Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Dielectric investigations on metal (Ni and Cu) tetrahydroxy phenyl porphyrins in PMMA polymer matrix

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ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Metalloporphyrins
PMMA polymer
Dielectrics
A.C conductivity

ABSTRACT

The present work reports on the dielectric behaviour of two different metallo porphyrins ($NiTPPOH_4$ and $CuTPPOH_4$) doped in poly (methyl methacrylate) (PMMA) polymer matrix. Different dielectric parameters such as dielectric constant, tangent loss and a.c. conductivity were measured at frequency ranges from 1- 100 kHz in the temperature range 35–100 °C. The dielectric constant ε' for $NiTPPOH_4$ and $CuTPPOH_4$ was found to be in the range of 2.42–5.45 and dielectric loss (tan δ) in the range of 0.0122–0.0756. The dielectric constant and loss are found to be higher for $CuTPPOH_4$. Variation in the dielectric loss with temperature at different frequencies show a shoulder peak indicating dipolar relaxation character. The a.c. conductivity of the materials increased with temperature and frequency. The activation energy was decreased with rise in temperature and shifting of relaxation regions towards low temperature is observed. Detailed analysis reveal that $CuTPPOH_4$ doped polymer exhibit significant dielectric properties.

Selection and peer-review under responsibility of the scientific committee of the 5th International Conference on Recent Advances in Material Chemistry

1. Introduction

Transition metal ion-polymer based composites have gained interest of many investigators by considering their suitability in developing optical detectors for highly efficient luminescent solar concentrators (LSC) [1]. Among various organic photoactive materials, porphyrins have received significant importance due to its high stable chemical structure, extended conjugation, broad absorption in the visible region and conductivity nature [2,3]. These properties enable porphyrins as an appropriate substrate material of luminescent devices in concentrating solar energy on to the surface edge of the cell furnish in achieving high solar efficiency. The key parameters for assessing suitability of porphyrin doped polymers depends on their dielectric properties such as dielectric constant, loss and a.c. conductivity with respect to certain temperature range and frequency. Reda et al., have investigated dielectric properties of phthalocyanines and hematoporphyrin doped in PMMA matrix [4]. The study demonstrates that a.c. conductivity increases with increasing temperature and frequency. Correlated barrier hopping mechanism was found to be dominated in all the samples.

The polymeric network doped with large macromolecules enable to increase in the degree of network disorder and furnish significant increase in the dielectric properties. The photophysical properties of the porphyrins were significantly altered in the solid matrix and show enhanced excited state parameters [5]. It results a significant increase in the conversion of solar energy and storage. In this report, we have explored the development of PMMA thin films doped with different metalloporphyrins and studied the dielectric properties as function of temperature and frequency.

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https://doi.org/10.1016/j.matpr.2021.10.027
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the 5th International Conference on Recent Advances in Material Chemistry

Please cite this article as: P. Prasanth, S. Talam, B. Ramakrishna et al., Dielectric investigations on metal (Ni and Cu) tetrahydroxy phenyl porphyrins in PMMA polymer matrix, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2021.10.027

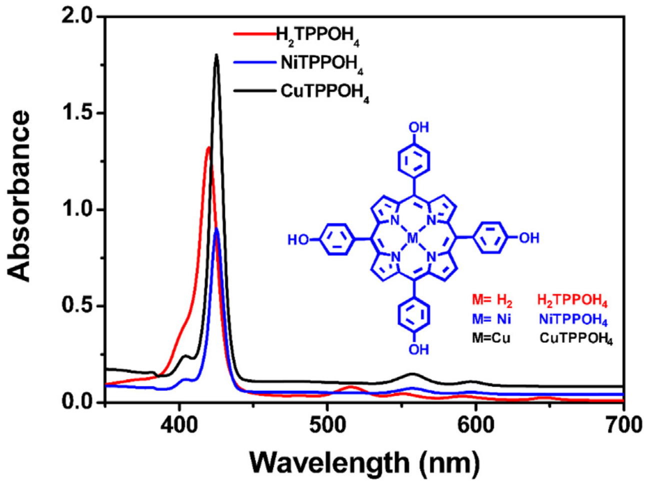

Fig. 1. Change in the absorption spectra of different porphyrins doped in PMMA matrix. The inset shows the molecular structure of porphyrins used in the present work.

2. Materials and methods

All the chemicals used are commercially available and were used without any further purification. Pyrrole, 4-Hydroxybenzaldehyde, propionic acid, Ni(II)acetate, Cu(II)acetate and PMMA were obtained from Sisco Research Laboratories Pvt. Ltd. (SRL), India. Absorption spectra was recorded in Ocean Optics HR-4000 spectrophometer. Surface morphology was recorded using Field Emission Scanning Electron Microscope (FE-SEM), FEI, Quanta 200. The dielectric measurements were carried out on LCR Meter (Hewlett-Packard Model-4263B) in the frequency range 10^2–10^5 Hz and in the temperature range 30–100 °C. The accuracy in the measurement of dielectric constant is ~0.001 and that of loss is $\sim 10^{-4}$. The sample was held in between two silver electrodes and the sample holder was heated by a 200 W nichrome heater. The heating was controlled by adjusting the current with a variac. For good thermal stability, cold water was circulated round the jacket. The readings were recorded after the sample was achieved a steady temperature. A chromel–alumel thermo couple was attached to the sample holder very close to the sample. The thermo emf developed across the junction was measured using digital PID temperature controller.

3. Results and discussion

Freebase and metalloporphyrins were synthesized according to the procedure described [6,7]. The inset of Fig. 1 shows the chemical structure of the porphyrins used in this work. Porphyrin doped PMMA thin films were prepared by taking 5 mg of metal (Cu, Ni) tetrahydroxy phenyl porphyrins in THF solution was added to 0.5 g of PMMA in 3 mL of THF. The resulting solution was allowed to stir for 30 min at room temperature. The whole solution was transferred into a petri dish and allowed for slow evaporation for 24 h. Finally, the thin films were dried at 50 °C for 12 h.

The absorption spectra of porphyrins doped PMMA films are shown in Fig. 1. $H_2TPP(OH)_4$ shows absorption at 420 nm corresponds to soret band and four Q-band peaks at 500–650 nm. Both $CuTPP(OH)_4$ and $NiTPP(OH)_4$ showed a red shifted absorption to 428 ± 2 nm and Q-band showed two absorptions at 557 and 598 nm respectively. The direct optical band gaps films were measured Urbach's equation and was found to be 2.97, 2.92 and 2.90 eV for $H_2TPP(OH)_{4,}$ $NiTPP(OH)_4$ and $CuTPP(OH)_{4.}$ On excitation at 425 nm, $H_2TPP(OH)_4$ show strong emission peak at 654 nm and another weak emission at ~ 718 nm corresponds to $S_1 \rightarrow S_0$ transitions. However, the metalloporphyrin doped films show very weak emission due to perturbation in the d-orbitals of the Ni and Cu metal ions. Fig. 2 shows SEM images of the pure PMMA and metalloporphyrins doped PMMA films. It is clear that pure PMMA shows an amorphous nature, while $NiTPP(OH)_4$ and $CuTPP(OH)_4$ shows a porous nature with flower petals. The SEM image of $CuTPP(OH)_4$ exhibits superior porous nature allows the free ions migration. The thickness of the developed films was measured to be 23 ± 2 μM. These films were further used to study the dielectric properties.

Variation of dielectric parameters such as dielectric constant ε', loss tan δ and a.c. conductivity was evaluated experimentally. Increase of three dielectric features with increase of temperature and frequency was observed. The dielectric constant and loss values for both the samples are found in the range 2.41 to 5.442 and 0.0122 to 0.0756 respectively. Increase of permittivity is associated with the favorable orientation of molecules with rise in the temperature. We have not observed any decrease in the permittivity due to some random thermal oscillations. All the samples were exhibited a similar trend of dielectric changes, where copper doped polymer exhibit high dielectric constant and loss 5.442 and 0.0756 corresponding to 1 kHz (Fig. 3). These changes were attributed due to enhancement of space charge polarization [9]. The divalent copper and nickel ions act as modifiers which in turn producing distortion in polymeric network causing bonding imperfections and further guides charge carriers through simple path lines leads to improvement in the constant and loss [10,11]. Variation of dielectric constant and loss has clearly confirmed the specific peak maximum which supports relaxation effects in both the samples (Fig. 4).

From the variation in dielectric loss with temperature, the half-width and height of the peak maximum were found to be increased for $CuTPPOH_4$ doped rather than that of $NiTPPOH_4$ doped films. This could be evidenced from the shifting of relaxation area from

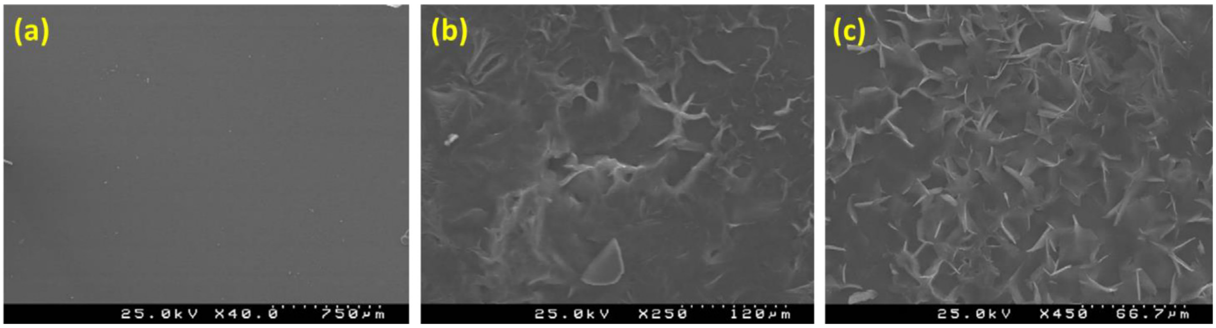

Fig. 2. SEM images of (a) pure (b) $NiTPPOH_4$ and (c) $CuTPPPOH_4$ doped PMMA films.

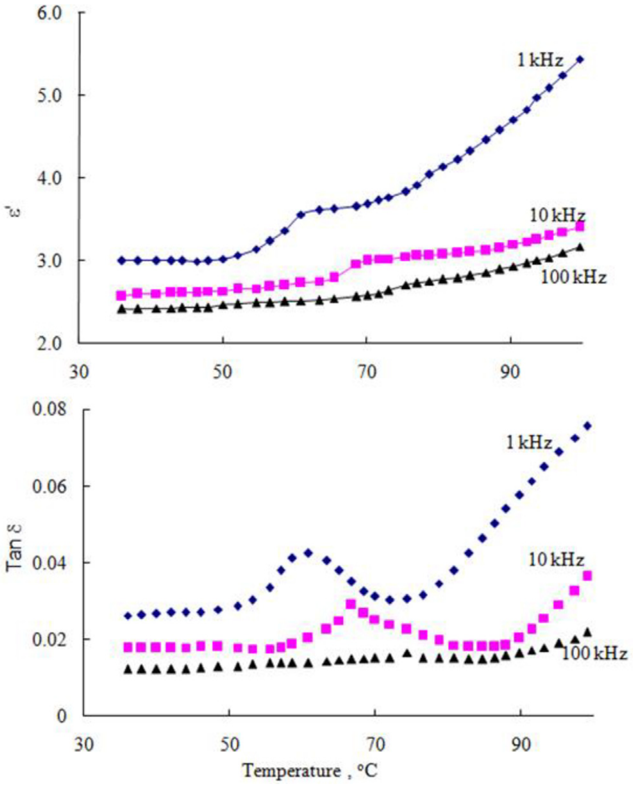

Fig. 3. Comparison plot of variation in dielectric constant and loss at different frequencies (1, 10 and 100 kHz) with varied temperatures for $CuTPPOH_4$ doped in PMMA matrix.

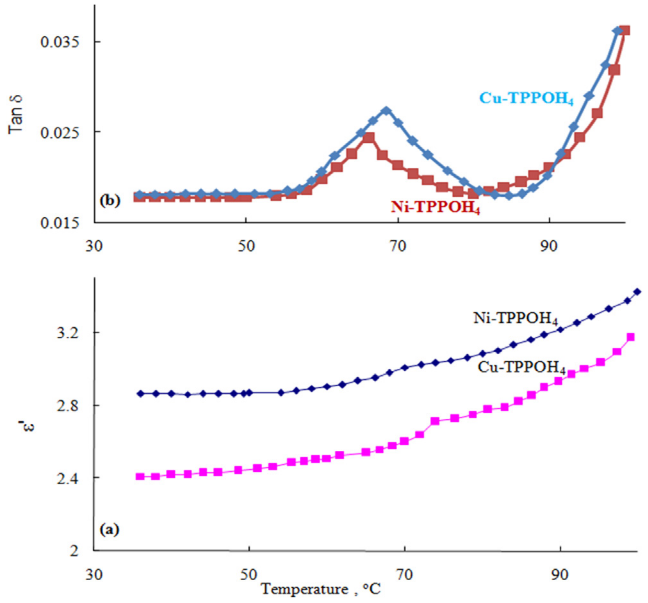

Fig. 4. (a) Comparison plot of variation in permittivity with temperature at 100 kHz (b) comparison plot of variation in dielectric loss with temperature at 10 kHz for $NiTPPOH_4$ and $CuTPPOH_4$ in PMMA matrix.

high temperature to low temperature. However, pure PMMA and H_2TPPOH_4 doesn't show such variation in the dielectric loss and dielectric constant. The following equation was used to measure the a.c. conductivity (σ_{ac}).

$$\sigma_{ac} = \omega\varepsilon_o\varepsilon'\tan\delta \tag{1}$$

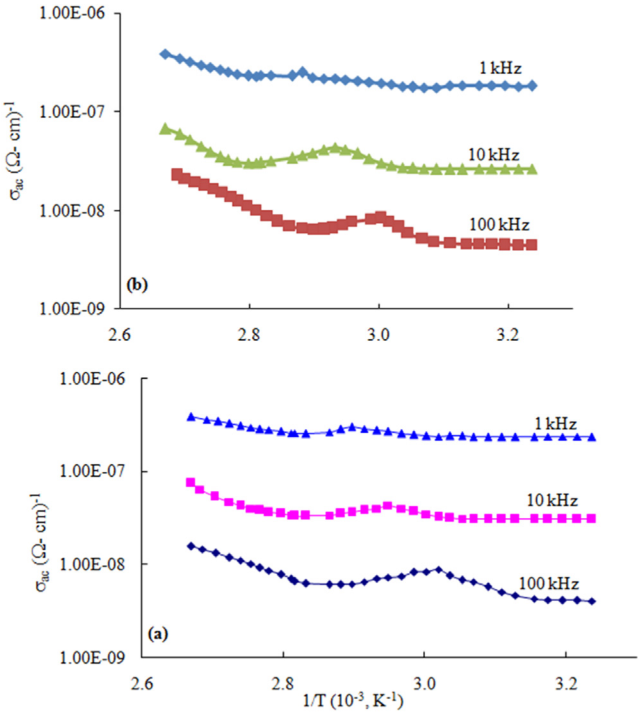

Fig. 5. Variation of a.c. conductivity with 1/T at different frequencies for (a) $NiTPPOH_4$ (b) $CuTPPOH_4$ doped in PMMA matrix.

Fig. 5 represents the variation in log σ_{ac} with 1/T at 1, 10 and 100 kHz frequencies. The measured values of a.c. conductivity for metlloporphyrins found to be in the range 4.04×10^{-9} to 3.78×10^{-7} and 4.37×10^{-9} to 3.84×10^{-7} $(\Omega\text{-cm})^{-1}$ respectively [8]. At low frequency of 1 kHz, $NiTPPOH_4$ exhibits low conductivity and act as a insulator. The linear dependence behavior was existed up to temperature 75 °C, thereafter, the conductivity started to show an increasing trend due to space charge polarization as per the quantum mechanical barrier hopping or tunneling model [4,8,11]. The conductivity of the samples were found to be increased with increase in temperature and frequency (Fig. 3). More specifically, a significant increase in the high temperature region is associated with increased mobility of charge carriers due to extra thermal energy. It is worth to mention that copper and nickel ions break the network inducing localized centres which affect the conduction mechanism prominently by favoring polymer molecules to get oriented into the field direction. For better and thorough understanding of dielectric relaxation affects, Tan δ_{max}, activation energy for dipoles and conduction are evaluated and depicted in Table 1. The effective activation energy (W_d) for the dipoles is evaluated using the following equation

$$f = f_0 e^{-W_d/K_B T} \tag{2}$$

The values of activation energies for $CuTPPOH_4$ found to be low and this observation is in good agreement with the variation of permittivity, loss and a.c. conductivity. Decrease in activation

Table 1
Summary of data on dielectric loss of metaloporphyrins doped in PMMA matrix.

Sample	(Tan $\delta_{max})_{avg}$	Temp. relaxation region (°C)$_{avg}$	A.E. for dipoles (eV)	A.E for conduction (eV)
$NiTPPOH_4$	0.0293	49–78	1.94	0.32
$CuTPPOH_4$	0.0262	55–76	1.85	0.35

energy and shifting of relaxation to downside with rise in frequency allows us to conclude that diploes can move freely to align into applied field.

4. Conclusions

Dielectric permittivity, loss and a.c. conductivity of different porphyrins doped polymer were measured in the frequency range 1–100 kHz. Investigations on dielectric parameters confirms that $CuTPPOH_4$ exhibits high conductivity while $NiTPPOH_4$ show insulating property. ε' and tanδ values are found to increased with temperature and frequency . The measured values of a.c. conductivity for both the samples lie in the range 4.04×10^{-9} to 3.78×10^{-7} and 4.37×10^{-9} to 3.84×10^{-7} (Ohm-cm)$^{-1}$. The variation in the conductivity was successfully demonstrated by quantum tunneling model. At low temperature region, change of log σ_{ac} with 1/T at three different frequencies is found to exhibit linear dependence. However, it show predominant growth in the high temperature zone due to large mobile charges by acquiring thermal energy.

CRediT authorship contribution statement

P. Prasanth: . **Satyanarayana Talam:** Conceptualization, Writing – review & editing. **Buthanapalli Ramakrishna:** Writing – review & editing. **Gunnam Nagarjuna:** Investigation. **Rambabu Busi:** Investigation. **M.C. Rao:** . **Venkatramaiah Nutalapati:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

NVR would like to thank SERB, India for funding through Startup Research Grant (SRG/2019/001023) and SRMIST for seed grant. NVR also thank to DST-FIST fund (No. SR/FST/CST-266/2015(c)) for improvement of S&T infrastructures to Department of Chemistry, SRMIST. Authors acknowledge to NRC, SCIF of SRMIST for the analytical characterization.

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