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Dielectric spectroscopy of Polyaniline/ Mixed metal oxide Composites

Sangshetty Kalyane* and U V Khadke

Department of Physics, BKIT Bhalki, Karnataka-585328, India.

Abstract

Metal oxide composites were prepared by microwave irradiation of different single metal oxides using a polyvinyl alcohol as a fuel. (ViO, CuO, and Fe_2O_3). Metal oxides are used to form metal oxide composites (MOC), Insitu polymerization of aniline was carried out in the presence of MOC to synthesize Polyaniline – MOC composites by chemical oxidation method with various compositions viz: 10 wt%, 30 wt% and 50 wt% of $NiCuFe_2O_3$ in PANI. The Dielectric constant was studied in the frequency range 10^2–10^7 Hz at room temperature. It is observed that, the dielectric constant is maximum for 50wt% of MOC in PANI. The dimensions of MOC particles in the matrix have a greater influence on the Dielectric constant values.

Keywords: Dielectric constant, Polyaniline, $NiCuFe_2O_3$ MOC

1. INTRODUCTION

Polymers have traditionally been considered as a good electrical insulators and a variety of their applications are depends on their insulating property [1]. However more than a decade now, researchers have shown that certain class of polymers which are conjugated, exhibit semiconducting behavior [2]. The discovery of doping has led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 S/cm. The presence of an extended π conjugation in polymers, however, confers the required mobility to charges that are created on the polymer

backbone (by the process of doping) and make them electrically conducting [3]. Conducting polymers have become the foci of much research in materials science and among all; polyaniline and polypyrrole have received greater attraction due to their favorable economics, easy synthesis, environmental stability and unique chemistry [4]. The electrical conductivities of the intrinsically and conducting polymer systems range from those insulators ($<10^{-5}$ and 10^{-10} S/cm) to those of typical semiconductors such as silicon ($\approx 10^{-5}$ S/cm) and to those greater than 10^4 S/cm (nearly to that of a good metal such as copper $\approx 5\times10^5$ S/cm) [5]. Applications of these polymers have begun to emerge a new era. These include coating and blends for electrostatic dissipation and electromagnetic interface (EMI) shielding [6, 7]. Electromagnetic radiation absorbs for welding (joining) of plastics, conductive layers for light emitting polymer devices and anti-corrosion for iron and steel [8]. Many attempts in the preparation of polypyrrole composites with inorganic particles were also performed, such as with montomorrillonite and *y*-zeolite [9]. Polypyrrole inorganic particles were also investigated for their applications in electroheological (ER) fluid and high-density information storage [10].

2. EXPERIMENTAL

Materials and Methods

Metal oxides NiO, CuO and Fe_2O_3 are used for the preparation of MOC. The Microwave method is used for the preparation of MOC. Ammonium persulphate $(NH4)_2S_2O_8$, Hydrochloric acid (HCl) of AR grade were used. Doubly distilled water and aniline is used as a solvent and monomer. Polyaniline is prepared by oxidative method and Polyaniline composites were prepared by insitu polymerization method with dispersion of MOC in polyaniline.

Synthesis of Polyaniline/ MOC Composites

Known quantity of NiO, CuO and Fe_2O_3 metal oxides are grinded well in a pestle & mortar. The mixture of metal oxides is mixed with polyvinyl alcohol with fuel in weight ratio 1:2 and again grinded. The same is heated in microwave oven for about 20 minutes at higher power level then allowed to cool the reaction product to room temperature. The mixure was again grinded well to obtain fine grains of MOC

Aniline was dissolved in 1m HCl to form PANI. MOC was added to PANI solution with vigorous stirring to keep the MOC suspended in the solution. To this reaction mixture, 0.1M of ammonium persulphate $[(NH_4)_2S_2O_8]$, acts as an oxidant, was added slowly with continuous stirring for 4-6 hours at 0-5^{O}C. The precipitated powder recover was vacuum-filtered and washed with deionizer water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. In the

similar manner pure PANI is prepared without adding MOC, composites were prepared in weight percent ratio in which the concentration of MOC (10 wt%, 30 wt% and 50wt%) was varied. The dielectric constant measurements were carried out at room temperature over the frequency range 10^2-10^7Hz using the Hioki LCR Q meter.

3. RESULTS AND DISCUSSION

1. SEM Study

SEM micrograph of pure conducting Polyaniline is shown in figure 1. It is observed that the SEM image of Polyaniline has clusters of some spherical shaped particles with elongated chain pattern. A granular morphology of the Polyaniline particle size is measured and found to be about 1 μm in diameter, which is consistent with other reports [1].

Figure 2 shows the SEM micrograph of MOC. It is observed that the particles are spherical in nature with close compacting of particles with few globular arrangement with compact netting. The change in morphology of the MOC dispersed PANI as compared with pure PANI and MOC. One can observe that, the increase in the compactness of the particles due to dispersion of MOC in to polymer matrix. The particles with spherical nature enhances the crystalline nature of PANI composite.

Figure 3 shows SEM photograph of Polyaniline- MOC composites of 50 wt% of MOC, shows clusters of spherical shaped particles and chain pattern, with the chains connecting the MOC particles. The chain pattern becomes meager visible and clusters of spherical shaped pattern are observed. A small variation in the particle dimensions of MOC so dispersed in polyaniline during SEM recording that as the weight percent of MOC in polyaniline increases, the porosity also increases.

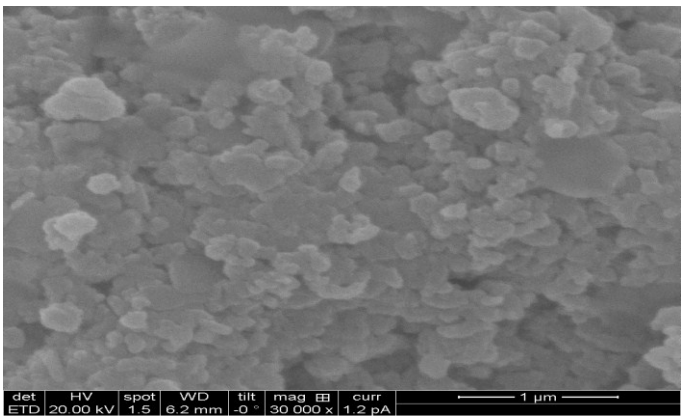

Figure 1. SEM Micrograph of polyaniline

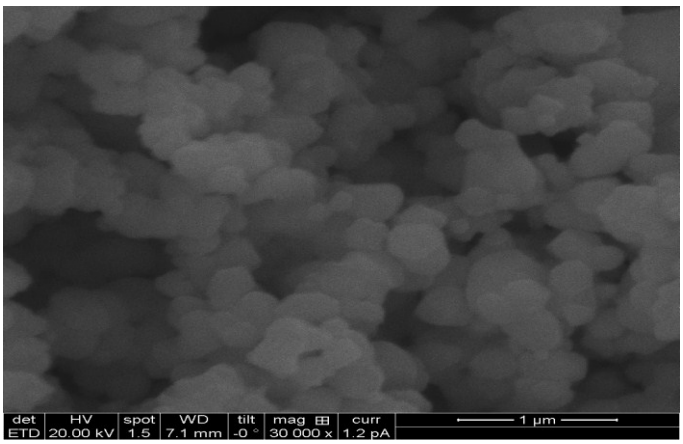

Figure 2. SEM Micrograph of pure MOC

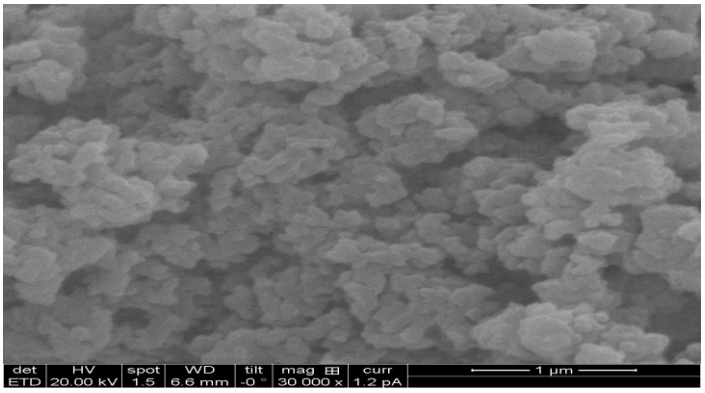

Figure 3. SEM Micrograph of polyaniline – MOC composites (50%)

Figure 4 shows X-ray diffraction pattern of Polyaniline. Careful analysis of x-ray pattern of Polyaniline suggests that, it has amorphous structure with a broad peak centered around $2\theta \approx 25^0$.

Figure 5 & 6 shows the XRD pattern of MOC and MOC dispersed polyaniline composite respectively. The observation of Bragg's reflections in MOC pattern shows the crystalline nature of the MOC sample. However the XRD pattern of MOC dispersed composite also shows the sharp Bragg's reflections. These peaks are due to inserted MOC and hence the crystalline nature for the amorphous polymer. MOC peaks in the polymer composite are identified on comparison with XRD pattern of MOC. The composite pattern further revels that the crystalline behavior of polymerization of aniline. Sharp peaks in the amorphous polymer pattern confirms formation of Polyaniline-MOC composite

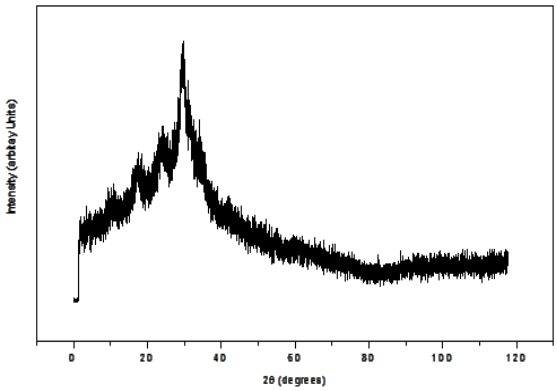

Figure 4. X-ray diffraction pattern of pure Polyaniline

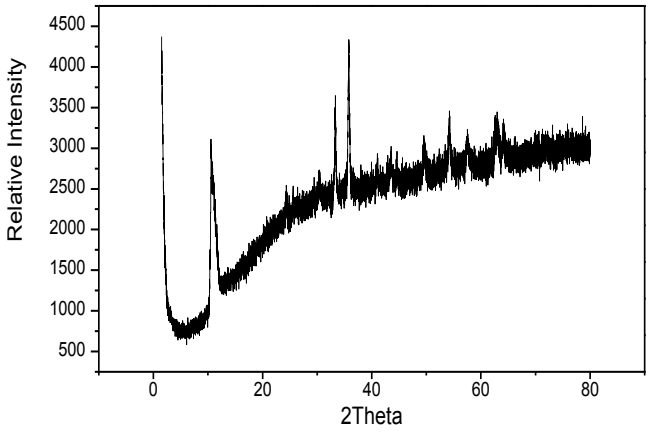

Figure 5. X-ray diffraction pattern of pure – MOC

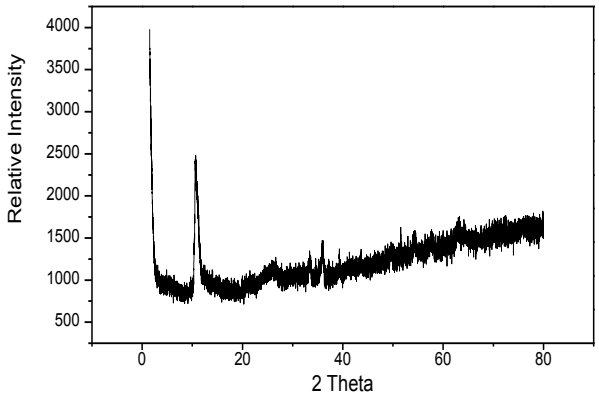

Figure 6. X-ray diffraction pattern of polyaniline – MOC composite (50 wt%)

Fig. 7 shows IR spectra of pure polyaniline where the percentage transmittance is plotted as a function of wave number in cm^{-1}. Careful observation in the IR spectra reveals the presence of intensity peaks at 2322.42, 2089.99, 1789.70, 1537.79, 1403.15, 1280.34, 925.41, 666.13, 502.42, 576.86, 552.64, 545.81and 538.62. The spectrum shows the presence of characteristic stretching frequencies at 1697, 1558, 1050 and 915 cm^{-1}. The intensity peaks at 1537.9, 925.41 and 538.62may be attributed due to the presence of C = N, N – H and C – N stretching frequencies.

The occurrence of various bands in IR spectra may be attributed to same factors which are given in table-01

Table 01

Frequency (cm^{-1})	**Observed band**
1610, 1593 and 1503	C = C stretching
1550 and 1500	C = N stretching
1040, 960 and 790	C – N stretching
1050	N – H bending deformation
726 and 1326	C – H bending deformation

The IR spectra of pure MOC are shown in Fig. 8. The important peaks observed in MOC are 1123, 660.17, 582.90, 560.87, 547.38, 543.28, 539.87, 535.49, 531.89 and 528.03 cm^{-1}. IR data suggests that the formation of MOC due to the presence of the characteristic stretching frequencies are observed at 1123 (M – M) and 543.23 (M – O) cm^{-1}. The IR spectra of polyaniline – MOC composite with 50wt% of MOC is shown in Fig. 9. The important peaks are observed in polyaniline - MOC composites are 2337.27, 1567.08, 1467.23, 1300.80, 1066.73, 991.58, 800.82, 563.93, 547.07, 543.31, 539.31, 532.01 and 527.30 cm^{-1}. By careful observation of IR spectra, some of the characteristic stretching frequencies are considerably shifted towards higher frequency side. The typical peaks are observed at 1567.08, 1066.73 and 547.07 cm^{-1}. These data suggests that, there is a Vander walls force of attraction between the polymeric chain and MOC.

The important peaks observed in case of polyaniline, MOC and polyaniline – MOC composites are given in the table-2.

Table-02: FTIR spectra of PANI, MOC &Polyaniline-MOC

Sample	**Observed band due to (cm-1)**
Pure Polyaniline	2322.42,2089.99,1789.70,1537.79,1403.15,1280.34,925.41,666.13,502.42, 576.86,552.64,545.81and 538.62
Pure($NiCuFe_2O_3$) MOC	1123, 660.17, 582.90, 560.87, 547.38, 543.28, 539.87, 535.49, 531.89 and 528.03
Polyaniline – MOC composite	2337.27, 1567.08, 1467.23, 1300.80, 1066.73, 991.58, 800.82, 563.93, 547.07, 543.31, 539.31,532.01 and 527.30

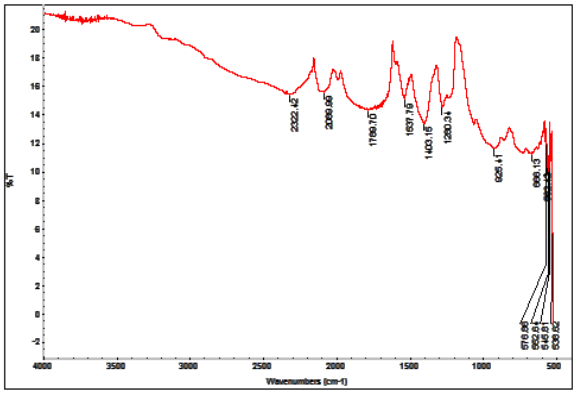

Figure 7. Infrared spectra of polyaniline

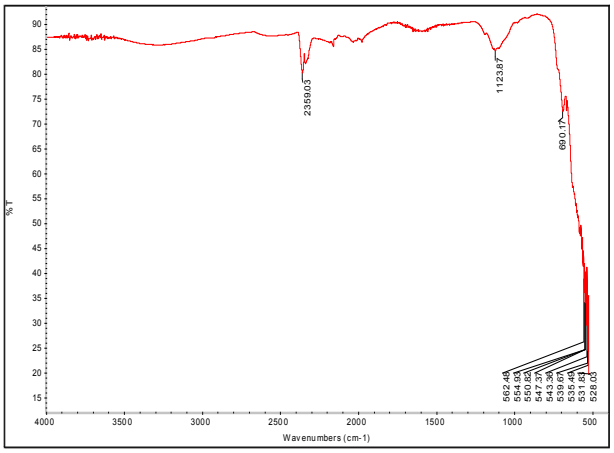

Figure 8. Infrared spectra of MOC

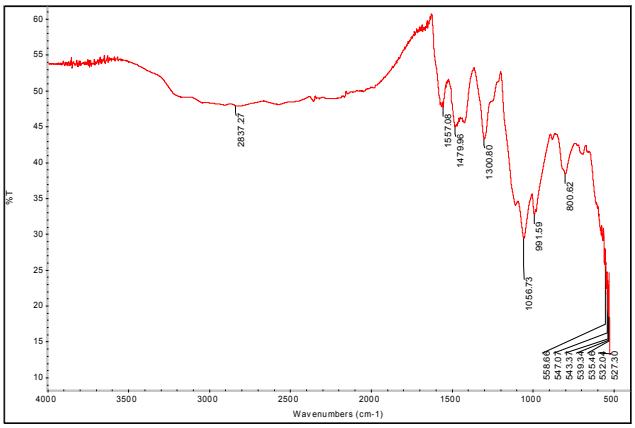

Figure 9. Infrared spectra of polyaniline – MOC composite (50 wt%)

Figure 10 shows the variation of dielectric constant as a function of frequency for Polyaniline. It is observed that a relatively high dielectric constant at low frequencies and low dielectric constant at higher frequencies for Polyaniline is observed here, which is a characteristic feature of conducting polymers and the results so obtained are in consistent with other reports[1].

Figure 11 shows the variation of ε' as a function of frequency for polyaniline – MOC composites (different wt %). In all the cases studied here, it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency but the dielectric constant is quite high for 50 wt%. The observed behavior may be due to Debye like relaxation mechanism taking place in these materials.

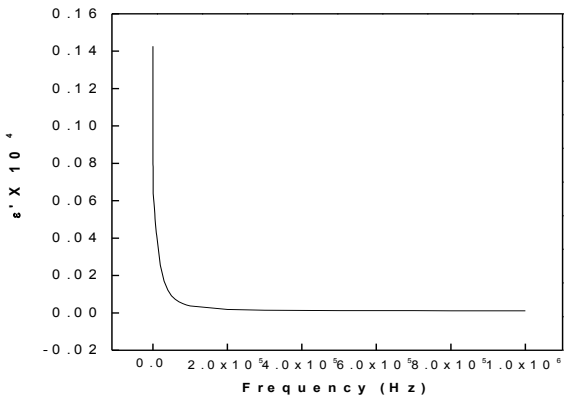

Figure 10 . Shows the variation of ε' as a function of frequency for Polyaniline

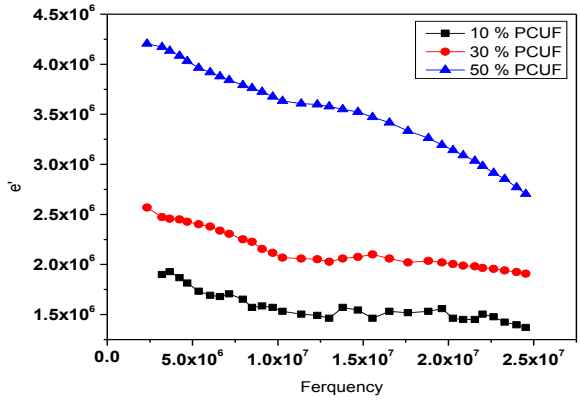

Figure 11. Variation of ε' as a function of frequency for Polyaniline- MOC

4. CONCLUSION

Efforts have been made to synthesize PANI/ MOC composites to tailor their properties. The results of dielectric constant show a strong dependence on the wt% of MOC in PANI.

REFERENCES

[1] V.R. Gowrikar, N.V. Vishwnathan, S. Jayadev, Polymer Science, Wiley Eastern Ltd., New Delhi, 1986.

[2] M.D. Ingram, H. Staesche, K.S. Ryder, J. Power Sources 129(1)(2004)107

[3] A.F. Diaz, B. Hall, J. Rev. Dev. 27(1983) 342

[4] ST Wellinghoff**,** T. Kedrowski**,** S. Jenekhe and H. Ishida**,** J**.** Phys**.** Colloq. (France), 44, (1983) C3-677.

[5] D.C. Trivedi, Handbook of Organic Conductive Molecules and Polymers, vol. 11, John Wiley and Sons Ltd., (1997).

[6] G.B. Street**,** T.C. Clarke**,** R.H. Geiss**,** V.Y. Lee, A. Nazzal**,.** P. Pfluger. &. J.C. Scott, J. Phys. (Paris) Colloque, C3(6)(1983), 599.

[7] S. Holta, T. Hosaka, W. Shimotsuma, Synth. Met. 6 (1985) 317.

[8] S.E. Lindsey, G.B. Street, Synth. Met. 10 (1988) 67.

[9] M. Salmon, A.F. Diaz, M. Krounbi, J.Bargon, Mol. Cryst. Liq. Cryst. 83 (1982)265.

[10] M. Raghu, S.V. Subramanyam, Phys. Rev. B 43 (1991) 4236.

[11] Narshima Parvatikar, M.V.N.Ambika Prasad, Journal of Applied Polymer Science,100 (2006)1403