Preparation and Dielectric Properties of Magnetite/Chitosan Nanocomposite Film

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ABSTRACT

Pure magnetite (Fe₃O₄) nanoparticles were synthesized and successfully coated with chitosan (CS). XRD patterns confirmed the formation of a pure spinel Fe₃O₄ structure without presence of any other phases. TEM results revealed that the Fe₃O₄ nanoparticles were 17.6-19.5 nm in size with a good homogeneously dispersion. The frequency dependences of the dielectric constant as well as the dielectric loss have been reported at different temperatures for pure CS and Fe₃O₄/CS nanocomposite films. Dielectric measurements showed that both of them recorded lower values with increasing frequency, whereas they showed a proportional relationship with temperature.

Key words: Magnetite, Chitosan, Electrical Properties

Introduction

Among all iron oxide nanoparticles, magnetite (Fe₃O₄) represents the most interesting properties due to its unique structure i.e. the presence of iron cations in two valence states, Fe³⁺ and Fe²⁺ on tetrahedral and octahedral sites with an inverse cubic spinel structure (Rahman et al., 2012). The electrons can hop between Fe³⁺ and Fe²⁺ ions in the octahedral sites at room temperature, rendering magnetite an important class of half-metallic materials (Ozkaya et al., 2009).

However, aggregation of Fe₃O₄ nanoparticles due to high surface area and magnetic dipole interaction between nanoparticles has limited their applications. This problem can perhaps be overcome by dispersing Fe₃O₄ nanoparticles in a biopolymer matrix (Kaushik et al., 2008, Kaushik et al., 2009). Among these biopolymers, Chitosan (CS) is a polyaminosaccharide produced by deacetylation of chitin naturally extracted from shells of crabs and shrimps, or isolated from the cell walls of fungi. It displays an excellent film-forming ability, good adhesion, biocompatibility, high mechanical strength and susceptibility to chemical modification due to the presence of reactive hydroxyl and amino functional groups (Kaushik et al., 2009). These composites are technologically important and have been used in many applications including magnetic recording media and magnetic fluids for the storage and retrieval of information, magnetic resonance image enhancement, and others (Gubin et al., 2009; Misra et al., 2004; Misu et al., 2011 and Yelenich et al., 2013).

In this study, pure Fe₃O₄ nanoparticles were prepared by hydrothermal method and successfully coated with CS biopolymer to form Fe₃O₄/CS nanocomposite film. Structural and morphological characteristics of the prepared nanoparticles were revealed. The dielectric measurements for pure CS and Fe₃O₄/CS nanocomposite films were studied as a function of frequency at different temperatures.

Experimental:

Preparation of Fe₃O₄ nanoparticles, CS film and Fe₃O₄/CS nanocomposite film:  
Fe₃O₄ nanoparticles were prepared by dissolving 2.5g of ferrous sulphate heptahydrate (SHAM LAB, Syria) in 30ml distilled water, then 10ml of PEG-20000 (England) was added to the solution at 30°C under vigorous stirring. During the reaction process, NH₄OH (ABCO CHEMIE, England) was added up to a pH value of 10. Then, 0.27ml of H₂O₂ (LOBA CHEMIE, India) solution was added to the stirred mixture and stirred for 20 min. The mixture was transferred into the autoclave and heated at 160°C in the oven for 15 h. The sample was washed by ethanol and distilled water several times. Finally, the sample was dried at 70°C (Li et al., 2008).

Fe₃O₄/CS nanocomposite film was synthesized by dissolving 1g of chitosan (MALLINCKRODT, France) in 1% CH₃COOH solution, then adding 0.05g of the prepared Fe₃O₄ nanoparticles. The solution was ultrasonicated for

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2 h. Finally, the mixture was poured into petridishes. Pure CS film was synthesized without addition of the prepared Fe$_3$O$_4$ of nanoparticles.

The prepared compounds were characterized by X-ray powder diffractometer (X’ pert pro. PANlytical, Holland), transmission electron microscopy (HR TEM-JEM 2100, JEOL, Japan). Dielectric measurements of the prepared samples had been measured over the temperature range (25-80°C) and frequency range (100 HZ-5 MHZ) using HIOKI Japan 3532-50 LCR HI TESTER that has been interfaced to a computer.

Results and Discussion

XRD results:

The crystal structures of pure CS, Fe$_3$O$_4$ nanoparticles and Fe$_3$O$_4$/CS nanocomposite film revealed by XRD are presented in (Fig. 1a-c). XRD patterns of pure CS showed distinct crystalline peaks at around 2θ values 20̊, 26.7̊ and 28.3̊, and this is because of presence of plenty of –OH and –NH$_2$ groups in the chitosan structure, which could form stronger inter and intramolecular hydrogen bonds (Ramya et al., 2012).

XRD patterns of Fe$_3$O$_4$ nanoparticles exhibited a typical Fe$_3$O$_4$ cubic spinel structure (Cuong et al., 2012). The positions and relative intensities of all diffraction peaks match well with those from the JCPDS card number 89- 4319 for Fe$_3$O$_4$. XRD patterns of Fe$_3$O$_4$/CS nanocomposite film showed intensity decreasing of the diffraction lines of the composite indicating that the Fe$_3$O$_4$ particles were successfully coated by amorphous CS (Salah El-Din et al., 2011). It is also evident that the CS coating process did not result in a phase change of Fe$_3$O$_4$ MNP (Chen et al., 2011). The average crystal size of pure Fe$_3$O$_4$ and Fe$_3$O$_4$/CS nanocomposite was 19.2 and 22.9nm, respectively.

![XRD patterns of (a) pure CS and (b) Fe$_3$O$_4$ nanoparticles and (c) Fe$_3$O$_4$/CS nanocomposite film](image)

TEM analysis:

TEM image of pure Fe$_3$O$_4$ revealed that the sample consists of uniform spherical particles with narrow size distribution and average particle size of 19.5 nm. This is consistent with XRD data calculated by the Scherrer’s formula. Whereas TEM image of Fe$_3$O$_4$/CS nanocomposite film, revealed a uniformly dispersion of Fe$_3$O$_4$ nanoparticles with 30.4 nm average particle size embedded inside CS matrix.
Electrical properties:
The frequency dependence of dielectric constant at different temperatures for pure CS and Fe\textsubscript{3}O\textsubscript{4}/CS nanocomposite films in the frequency range 100Hz-5MHz was shown in Fig. 3a and b. It could be noticed that the dielectric constant for the samples presented a relatively high value at low frequency range, decreased with increasing frequency and almost remained independent of applied external field at high-frequency division. It can be realized that, at lower frequency, the dipoles in the system can reorient themselves to respond to applied electric field. Whereas at higher frequency, the decrease of dielectric constant values was attributed to the lag of molecules towards the applied electric field and this could be explained by the difficulty of dipoles orientation in this frequency range (Srivastava et al., 2014). Moreover, it was also observed that the dielectric constant ($\varepsilon'$) of Fe\textsubscript{3}O\textsubscript{4}/CS nanocomposite film was greatly influenced and was found to be higher than that of pure CS film. On the other hand, the dielectric constant increased with increasing temperature and this increase may be due to the thermal energy supplied to the material which is sufficient enough to free the localized dipoles and they align themselves in the direction of applied field (Joshi et al., 2014).

Fig. 3: Variation of dielectric constant with frequency at different temperatures for (a) pure CS film and (b) Fe\textsubscript{3}O\textsubscript{4}/CS nanocomposite film.

Fig. 4a and b demonstrated the dielectric loss of pure CS and Fe\textsubscript{3}O\textsubscript{4}/CS nanocomposite films, respectively as a function of frequency at different temperatures. It was observed that the dielectric loss ($\varepsilon''$) of the samples decreased as the frequency increased and almost remained constant at higher frequency. The trend observed could be ascribed to dipole polarization. Moreover, it was also observed that the dielectric loss of Fe\textsubscript{3}O\textsubscript{4}/CS nanocomposite film was greatly influenced and was found to be higher than that of pure CS film. On the other hand, the increase in dielectric loss with increasing temperature may be attributed to increasing lattice vibrations and creation of some phonons which interact with the charge carriers giving rise to electron phonon scattering (Joshi et al., 2014).

Fig. 2: TEM images of (a) Fe\textsubscript{3}O\textsubscript{4} nanoparticles and (b) Fe\textsubscript{3}O\textsubscript{4}/CS nanocomposite film.
Fig. 4: Variation of dielectric loss with frequency at different temperatures for (a) pure CS film and (b) Fe3O4/CS nanocomposite film.

Conclusion

Pure Fe3O4 nanoparticles were prepared by hydrothermal method and successfully coated with CS biopolymer. XRD patterns and TEM micrographs confirmed formation of a pure spherical Fe3O4 and a mean diameter of 19.5. The dielectric constant and dielectric loss values decreased with increasing frequency and increased with temperature increase.

Acknowledgements

Authors are thankful to Prof. Dr. Mahmoud Farag Zawrah, Professor of Chemistry of Advanced Materials and Nanotechnology (National Research Center), who allowed for doing this work at his lab.

References


