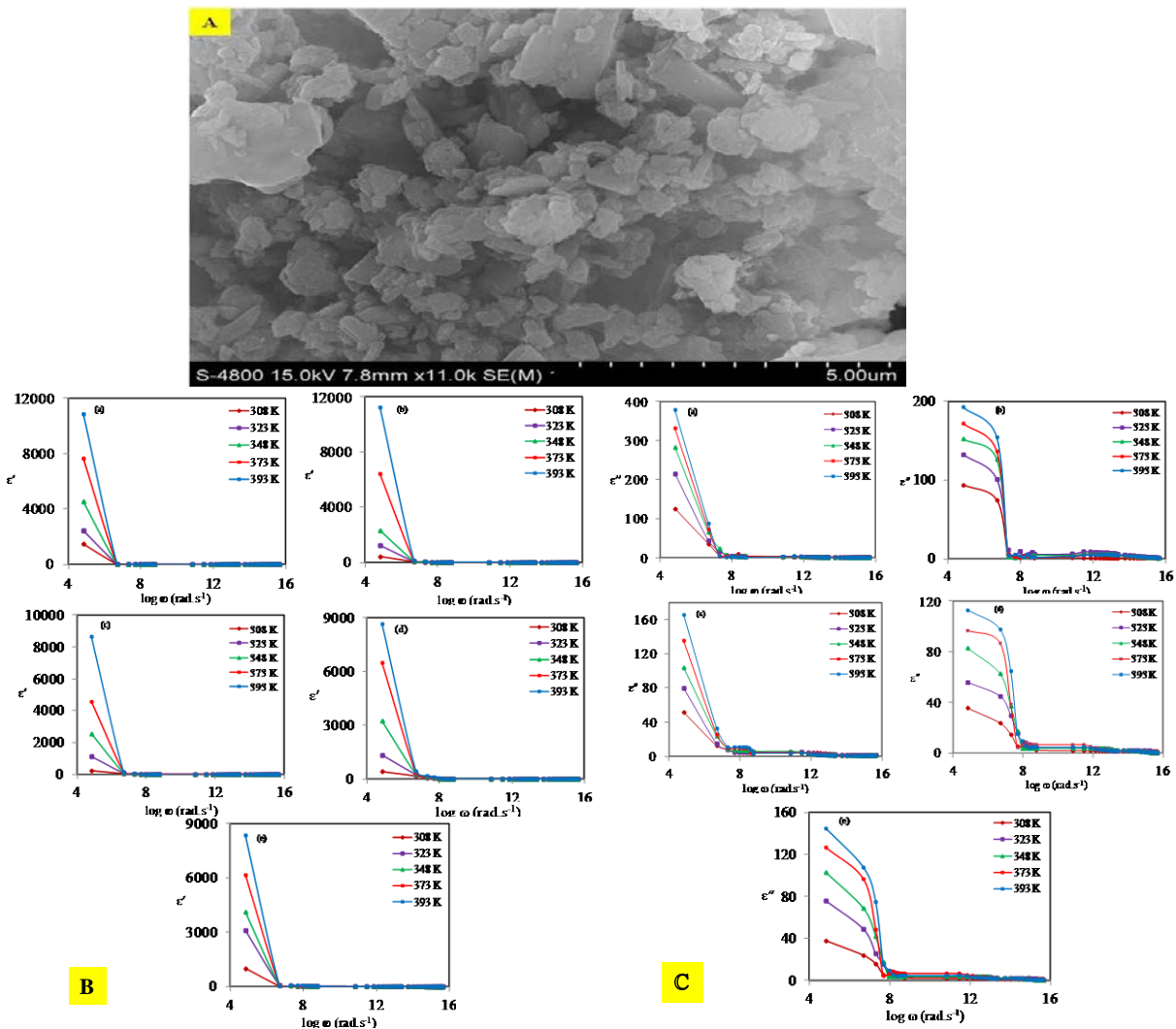


Fig. 1 - (A) FE-SEM micrograph of optimized PIn sample.; (B) The real part of dielectric constant (ϵ') as function of frequency for PIn samples; (C) The imaginary part of dielectric constant (ϵ'') as function of frequency for PIn samples.

4. Conclusions

In the summary of present work, we have successfully made an attempt for one pot chemical synthesis of PIn using FeCl_3 as an oxidant at room temperature in aqueous solution. The amorphous nature of as-synthesized optimized sample was confirmed through FE-SEM analysis. The complex dielectric constant of as-synthesized materials was studied by using ac impedance analyzer in the frequency and temperature ranges 20 Hz-1 MHz and 303-393 K respectively. The dielectric constant of the sample decreases with the increase in frequency and increases with increase in temperature. This behavior can be ascribed to the fact that at low frequencies, dielectric constant is the result of contribution of several kinds of polarizations as deformational (electronic, ionic) as well as relaxation (orientational and interfacial). When the frequency is increased, the electric dipoles cannot follow the field which leads to the decrease of orientational polarization. The decrease in dielectric constant with frequency is attributed to polar nature of the material

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