World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:10, No:10, 2016

Open Science Index, Materials and Metallurgical Engineering Vol:10, No:10, 2016 publications.waset.org/10005639.pdf

Structural and Electrical Characterization of Polypyrrole and Cobalt Aluminum Oxide Nanocomposites

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***Abstract*—**To investigate electrical properties of conducting polypyrrole (PPy) and cobalt aluminum oxide (CAO) nanocomposites, impedance analyzer in frequency range of 100 Hz to 5 MHz is used. In this work, PPy/CAO nanocomposites were synthesized by chemical oxidation polymerization method in different weight percent of CAO in PPy. The dielectric properties and AC conductivity studies were carried out for different nanocomposites in temperature range of room temperature to 180 °C. With the increase in frequency, the dielectric constant for all the nanocomposites was observed to decrease. AC conductivity of PPy was improved by addition of CAO nanopowder.

***Keywords*—**Polypyrrole, dielectric constant, dielectric loss, AC conductivity.

I. INTRODUCTION

FUNCTIONAL organic-inorganic materials and polymers, with nanoparticles are embedded in the polymer network will enhance its functionality and its electrical properties. Synthesis of nanocomposites plays important role in fabrication of materials with high dielectric constant and low dielectric loss which are important in integrated electronic circuits, random access memories, supercapacitors. Recently, composites synthesized from PPy and ternary oxides like graphene supported PPy/Li2SnO3 for lithium ion batteries [1], NiCo2O4/PPy core/sheath nanowire arrays on Ni foam for high performance supercapacitors [2] are reported. Dielectric properties and AC conduction can be improved by the addition of CAO nanoparticles in PPy.

In the present work, PPy/CAO nanocomposites of different weight percent have been synthesized by chemical oxidation method and frequency dependent AC conductivity and their dielectric properties at different temperature has been studied in detail.

II. EXPERIMENTAL

CAO nanopowder from Sigma Aldrich, monomer Pyrrole of AR grade from Spectrochem Pvt. Ltd., oxidant ammonium persulphate (APS) from Fisher Scientific were used as received.

III. SYNTHESIS OF PURE PPY AND PPY/CAO NANOCOMPOSITES

0.3 M of pyrrole solution is measured and poured into a round bottomed flask. In this pyrrole solution, 0.06 M APS solution is added continuously but drop wise by using burette. The temperature surrounding the pyrrole solution is maintained between 0 °C and 5 °C, and the reaction is allowed for 5 hours under continuous stirring. The precipitated PPy is filtered and kept overnight for drying. Then, PPy powder is kept at temperature 100 °C in a muffle furnace for 2 hours. The weight of the PPy powder is 2.9 g (100 wt.%) [3].

0.29 g (10 wt.%) of CAO Nano powder is mixed thoroughly in 0.3M pyrrole solution and in-situ polymerization of polymer nanocomposite is carried out by adding 0.06 M ammonium persulphate drop wise to get a PPy/CAO 10 wt.% composite. Same method of polymerization is used to synthesize 20, 30, 40, and 50 wt.% nanocomposites.

After the synthesis and drying of all nanocomposites, pure PPy and PPy/CAO powder is hydraulically pressed with pressure of 7-8 tons to get the pellets of 10 mm diameter and 1-2 mm thickness. The electrical measurements were done by using 6500B Wayne Kerr precision impedance analyzer in frequency range of 100 Hz to 5 MHz after applying conducting silver paste to the pellets of synthesized composites.

IV. RESULT AND DISCUSSION

A. X-Ray Diffraction (XRD)

Fig. 1 shows the XRD patterns of (a) pure PPy, (b) CAO nanoparticles and (c) PPy/30 wt.% CAO Nano composite. Fig. 1 (a) has no characteristic peak which shows the amorphous nature of PPy. Fig. 1 (b) represents the XRD pattern of the CAO revealing the high degree of crystalline nature. The XRD pattern of the PPy/30 wt.% CAO Nano composite is shown in Fig. 1 (c). The main peaks were observed at 31.22°, 36.72°, 44.68°, 55.51°, 59.19°, and 65.03° with respect to interplanar spacing (d) 2.86 Å, 2.44 Å, 2.02 Å, 1.65 Å, 1.55 Å, and 1.43 Å, respectively. The peaks, which have spike nature represent the crystalline nature and double peaks, represent semi-crystalline nature [4]. The XRD of the PPy/30 wt.% CAO nanocomposite shows semi crystalline behavior.

B. SEM Analysis

Fig. 2 (a) represents the SEM micrograph which shows the spherical as well as elongated chain pattern of pure PPy particles. The particle sizes were in the range between 520 nm

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and 890 nm. Fig. 2 (b) is the SEM micrograph of the PPy/30 wt.% CAO nanocomposite, the image shows that $CoAl_2O_4$ nanoparticles were embedded in the PPy chains. It is observed that, after addition of $CoAl_2O_4$ nanoparticles in PPy, cluster size has decreased [5].

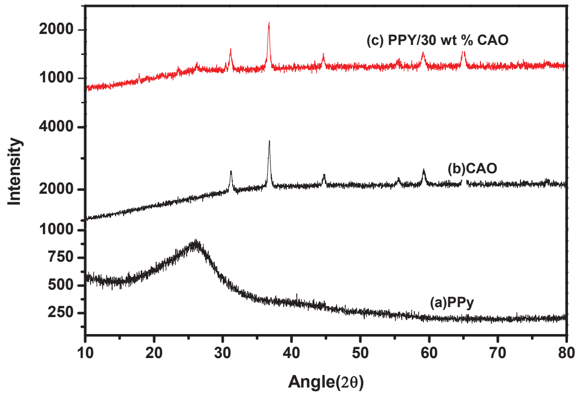

Fig. 1 XRD patterns of (a) pure PPy, (b) CAO nanoparticles and (c) PPy/30 wt.% CAO nanocomposite

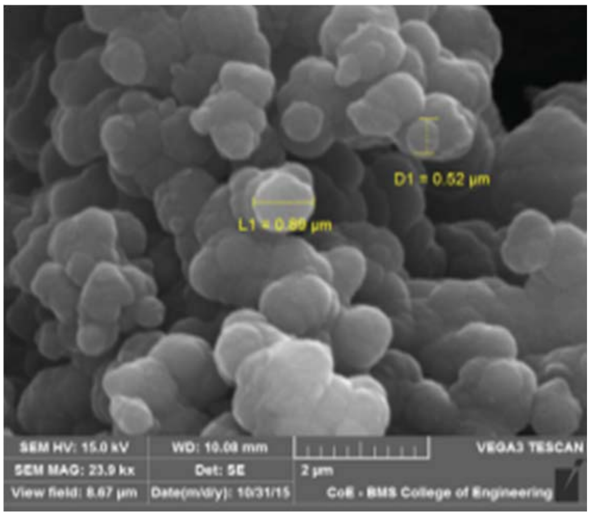

Fig. 2 (a) SEM micrograph of pure PPy

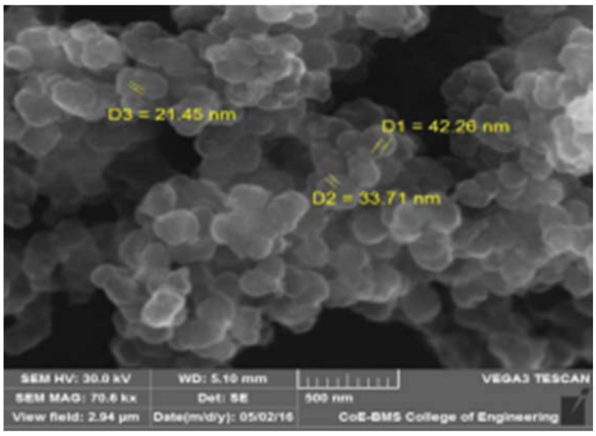

Fig. 2 (b) SEM micrograph of PPy/30 wt. % CAO Nano composite

C. Dielectric Spectroscopy

Dielectric properties of pure PPy and PPy/CAO nanocomposites were studied in the frequency range between 100 Hz to 5 MHz. The dielectric constant of the system subjected to an external oscillating electric field is calculated by (1)

$$\varepsilon'(\omega) = \frac{C*t}{\varepsilon_0 * A} \tag{1}$$

where the C is the capacitance in Farad, t is the thickness in cm, and A is the area of the sample in cm^2.

The frequency dependence of the dielectric constant (ε'(ω)) at room temperature for the pure PPy and PPy/CAO nanocomposites with different weight percent of CAO is shown in Figs. 3 (a) and (b).

Due to different polarization mechanisms like ionic, electronic, orientation, and space charge which have different relaxation frequencies, there is decrease in ε'(ω) with frequency [6]. Dielectric constant ε'(ω) is comparatively high at lower frequencies and gradually decreasing with increase in frequency. This is due to the interfacial and space charge polarization at PPy/CAO interface. The CAO creates nano-dielectric domains which give high dielectric constant value at PPy/CAO interface. This behavior is in accordance with the Maxwell Wagner type of polarization mechanism [6]. Fig. 3 (b) is the enlarged graph of Fig. 3 (a) from frequency 1 MHz to 5 MHz.

The frequency dependence of the dielectric constant (ε'(ω)) at room temperature and at higher temperature is shown in Fig. 4 (a) pure PPy, (b) PPy/30 wt.% CAO composite. It is observed from Fig. 4 (a) that dielectric constant for pure PPy is increased with the increase in temperature up to temperature 160 °C. But, at 180 °C temperature, due to absorption of more heat, orientation in molecule becomes random, and hence, there is reduction in the dielectric constant.

From Fig. 4 (b), at room temperature, polarization is observed due to oscillating electric field only. But as temperature is increased from room temperature till 90 °C the value of dielectric constant is found to be increased. This shows that increase in temperature influences the polarization in PPy/30 wt.% CAO composites. As temperature increases from 120 °C to 180 °C, molecules gain thermal energy and vibrate with higher amplitude [7].

The frequency dependence of the dielectric loss at room temperature for the Pure PPy and PPy/CAO nanocomposites with different weight % of CAO is shown in Fig. 5. It is found from Fig. 5 that dielectric loss also shows same trend as dielectric constant, i.e. as frequency increases dielectric loss decreases sharply for pure PPy and for all nanocomposites.

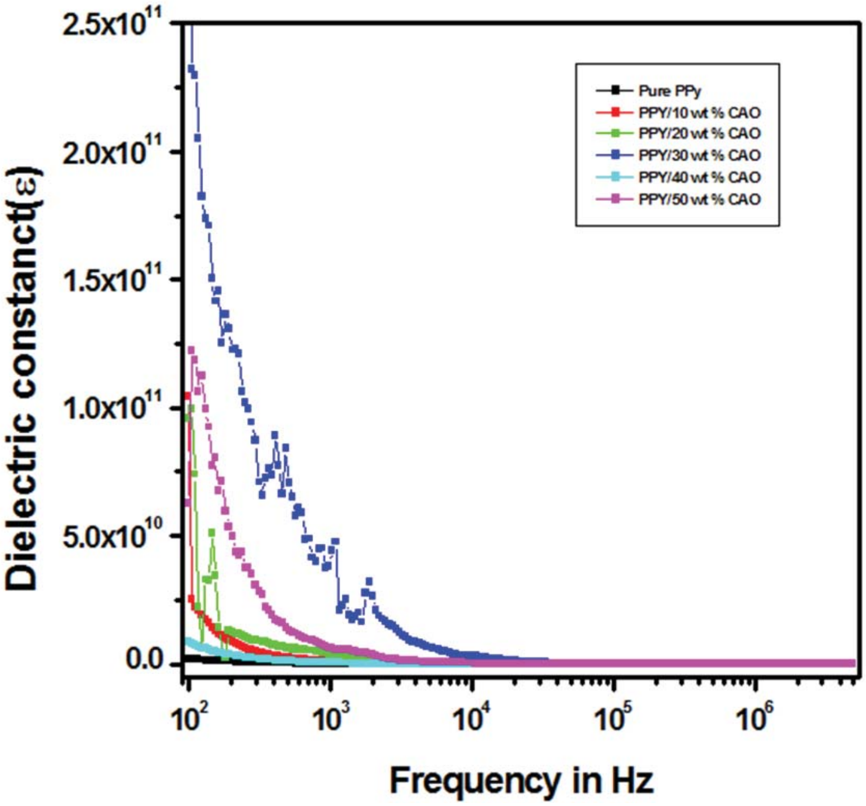

Fig. 3 (a) Frequency dependence of the dielectric constant at room temperature for the pure PPy and PPy/CAO nanocomposites

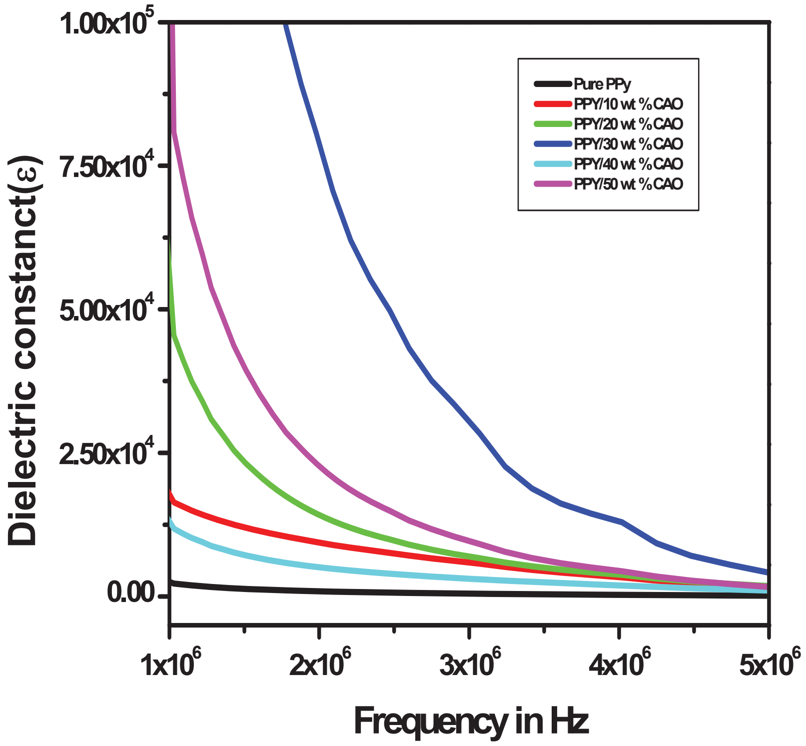

Fig. 3 (b) Frequency dependence of the dielectric constant at room temperature for the pure PPy and PPy/CAO nanocomposites

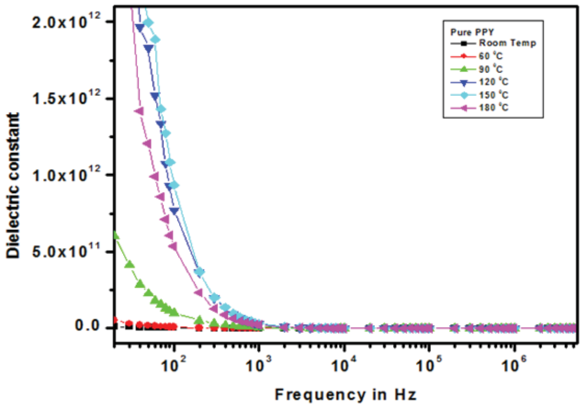

Fig. 4 (a) The frequency dependence of the dielectric constant (ε'(ω)) at room temperature and at higher temperature for pure PPy

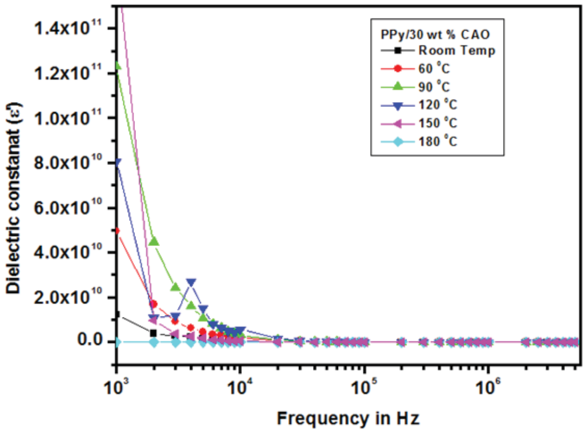

Fig. 4 (b) The frequency dependence of the dielectric constant (ε'(ω)) at room temperature and at higher temperature for PPy/CAO 30 wt.% nanocomposites

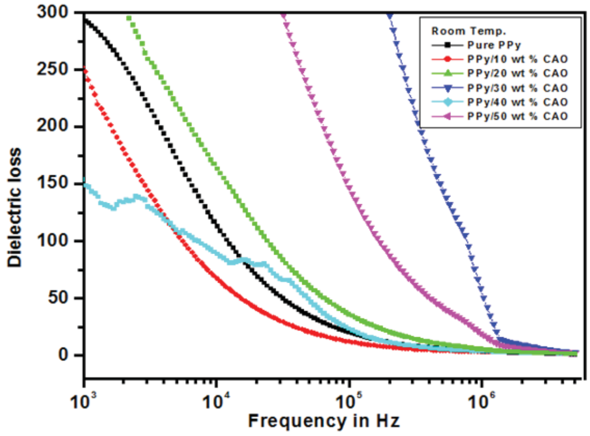

Fig. 5 The frequency dependence of the dielectric loss at room temperature for the pure PPy and PPy/CAO nanocomposites with different wt.% of CAO

Since nanocomposites contain heterogeneous molecules like polymer chains and oxide nanoparticles, there are two types of charge carriers. One is due to n-polaron molecules where charge carriers move along the polymer chains, and the other is dipole of $CoAl_2O_4$ particles where charge carriers have limited mobility and favor for polarization in polymer nanocomposite system.

At lower frequency, the value of dielectric loss is more because of mobility of ions in the PPy/CAO nanocomposites. At moderate frequencies, dielectric loss is contributed because of ion hopping, loss in conduction of ions mobility, and loss of polarization of ions. Due to vibration of ions, there is decrease in dielectric loss at higher frequencies [8].

The temperature dependence of dielectric loss ε"(ω) calculated at 5 MHz for PPy and PPy/30 wt.% CAO composite is shown in Fig. 6.

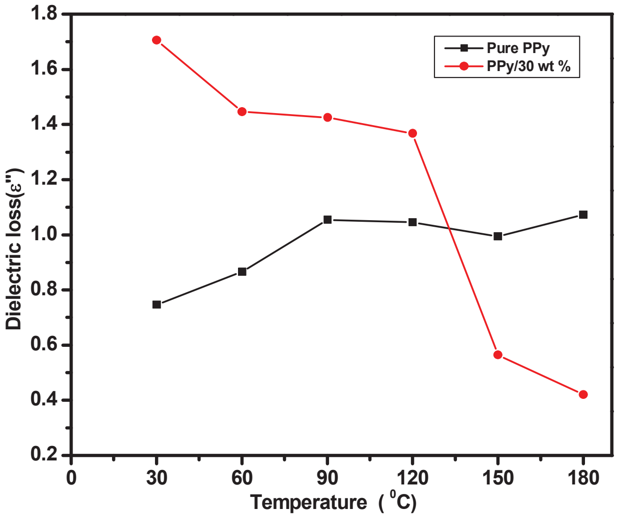

Fig. 6 The temperature dependence of dielectric loss ε"(ω) calculated at 5 MHz for PPy and PPy/30 wt.% CAO composite

From Fig. 6, it is clear that dielectric loss for PPy and PPy/30 wt.% CAO composite depends on temperature. For PPy dielectric loss is increased till temperature 90 °C and decreased afterwards. And for PPy/30 wt.% CAO composites, dielectric loss is decreased with increase in temperature.

D. AC Conductivity

By measuring the conductance (G), thickness and area of pellets of PPy/CAO nanocomposite, the AC conductivity σ_{ac} (ω) in the frequency range of 100 Hz to 5 MHz was calculated with (2) [9]:

$$\sigma_{ac}(\omega) = G(\omega)\frac{t}{A} \qquad (2)$$

where t is the thickness of the sample in cm, and A is the area of cross-section in cm^2 of the pellet.

The variation of AC conductivity at room temperature with frequency for pure PPy and different PPy/CAO nanocomposites is shown in Fig. 7 (a), and the change in AC conductivity with different wt.% of CAO in PPy is shown in Fig. 7 (b).

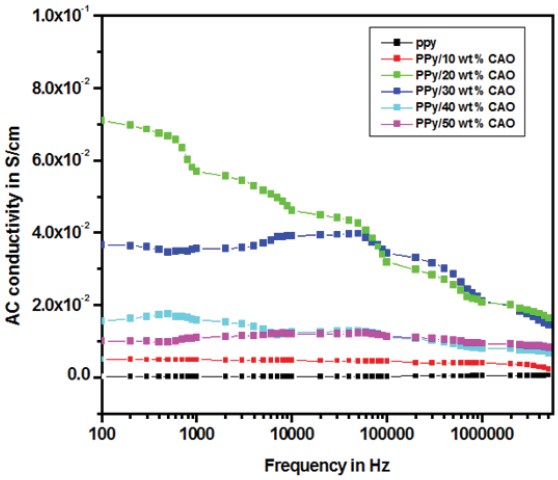

Fig. 7 (a) The variation of AC conductivity at room temperature with frequency for pure PPy and different PPy/CAO nanocomposites

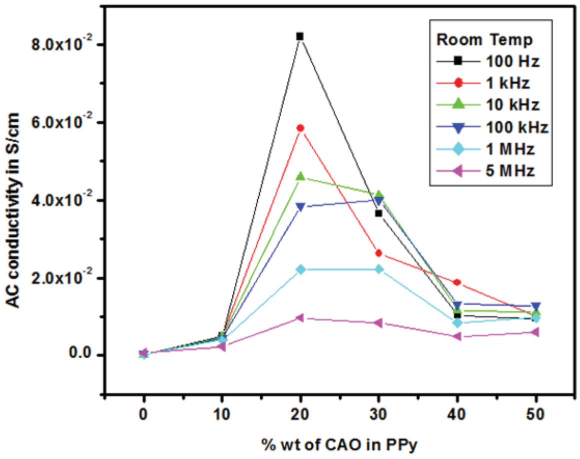

Fig. 7 (b) The change in AC conductivity with different wt.% of CAO in PPy

From Figs. 7 (a) and (b), AC conductivity is almost constant for all nanocomposites over the entire range of frequency except for 20 and 30 wt.% composites. For these two composites (20 and 30 wt.%), conductivity is increased at lower frequency which is due to the increase in localized sites for hopping process of charge carriers [10]. But, for more concentrations, namely 40 and 50 wt.% of CAO, nanoparticles oppose flow of charge carriers; hence, decrease in AC conductivity is observed.

The variation of AC conductivity σ_{ac} (ω) as a function of frequency at room temperature and at temperature 90 °C for PPy and PPy/CAO nanocomposites is shown in Figs. 8 (a) and (b).

It is observed that the nanocomposites exhibit higher AC conductivity in magnitude than that of the pure PPy for room temperature as well as at higher temperature. At room temperature, AC conductivity is increased from 0.0015 S/cm to 0.0065 S/cm, and at temperature 90 °C, it is changed from 0.0038 S/cm to 0.014 S/cm.

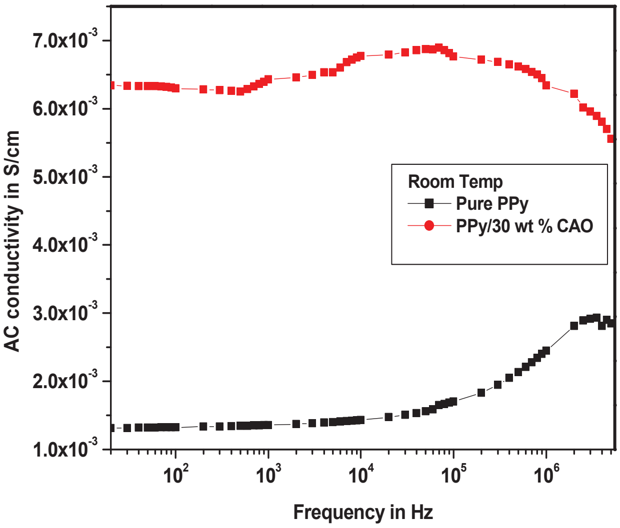

Fig. 8 (a) The variation of AC conductivity σ_{ac} (ω) as a function of frequency at room temperature for PPy and PPy/CAO nanocomposites

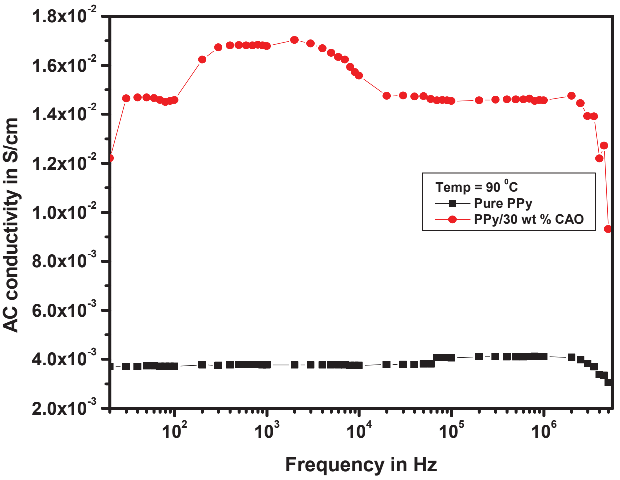

Fig. 8 (b) The variation of AC conductivity σ_{ac} (ω) as a function of frequency at temperature 90 °C for PPy and PPy/CAO nanocomposites

The conductivity in polymer nanocomposites varies macroscopically due to compactness between polymer and added nanoparticles, orientation of nanoparticles embedded in polymer and inhomogeneity in nanocomposites. And microscopically speaking, conductivity depends on doping percent of nanoparticle's and polymer chain length. This phenomenon is mostly observed in polymer-based composites [11]-[14].

V. CONCLUSIONS

Synthesis of PPy/CAO nanocomposites is carried out by in-situ chemical oxidative polymerization method. Dielectric properties and AC conductivity studies have been investigated at room temperatures and at higher temperature. It is observed that electrical properties depend on wt.% of CAO in PPy as well as temperature. Increase in dielectric constant and dielectric loss with addition of CAO is due to the increase in ordering and hopping of ions, respectively. Dielectric constant and dielectric loss is increased till 30 wt.% of CAO/PPy nanocomposites and it is decreased for higher wt.% of CAO in PPy. Dielectric constant for 30 wt.% of CAO/PPy nanocomposites is increased till temperature 90 °C, and dielectric loss is decreased with respect to temperature. There is reduction in dielectric constant and dielectric loss for higher temperatures. Increase in AC conductivity with the content of CAO is because of increase in conjugation length of PPy. The 20 and 30 wt.% of CAO/PPy show higher conductivities. The AC conductivity also increased from room temperature to 90 °C.

ACKNOWLEDGMENTS

The authors would like to acknowledge the World Bank funded project TEQIP – II and Centre of Excellence on Advanced Materials Research under TEQIP 1.2.1.

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