A Study on Conductivity Behaviour of Supramolecular Polymer Functionalized Magnetic Nanoparticles

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Abstract- **The present investigation deals with the synthesis and characterisation study of supramolecular polymeric nanocomposites. The nanocomposites are prepared by doping the magnetic ferrite nanoparticle into the synthesised Uriedo-pyrimidinone based supramolecular polymers. Magnetic nanoparticles have attracted intensive attention for their wide applications as biomaterials and energy storage devices. Supramolecular polymer composite is characterised by Fourier transform infrared spectroscopy (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The morphology of magnetic nanoparticles and a fracture surface of the composite material are analysed using the scanning electron microscope. The X-ray diffraction analysis enabled the identification of magnetic nanoparticles in polymer matrix. SEM images shows the dispersion of nanoparticles in the polymer matrix which are of different sizes. Dielectric measurements are performed on these composites on a LCR meter in the temperature range from 30°C to 100°C and in the frequency range 1 kHz - 10 kHz. The effect of temperature and frequency variation on dielectric constant (’), dielectric loss (tan) and a. c. conductivity ($_{a.c.}$) are determined. The result shows that the conductivity increases with rise in temperature. The dielectric constant, dielectric loss and conductivity of the supramolecular polymer were compared with magnetic nanoparticle doped composite.**

*Keywords-***Supramolecular polymer; magnetic nanoparticle; dielectric loss; nanocomposite.**

I.INTRODUCTION:

Supramolecular polymer electrolytes [SPE] are among the important class of macromolecules. These polyelectrolytes are charged with magnetic nanoparticles containing a large number of ionizable or ionic groups [1]. Ureido-Pyrimidinone based Supramolecular polymer nanocomposites are usually one dimensional in nature and the indepentant nanoparticles aggregates continue to exist either in melt or in dilute solutions [2]. The supramolecular polymer nanocomposites containing magnetic nanoparticles are usually investigated due to their unique electrical characteristics [3].

Ferrites which have a general structure of $[M^{2+}]_{tet}[Fe^{3+}]_{octa}O_4$ exhibit magnetic, electrical and catalytic characteristics among magnetic materials [4,5]. Due to their wide uses in several technologies and applications, spinel ferrites MFe_2O_4 (where M is often a transition metal atom) are kind of most important magnetic materials which are still widely investigated [6]. Polymer-blended magnetic materials are now extensively studied because of their high processability, versatility and low cost [7], and because of their fascinating physical properties that appear when the supramolecular polymer is added to the magnetic nanoparticles [8]. Among recent research articles concerned with polymer blended magnetic materials, Xiaowei et al [9] demonstrated a viable strategy for preparing polymer-coated functional metal oxides, which are potentially useful in biological and nanoelectronic applications. In the recent years, studies on the electrical properties of supramolecular polymer nanocomposites have attracted much attention in view of their application in electronic devices [10].

In this investigation, we report on the nitrogen-containing ureido-pyrimidinone based supramolecular polymers containing ferrite nanoparticles, which may significantly enhance the electrical conductivity of supramolecular polymer nanocomposites.

II. EXPERIMENTAL METHODS:

A.Materials

Zinc chloride ($ZnCl_2$), iron chloride ($FeCl_3.6H_2O$) and NaOH were purchased from Merck; Poly(tetrahydrofuran) diol ($PTHF(OH)_2$), 2-amino-4-hydroxy-6-methylpyridine, 2,4-toluene diisocyanato toluene, and dibutyl tin dilaurate (DBTDL) were purchased from Aldrich. PTHF ($OH)_2$ was dried at 60^oC for at least 24 hrs and 2-amino-4-hydroxy-6-methylpyrimidine was dried at 70^oC for 6 hrs before synthesis. Chloroform, DMF and Hexane were dried using common drying agents, distilled and stored prior to use.

B. Procedure

Synthesis of UPy based supramolecular polymer nanocomposites

Synthesis of UPy synthon was reported in our previous investigation [11]. The ferrite nanoparticles are synthesised by co-precipitation method [12]. The nanocomposite was prepared by mixing stoichiometric amount of synthesised supramolecular polymer in a dispersion of $ZnFe_2O_4$ nanoparticles in 30 ml of water at room temperature with constant stirring. The product formed and dried for the solvent was evaporated under reduced pressure. The resulting supramolecular polymer –magnetic ferrite nanocomposite was dried at room temperature for 6 h.

C. Characterisation

The synthesized supramolecular polymer magnetic nanocomposites was characterised by the XRD technique from powder crystalline samples at ambient temperature in a 2 range of 20° to 90°. Fourier transformed infrared (FT-IR) spectra were measured in the range 400-4000 cm^{-1} were recorded in order to investigate the nature of the chemical bonds formed. The morphology of the nanocomposite sample was obtained from scanning electron microscopy. The real (') and imaginary (") parts of nanocomposite dielectric permittivity and ac conductivity have been calculated over a wide range of temperatures (30^oC and 100^oC) and frequencies (10 and 100 kHz) using dielectric-impedance analyser.

III. RESULTS AND DISCUSSION:

A.FT-IR analysis

FT-IR spectra of the synthesised supramolecular polymer nanocomposites shown in figure 1. Two absorption bands are observed at 599 and 561 cm^{-1}, which can be attributed to the coupling between Fe-O stretching modes of tetrahedral and octahedral sites as expected from normal spinal structure. The peak at 3332 cm^{-1} indicates the N-H stretching of secondary amine. The peak at 1566 cm-1 is attributed to the characteristic C=C stretching of the benzene ring and 1348 cm^{-1} is assigned to C-N stretching of the benzene ring. The peaks at 3612, 2939.52 cm^{-1} corresponding to the stretching and bending vibration of O-H and C-H respectively as shown in Fig.1.
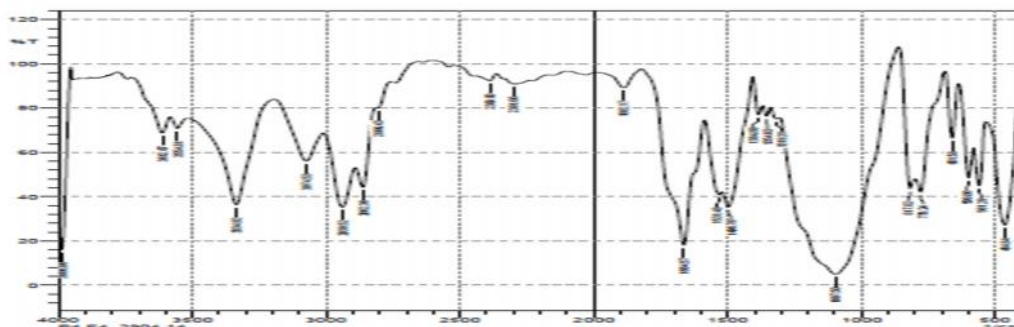

Fig. 1 FT-IR spectra of UPy based polymer nanocomposites

B. XRD analysis

The formation of magnetic nanoparticles and Ureido-pyrimidinone based supramolecular polymer doped nanoparticles was confirmed from XRD pattern (Fig.2). The average crystalline diameter has been calculated using Debye-Scherrer's equation as shown below,

$$D = 0.9\,\lambda / \beta \cos\theta$$

Where β is the line broadening at the full-width at half maximum (FWHM) of the most intense peak, θ is the Bragg's angle and λ is the X-ray wavelength. The result shows that the particle size of supramolecular polymer funtionalised magnetic nanoparticles was calculated as 93.4 nm.
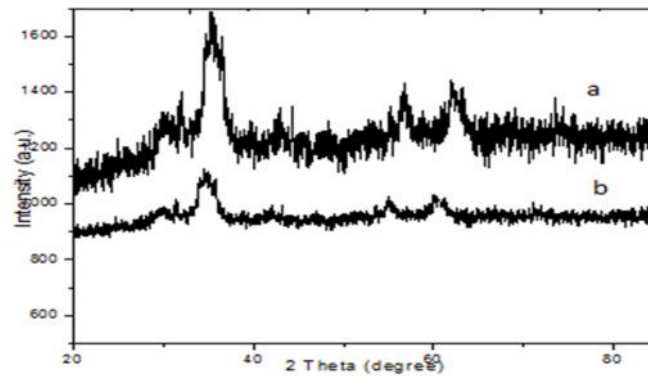

Fig. 2. X-ray diffraction of (a) magnetic nanoparticles (b) polymer doped magnetic nanoparticles

C. SEM analysis

Fig. 3 shows the SEM images for samples magnetic nanoparticles, supramolecular polymer and supramolecular polymer nanocomposites. From Fig. 3, it can be observed that the magnetic nanoparticles are in highly agglomerated form whereas supramolecular polymer doped nanoparticles show well dispersed characteristic.
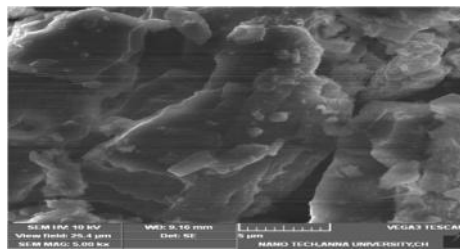

Fig.3. SEM image of Supramolecular polymer doped magnetic naocomposites.

D. Electrical conductivity studies

The effect of temperature and frequency variation on dielectric constant (ε'), dielectric loss (tan δ) and a. c. conductivity ($\sigma_{a.c.}$) are determined by the ac impedance analysis.

E. AC ionic conductivity

The ionic conductivity of the supramolecular polymer nanocomposites was derived from the impedance plots (Z' vs Z'') in the composites are carried out at two different temperatures. from the complex impedance spectrum and given in Figure 4 (a) and (b).

A bulk ionic conductivity values are 3.97×10^{-4} ohm^{-1} cm^{-1} and 15.12×10^{-4} ohm^{-1} cm^{-1} at 30°C and 100°C respectively was calculated by using the equation,

$$\sigma_b = L/R_b\, A$$

where L is the thickness of the polymer nanocomposite pellet and A is the surface area of it. The resistance of the nanocomposite (R_b) was determined from the intercept of the impedance spectrum on the Z' real axis. The increase in σ_{ac} with temperature can be explained on the basis that raising the temperature causes more structure relaxation and releasing ability of magnetic nanoparticles.
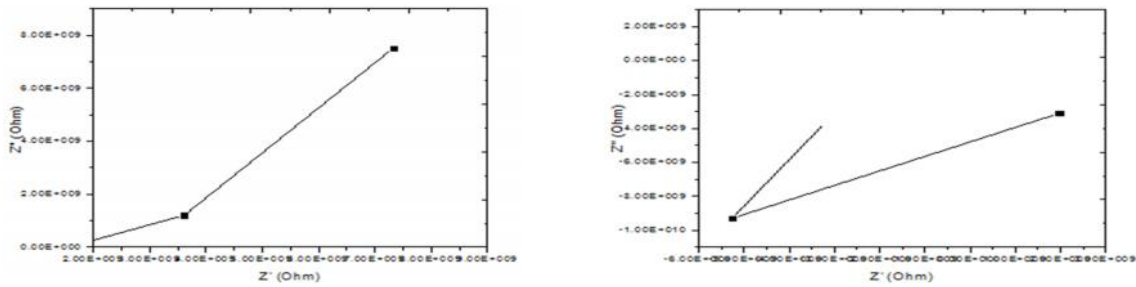

Fig.4 (a) and (b) Plot of Z' vs Z'' for nanocomposite at 30°C and 100°C

F. Dielectric Permittivity and Loss Studies

Figures 5 (a) and (b) show the variation of dielectric constant and dielectric loss of supramolecular polymer nanocomposites. Both ε' and ε'' of polymer nanocomposites initially decrease by increasing the applied frequency. This behavior is may be due to the fact that at low frequencies the dipoles have sufficient time to align with the polymer matrix before it changes its direction and consequently, the dielectric constant is high.
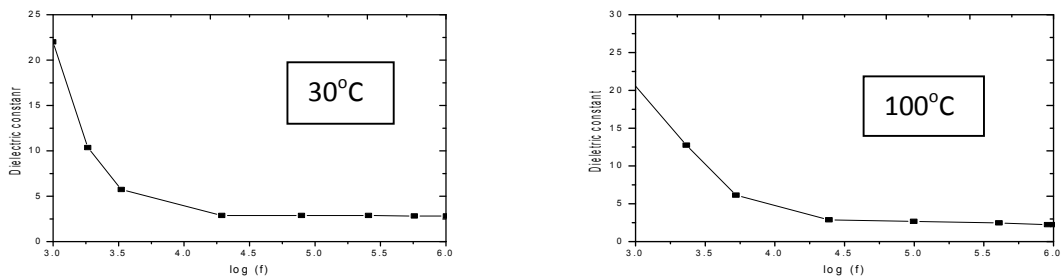

Fig 5: (a) and (b): Variation of dielectric constant at different temperatures.

IV. CONCLUSION:

In this study, the synthesis, conductivity and permittivity characterization of the supramolecular polymer nanocomposites have been reported. Polymer doped magnetic nanoparticles in the form nanocomposites were obtained through interfacial interactions between Ureido-pyrimidinone based supramolecular polymer and ferrite nanoparticles. The highest conductivity ($\sigma = 15.12 \times 10^{-4}$ ohm^{-1} cm^{-1}) was obtained at 100°C for nanocomposite, which is much higher than that of 30°C ($\sigma = 3.97 \times 10^{-4}$ ohm^{-1} cm^{-1}). These high values of electrical conductivity, dielectric permittivity and dielectric loss at room temperature lead to make the sample as a promising material in the solid state electrochemical devices.

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