Conductivity and dielectric properties of PANI-Fe_2O_3 composites synthesized by in situ polymerization technique

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Abstract

In the present work we report the synthesis of PANI-Fe_2O_3 composites by in situ polymerization technique. The Fe_2O_3 content in the composites was varied from 10 to 50 wt%. Morphological and structural characterization of the as synthesized composites was carried out using scanning electron microscope and X-ray diffraction technique. The AC conductivity and dielectric constant of composites were studied as a function of frequency. With the increase in Fe_2O_3 content in composites from 10% to 50% the conductivity is found to increase at higher frequencies. The dielectric constant measurements showed that with the increase in Fe_2O_3 concentration the dielectric constant was found to be increasing and was highest for composite with 50% Fe_2O_3 content.

Keywords: PANI-Fe_2O_3, Scanning electron microscopy, X-ray diffraction

I. Introduction

In past few years polymeric materials have been quite popular for solid state devices mainly due to electrical transport properties. When combined with appropriate filler materials with suitable compositions unique conducting polymer composites with desired properties can be obtained. The field of conducting polymers has been a huge attention due to potential applications like electromagnetic interference shielding, molecular electronics and light emitting diodes due to their high durability, light weight and high efficiency. Among various conducting polymers, polyaniline is quite popular because its electrical properties could be tunable by charge transfer doping and protonation as well. In addition to this it can be synthesized easily and by inexpensive method and is light in weight. PANI can be synthesized by electrochemical and chemical routes in which in situ polymerization technique is quite popular.Although PANI is quite attractive but due to its insolubility in common solvent and poor mechanical properties are obstruction for many potential applications. So in order to overcome such issues PANI is incorporated with either metal or metal oxide particles. These filler materials are found effective in improving the optical, mechanical and physical properties. All these properties are highly influenced by filler particles content, shape and size. In particular the electrical conductivity of the composites tends to increase with the incorporation of filler particles as they tend to act as conductive junctions between the chains of PANI [1-3].

Among the available metal oxides, Fe_2O_3 are popular due to their electrochemical, magnetic and photocatalytic properties. This metal oxide is quite popular for gas sensing properties and is capable of sensing a number of gas vapours such as H_2, CO, NO_2, NH_3, acetone and ethanol. Fe_2O_3 metal oxide particles can be synthesized by various routes which includes flame spray pyrolysis, solvothermal, hydrothermal, microwave or laser induced ablation. On the other hand the functional properties of conducting polymer used for gas sensing applications can be further improved by adding metal oxide particles like Fe_2O_3. Because many conducting polymers like polypyrrole and PANI are already in use for deducting inflammable gases and other volatile organic compounds due to their high sensitivity. PANI has been used in gas sensing and deducting volatile organic compounds due to its singular redox properties.In particular PANI is used for hazardous NH_3 gas sensing applications for monitoring air quality in various industries. Improvement in properties of the Fe_2O_3/polymer composites can be achieved but it depends on various factors like morphology, content and interface of individual components of the composites [4-6].

Many attempts have been made for developing Fe_2O_3 based composites for broad range of applications. Bandgar et al [7] developed the camphor sulfonic acid based PANI/α-Fe_2O_3nanocomposite for ammonia gas sensing applications. Uniform and flexible nanocomposite films of different compositions (10-50%) were synthesis by in-situ polymerization technique.The gas selectivity test was performed for different gases like NH_3, NO_2, LPG and C_2H_5OH.The gas sensing measurements showed that the out of all the 30%camphor sulfonic acid based nanocomposite flexible films were highly sensitive to ammonia gas by showing maximum response of 72% at room temperature. Here the gas sensing mechanism was described on the basis of variation in resistance of nanocomposite after interaction with NH_3 gas. Further the developed nanocomposites were able to detect the NH_3 of very small concentration of 2.5 ppm. In another work, Sonker and Yadav [8] studied the NO_2 gas detection behaviour of PANI/α-Fe_2O_3 at room temperature. The composite films were developed using spin coating technique and the Fe_2O_3nanoparticles concentration was varied from 1, 3, 5 and 10%. The composite film showed high sensing response of ~2.29×10^2 towards 20 ppm of NO_2 gas with a moderate response time of 2.35 minutes. Here the improvement in sensing properties of composite films was attributed to Fe_2O_3 nanoparticles which not only tunes the active sites for adsorption but also desorption of NO_2 gas. In the present

we report the synthesis of polyaniline-Fe_2O_3 composites prepared by in situ polymerization technique with varying Fe_2O_3 content. The developed composites were characterized using X-ray diffraction, Scanning electron microscopy and Fourier transformation infrared spectroscopy (FTIR). The AC conductivity and dielectric properties of composites as function of frequency with varying Fe_2O_3 concentration was also studied.

II. Experimentation

Synthesis

Synthesis of the PANI–iron oxide (Fe_2O_3) composites was carried out by polymerization *in situ*. Aniline (0.2 M) was dissolved in 1 M HCl and stirred for 2hrs to form aniline hydrochloride. Iron oxide was added in the mass fraction to the above solution with vigorous stirring in order to keep the Fe_2O_3 homogeneously suspended in the solution. To this mixture, 0.2 M of ammonium persulphate, which acts as an oxidant was slowly added drop-wise with continuous stirring at room temperature for 8 hrs to completely polymerize the monomer aniline. The precipitate was filtered, washed with demonized water, and finally dried in an oven for 24 hrs to achieve a constant mass. In this way, PANI–Fe_2O_3 composites containing various mass fractions of Fe_2O_3 (10%, 20%, 30%, 40% and 50%) in PANI were synthesized.

III. Characterization

The powder morphology and the structural characterization of PANI–Fe_2O_3 composites synthesized by in situ techniquewere studied using scanning electron microscopy (SEM, JSM-6360LV, Japan) and X-ray diffraction (XRD). The X-ray diffraction patterns of the powders were taken using Philips XPERT diffractometer using Cu Kα radiation (λ = 1.54 A˚). The AC conductivity and dielectric properties of all the composites with different Fe_2O_3 content were studied in the frequency range of 0.2 to 10 MHz using LCR-Q meter (Wayne Kerr, 4300) analyser. The Fourier transform infrared spectra (FTIR) were taken using Perkin Elmer (model 783) IR spectrophotometer in KBr medium to confirm the presence of Fe_2O_3 in PANI in the frequency range of 400 – 4000 cm^{-1}.

IV. Results and discussion

Characterization: SEM and X-ray diffraction

Figure 1 a - e shows the SEM micrographs depicting morphology of PANI–Fe_2O_3 composites with varying Fe_2O_3 content from 10% to 50%. From the SEM micrographs it can be observed that various sizes of Fe_2O_3 particles are embedded in the lumps of the composite. Careful examination of images reveals that the Fe_2O_3 particles are dispersed uniformly on the surface of PANI. Further the PANI chains were found to be surrounded by the Fe_2O_3 particles. Here morphological aspects like the roughness and porosity of the composite films was dependent on the Fe_2O_3 content which is quite advantageous for gas sensing applications mainly due to large surface area. The X-ray diffraction patterns of PANI–Fe_2O_3 composites with different Fe_2O_3 content are shown in figure 2. Many well defined and broad peaks were observed at different 2θ angles = 35.8°, 49.8°, 53.6° and 62.4° to (3 1 1), (4 0 0), (4 2 2) and (5 1 1) planes of Fe_2O_3. All these peak positions obtained for Fe_2O_3 are well in line with that of values reported for γ-Fe_2O_3. Here the all these planes corresponds to rhomohedral crystal structure of Fe_2O_3 while close observation shows the (1 0 0) plane corresponding to that of PANI was seen in XRD patterns with higher Fe_2O_3 content composites. Further the sharp nature of the peaks suggests that the composites produced are crystalline behaviour. However the wide peaks obtained for the composites for the 2θ in between 18° and 31° suggests the mixture of crystalline Fe_2O_3 phase and amorphous phase of PANI [9, 10].

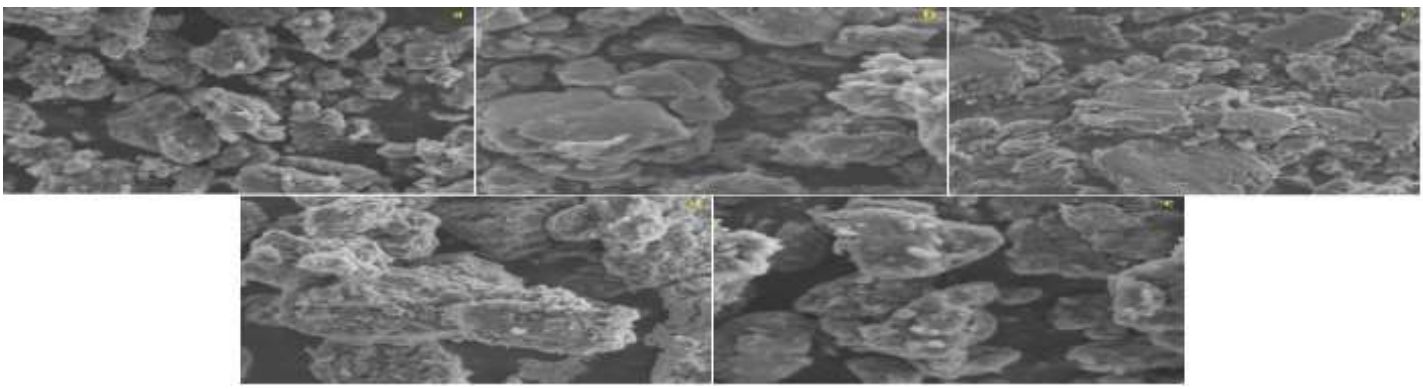


Figure 1 SEM micrographs of PANI-Fe_2O_3 composites with different Fe_2O_3 content: (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 wt%.

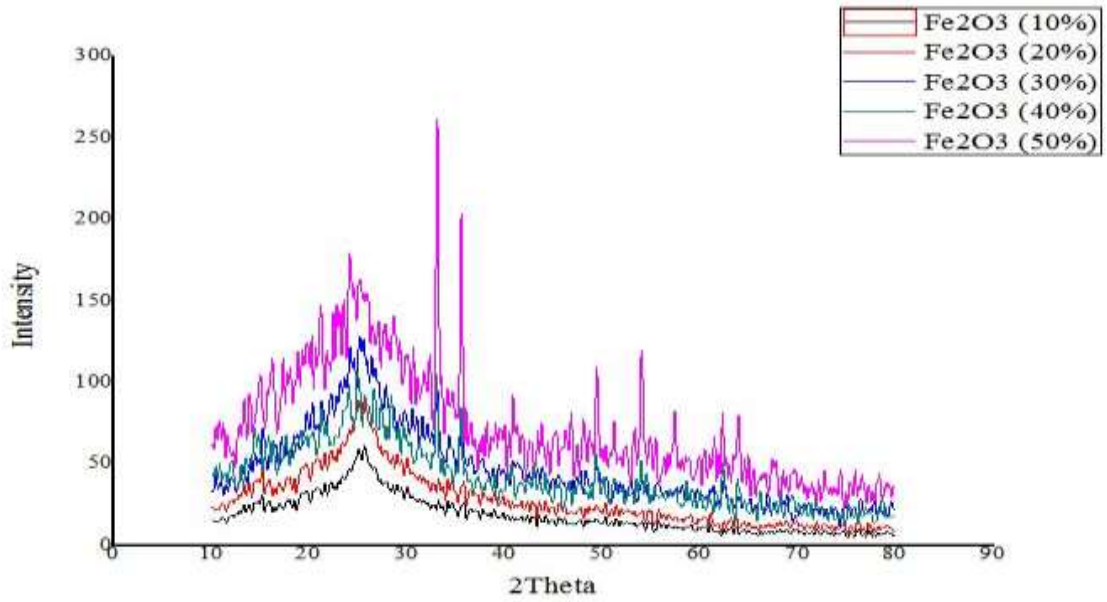
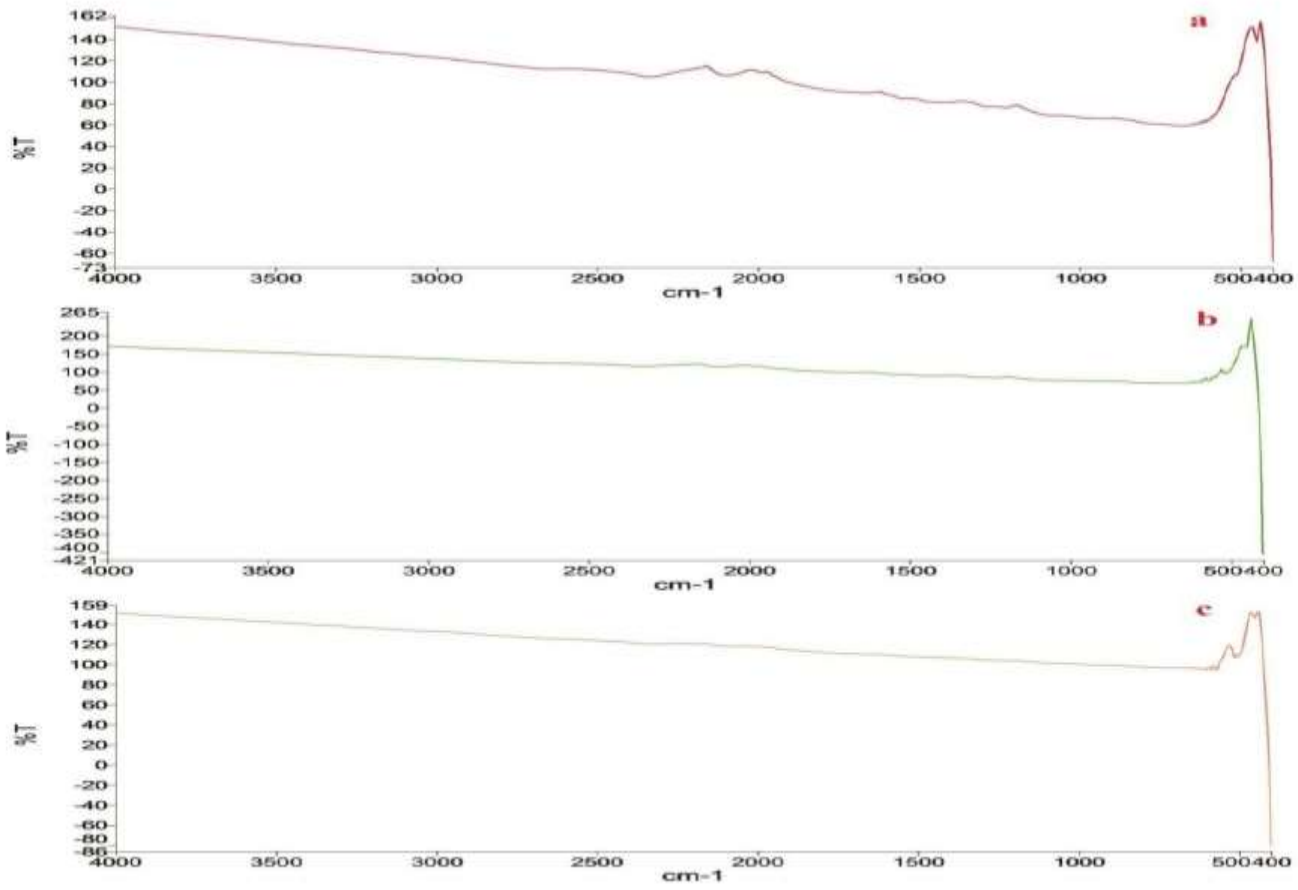


Figure 2 X-ray diffraction patterns of PANI-Fe_2O_3 composites with different Fe_2O_3 content.

V. Functional group identification



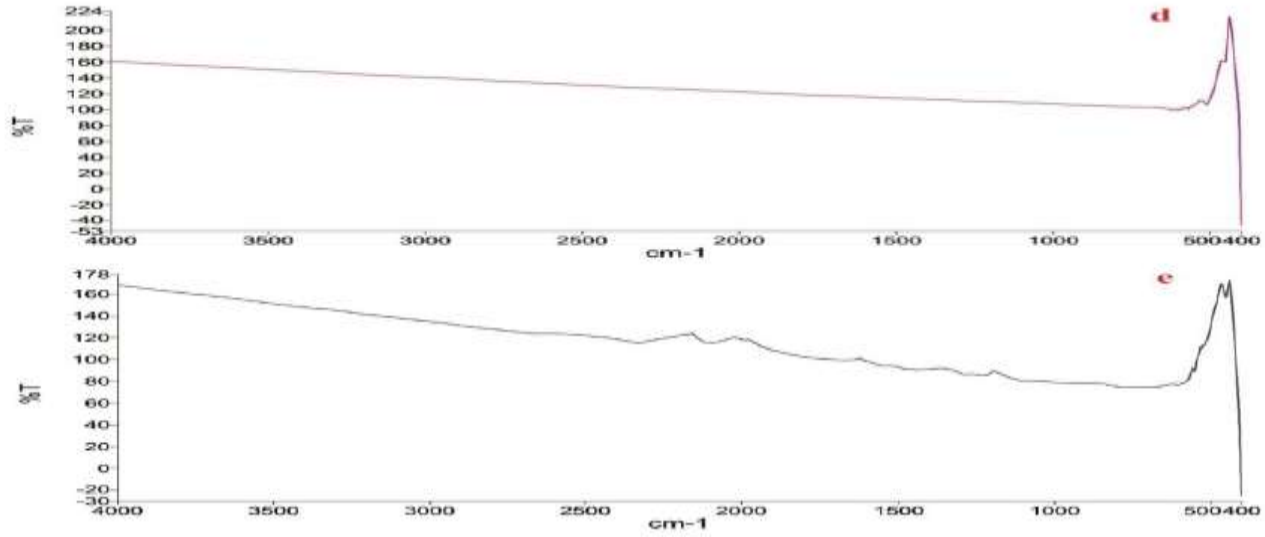


Figure 3 FTIR spectra of PANI-Fe_2O_3 composites with different Fe_2O_3 content: (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 wt%.

Figure 3 a - e shows the characteristic of functional groups of PANI–Fe_2O_3 composites with varying Fe_2O_3 content from 10% to 50%. A broad peak observed at 2201 cm^{-1} is attributed to overlapping of Fe-OH stretching vibration on N-H stretching vibration. Further the peak observed at 1380 cm^{-1} belongs to stretching vibration of NO_3^- ions. Finally a sharp peak observed at 512 cm^{-1} corresponds to stretching of Fe-O bond. Generally this peak is observed at 530 cm^{-1}, but in present case due t interaction with PANI the peak is shifted from 530 cm^{-1} to 512 cm^{-1}[11].

AC conductivity of PANI-Fe_2O_3composites

The AC conductivity of all the composites as a function of frequency with varying Fe_2O_3 content is shown in figure 4. The observation tells us that all composites show similar behaviour up to a frequency of 2×10^5 Hz and after that the conductivity increases significantly. With the increase in Fe_2O_3 content in composites from 10% to 50% the conductivity is found to increase at higher frequencies. High conductivity is observed in composites with Fe_2O_3 content of 50%.The increase in AC conductivity of the composites is mainly due to extended chain length of PANI which helps in polarisation of charge carriers between localized sites and offers a lot of conductive path. According to percolation theory the metal oxide particles like Fe_2O_3 and conducting polymer like PANI, a conductive path is formed in their composite for the flow of current resulting in the increase in AC conductivity. However there are some works where the authors [10] have reported drop in AC conductivity beyond 20% of Fe_2O_3 content which was attributed to blockage of charge hop carriers.

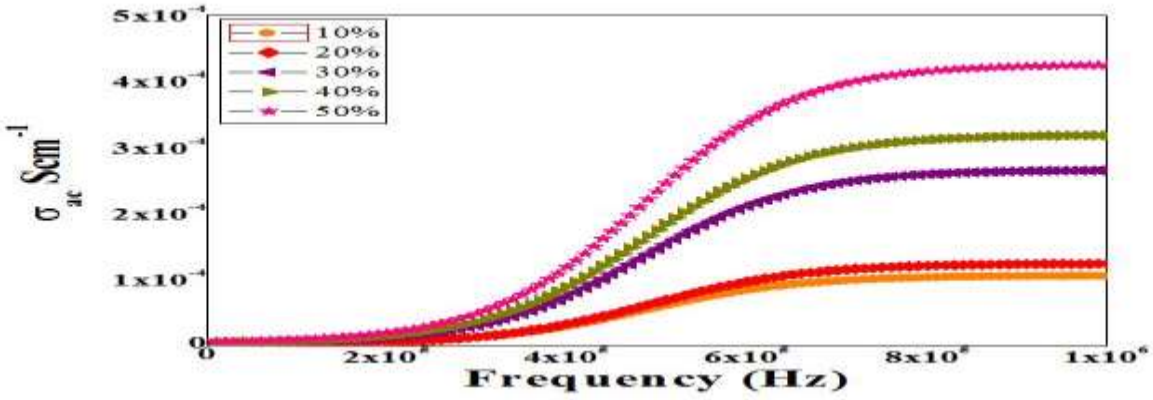


Figure 4 AC conductivity of PANI-Fe_2O_3 composites as a function of frequency for different Fe_2O_3 content.

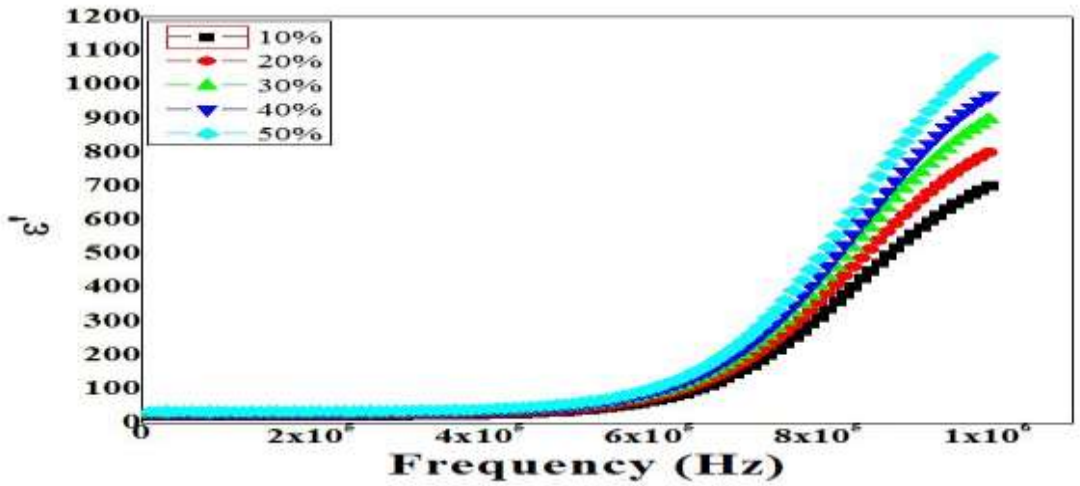


Figure 5 Variation of ε' for PANI-Fe_2O_3 composites as a function of frequency for different Fe_2O_3 content.

Dielectric behaviour of PANI-Fe_2O_3 composites

Figure 5 shows the dielectric behaviour (ε') as a function of frequency for PANI-Fe_2O_3 composites with varying Fe_2O_3 content. It can be observed that the dielectric constant ε' up to 4×10^5 Hz for all the composites is constant. Later the dielectric constant tends to increase with the increase in frequency as well as with the increase in Fe_2O_3 content. Incorporation of Fe_2O_3 resulted in significant increase in dielectric constant of the composite. Further as the Fe_2O_3 content in composite is increased from 10 to 50% the dielectric constant tends to increase. The variation in the dielectric constant is mainly due to the concentration of Fe^{3+} ions in the composites. It is well known that the Fe^{3+}ions have spherical symmetry which on addition of extra electrons is found to be disturbed. So this result in charge transfer $Fe^{3+}\leftrightarrow Fe^{2+}$ causing displacement of electron and leading to polarization. Due to increase in Fe^{2+} ions resulting in increase in polarization, it is found that the increase in Fe_2O_3 content in composite resulted in increase in dielectric constant. Further the increase in the dielectric constant can also be attributed to increase in the AC conductivity of the composites. This indicates better the dielectric constant higher is the ability of composites to store electric energy [12].

VI. Conclusions

The following conclusions were drawn from the current study,

- PANI-Fe_2O_3 composites with varying Fe_2O_3 content from 10% to 50% have been successfully synthesized by in situ polymerization technique.
- The composites showed higher AC conductivity values at higher frequencies due to extended chain length of PANI which helps in polarisation of charge carriers between localized sites.
- Out of all, the composite with highest Fe_2O_3 content of 50% was found to possess highest AC conductivity indicating charge transport as dominant mechanism.
- The dielectric constants measured for all composites displayed increase in values with the increase in Fe_2O_3 content. The increase in dielectric constant is attributed to increase in Fe^{2+} ions which contribute to increase in polarization.

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