

Electric Modulus Properties of Ppy/Cuznfe₂o₄ Nanocomposites

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Abstract: Frequency and temperature dependences of electric modulus of pure Polypyrrole and Polypyrrole doped with CuZnFe₂O₄ nanoparticles were investigated using ac impedance spectroscopy in the frequency range 100 to 5MHz, at temperatures 30 °C, 100 °C, 150 °C and 200 °C. In addition, the real (M') and imaginary (M'') components of the electrical modulus were calculated from the values of ε' and ε''. Using the electric modulus formalism It has been found that the Cole – Cole equation of dielectric relaxation expressed in the electric modulus form is capable of quantitatively describing the experimental data from which we extract the relaxation time and a parameter which gauges the broadening of the loss spectrum.

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I. Introduction

Composite materials are considered as the materials of two or more constituents with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure. These composites have good potential for various industrial fields because of their excellent properties such as high hardness, high melting point, low density, low coefficient of thermal expansion, high thermal conductivity. Polymer nanocomposites are a special class of advanced materials in which nanomaterials are dispersed in polymers. They exhibit amazing combination of properties and hence find applications in EMI shielding, electronic devices, Microwave absorbers, sensors, rechargeable batteries etc;[1]. In polymer nanocomposites conductivity depends on various factors such as filler morphology, size, loading concentration, compactness and interfacial interaction. Electrical transport process parameters such as carrier/ion hopping rate; conductivity relaxation time, etc. in the material can be analyzed via complex electric modulus formalism. The electric modulus corresponds to the relaxation of the electric field in the material when the electric displacement remains constant, so that the electric modulus represents the real dielectric relaxation process,

Modulus representation is now widely used to analyze ionic conductivities[2]. Polypyrrole (PPy) is one of the most attractive polymers due to its special transport properties, facile synthesis, higher conductivity and good environmental stability. Polypyrrole has the advantages real applications in batteries, electronic devices, optical switching devices, functional electrodes, sensors and so on[3]. Nano crystalline ferrites are materials of considerable interest due to their unique dielectric, magnetic and optical properties. Copper zinc iron oxide nano particles (copper zinc nano ferrites) are used in sensors - LPG sensing [4]. Copper zinc iron oxide nano particles of size <100nm are selected for our investigation.

In this article we report the temperature and frequency dependence of the electric modulus (real and imaginary part) in CuZnFe₂O₄ Polymer nanocomposites at frequencies 10² –10⁶ Hz at temperatures 30 °C, 100 °C, 150 °C and 200 °C.

II. Experimental Details

Chemicals - The monomer pyrrole, oxidising agent Ammonium persulphate, nanopowder Copper zinc iron oxide, acetone were purchased from Sigma Aldrich. All chemicals were of analytical grade and used as received without any further treatment.

2.1. Synthesis of Polypyrrole

Polypyrrole was synthesized by in-situ polymerization of monomer pyrrole in the presence of oxidising agent ammonium persulphate. 0.3M pyrrole taken in a round bottomed glass flask was placed in an ice tray mounted on a magnetic stirrer. 0.6M Ammonium persulphate was added drop wise using a burette to the above 0.3M pyrrole. The reaction was carried out for 5 hours under continuous stirring maintaining temperature of 0 to 5 degree Celsius. The resulting precipitate was removed by filtration by suction. The

polypyrrole powder thus obtained was then dried in a hot air oven and subsequently in a muffle furnace at a temperature of 100 degree Celsius. The yield was 2.15 gm, taken as 100Wt% [5].

PPy/CuZnFe₂O₄Nanocomposites were synthesized by in-situ polymerization of monomer Pyrrole using ammonium persulphate as oxidising agent reported in detail elsewhere. [6].

The pure polypyrrole and PPy/CuZnFe₂O₄ nanocomposites are pressed in the form of pellets of diameter 10mm and thickness 1 to 3 mm, using hydraulic press by applying 10-12 tons of pressure. The pellets of the synthesized composites are coated with silver paste on either side of the surfaces to obtain better contacts for conductivity measurements[7].

III. Results And Discussion

The electric modulus corresponds to the relaxation of the electric field in the material when the electric displacement remains constant, so that the electric modulus represents the real dielectric relaxation process, which can be expressed as

$$M^* = \frac{1}{\epsilon^*} = M' + iM''$$

It is the reciprocal of the permittivity $M^* = \frac{1}{\epsilon^*}$ [8]

Fig.5.22 shows variation of real and imaginary part of Electric modulus (M' and M'') of PPy-CuZnFe₂O₄ with frequency.

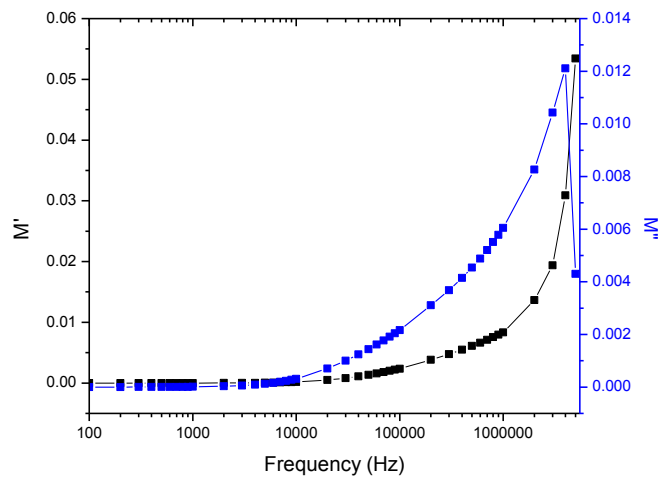


Fig. 1 - PPy

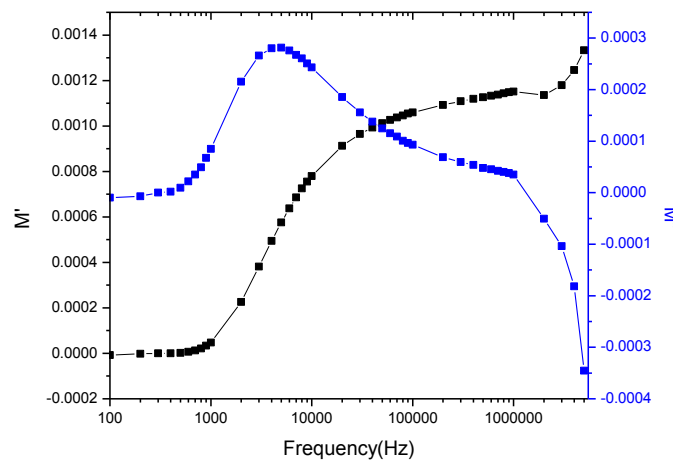


Fig. 2a - 10%

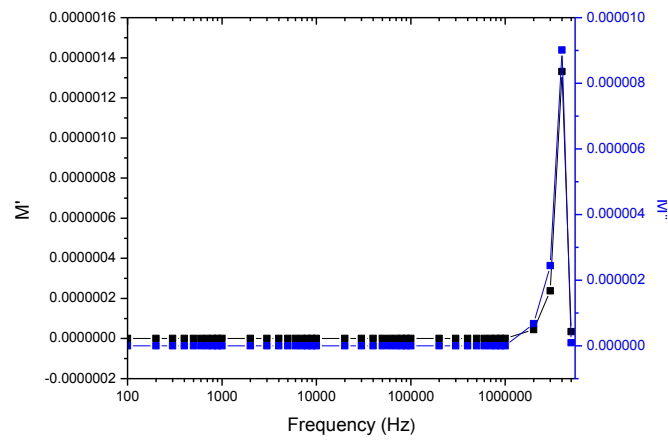


Fig. 2b - 20%

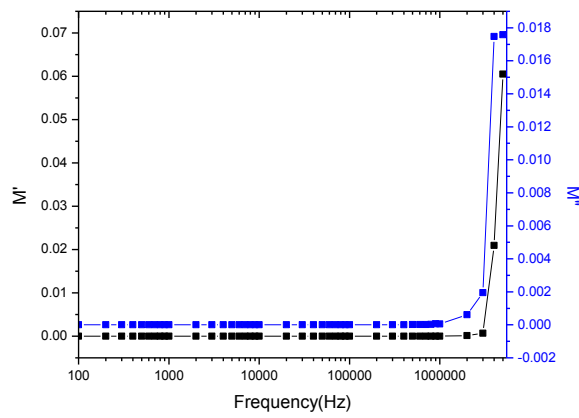


Fig. 2c - 30%

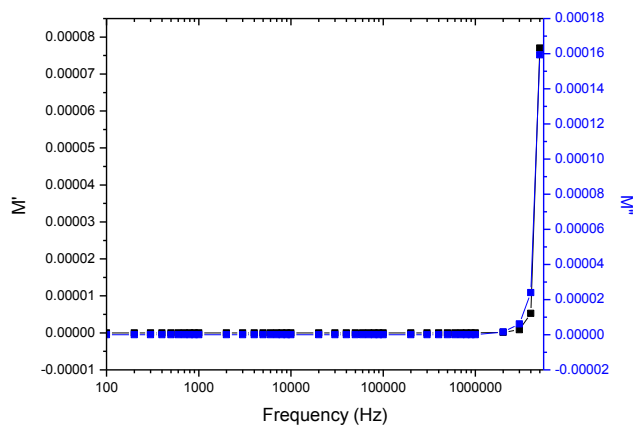


Fig. 2d - 40%

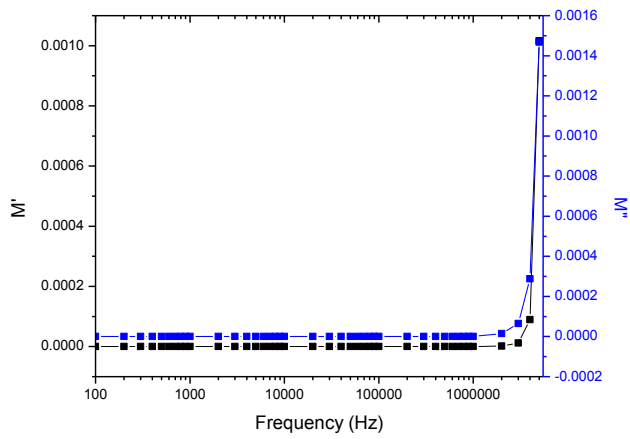


Fig. 2e - 50%

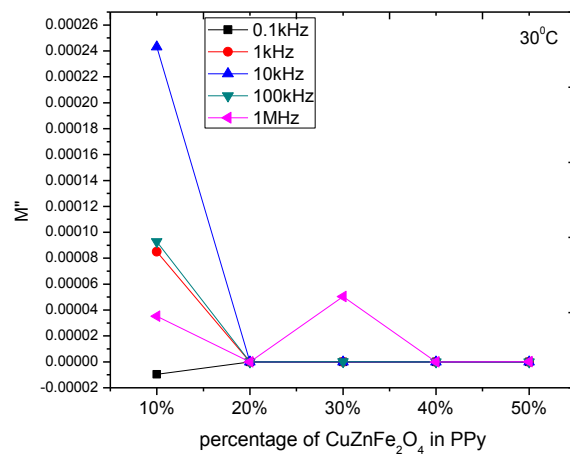


Fig. 3a

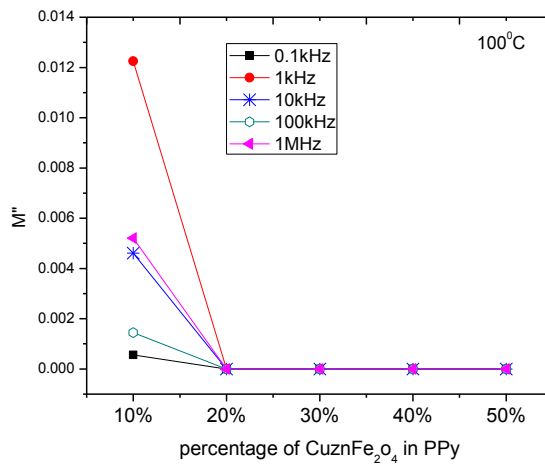


Fig. 3b

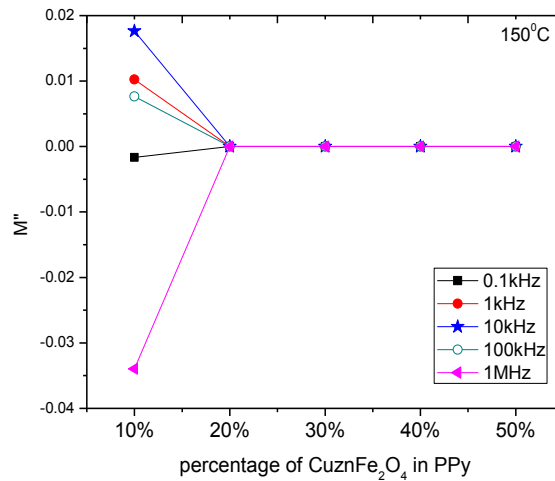


Fig. 3c

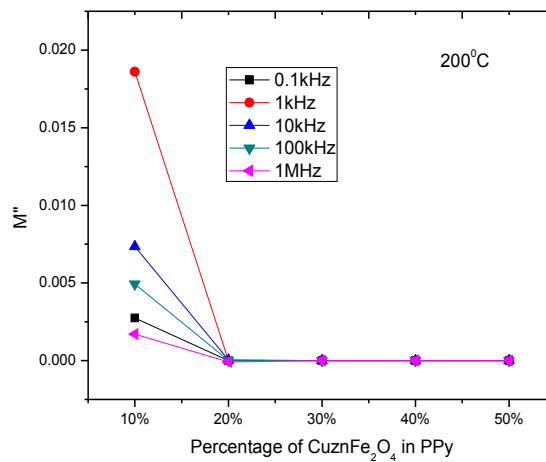


Fig. 3d

It is clear from the fig. that for 10% composites M' remains constant upto 1000Hz and beyond that it increases with frequency. M'' increases upto 4.5kHz and thereafter decreases till 5MHz. For the composites of 20wt% both M' and M'' remains constant upto 1MHz, becomes maximum at 4MHz and decreases at 5MHz. For, 30, 40 and 50Wt% , both M' and M'' remains constant upto 1MHz, and beyond that it increases with frequency. This reiterates our previous results ie dielectric nature of nanocomposites[8-10].

The percent variation of imaginary part of Electric modulus (M'') with temperature at selected frequencies is shown in Fig.5. It is clear from the figure that the electric modulus M'' also shows the same trend as M' . At every temperature the modulus has maximum value at high frequencies and approaches zero at lower frequencies. This confirms the presence of ionic polarization in the studied temperature at higher frequencies for all composites. It remains same for all composites at all temperatures except for 20% in which the modulus increases at high frequencies due to increase in the relaxation of the field.

Cole-Cole Plot

Cole-Cole plot is a graphical representation of frequency dependent dielectric functions. It is plot of imaginary v/s real part of electric modulus. This plot is useful in analysing the dielectric relaxation process.

Cole-Cole plot of PPy/CuZnFe₂O₄ Nanocomposites

The Cole-Cole plots for PPy and PPy-CuZnFe₂O₄ are shown in Fig. 4a and 5(a) to 5(e) respectively. The Cole-Cole plot of PPy is a semicircle showing typical behavior of dielectric obeying Debye's relaxation process. The ideal complex modulus spectra M'' vs. M' represent a semicircle in the complex plane as shown in fig.

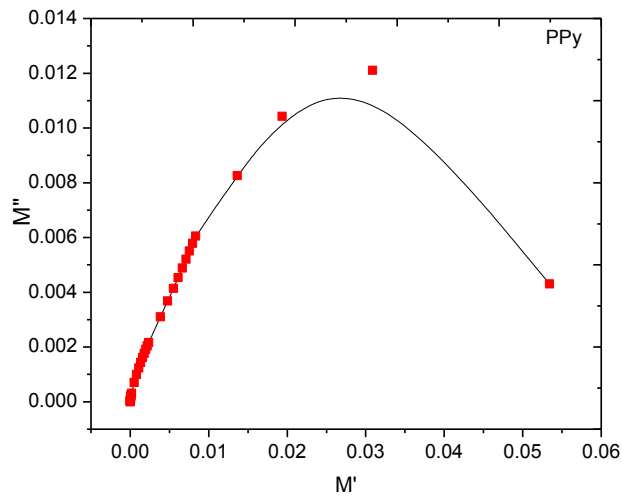


Fig.4a. Cole –Cole plot of PPy

For nanocomposites of low Wt% (10wt%) the plot is a semicircle similar to PPy and for other nanocomposites Cole-Cole plot shows part of semicircle at low frequencies and at high frequencies, asymptotic approach is observed, if the plot data would have extended to very high frequencies, probably the plot would have been a semicircle. It is also evident from the Fig. 5 that the relaxation time is not varying linearly with composition.

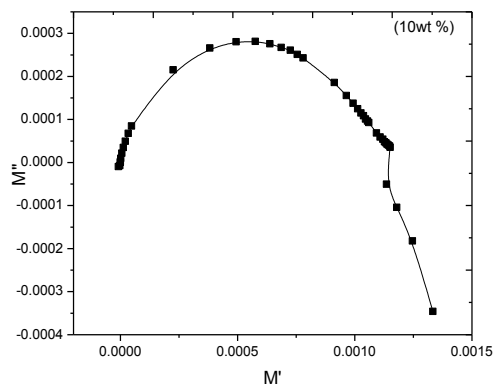


Fig. 5.(a)

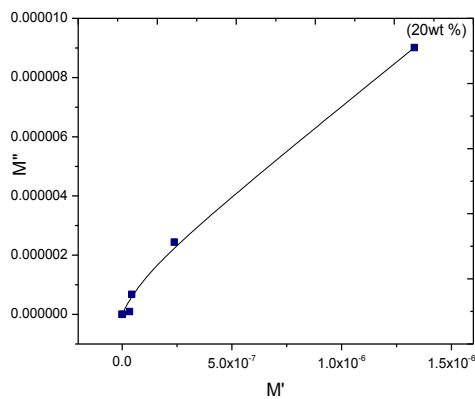


Fig. 5 (b)

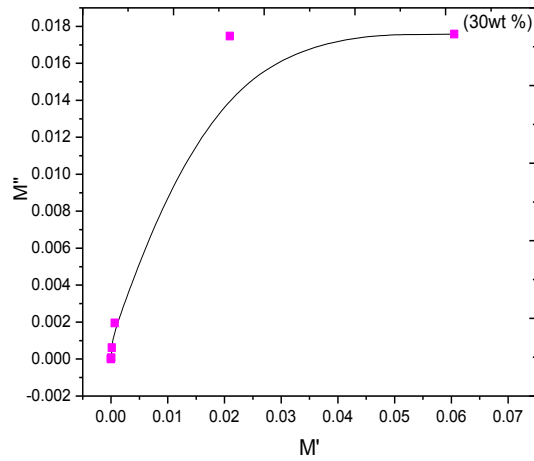


Fig.5. (c)

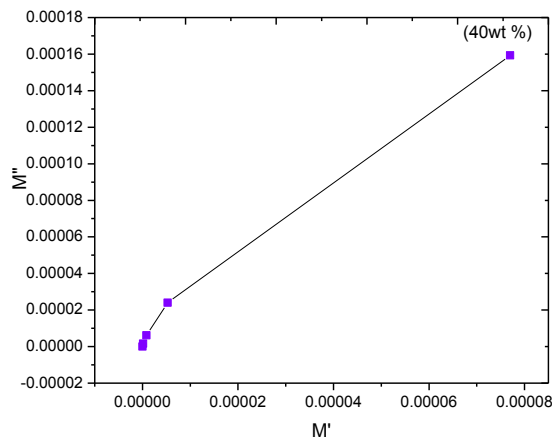


Fig. 5.(d)

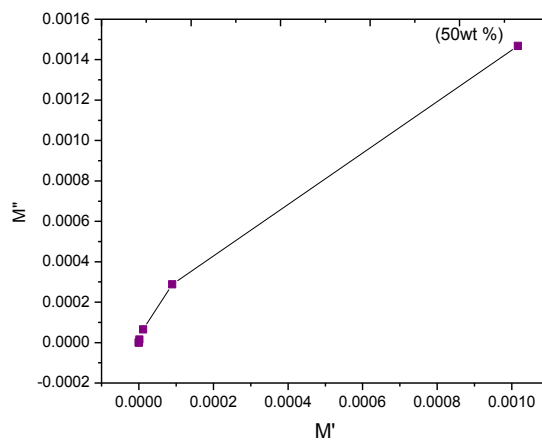


Fig. 5 (e)

Fig. 5.29 Cole – Cole plots of PPy-CuznFe₂O₄ composites

This is attributed to non uniform mass distribution of nanoparticles in polymer matrix which results in different orientation of dipoles. A comparison of Cole-Cole plot of PPy and PPy- nanocomposites is shown in Fig.5.3. It is also evident from Fig. 5.30 that the magnitude of M'' is more for 30Wt% when compared to PPy and other nanocomposites, which supports the uniqueness of nanocomposites.

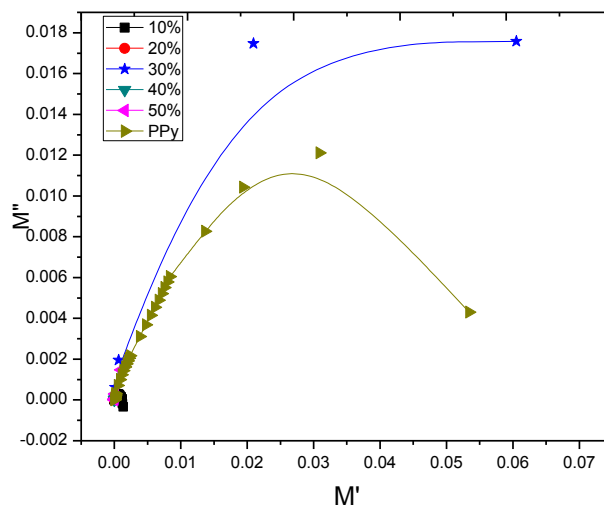


Fig. 5.30 Comparison of Cole – Cole plots of PPy-CuznFe₂O₄ composites

In the Cole plots of nanocomposites, the line through the origin is displaced to the right indicating the presence of DC conductance.[11-12]

IV. Conclusions

In summary, we have successfully synthesized polypyrrole nanocomposites by in-situ polymerization method. The real and imaginary part of the electric modulus remains constant upto 1 MHz, and increases thereafter. This is in conformity with the dielectric behaviour. The percent variation of electric modulus (real part) with selected frequencies at different temperature is shown in Fig.3a-d. The electric modulus of all nanocomposites remains constant with frequency at all temperatures. But the electric modulus of nanocomposites of 10wt% varies with frequency at all temperatures.

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