ELSEVIER

Materials Science and Engineering B 135 (2006) 113–119

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Structural and electrical studies on tetrameric cobalt phthalocyanine and polyaniline composites

S. Saravanan [a,*], M.R. Anantharaman [a,**], S. Venkatachalam [b]

[a] *Department of Physics, Cochin University of Science and Technology, Cochin 682022, India*
[b] *Vikram Sarabhai Space Centre, Trivandrum 695022, India*

Received 16 March 2006; received in revised form 16 August 2006; accepted 20 August 2006

Abstract

Polyaniline and oligomeric cobalt phthalocyanine are blended in different proportions by chemical methods. These blends are characterised by spectroscopic methods and dielectric measurements. Dielectric studies on the conducting polymer blends are carried out in the frequency range of 100 kHz to 5 MHz from room temperature (300 K) to 373 K. Dielectric permittivity and dielectric loss of these blends are explained on the basis of interfacial polarisation. From the dielectric permittivity studies, ac conductivity of the samples were calculated and the results are correlated. In order to understand the exact conduction mechanism of the samples, dc electrical conductivity of the blends is carried out in the temperature range of 70–300 K. By applying Mott's theory, it is found that the conducting polymer composites obey a 3D variable range hopping mechanism. The values of Mott's temperature (T_0), density of states at the Fermi energy ($N(E_F)$), range of hopping (R) and hopping energy (W) for the composites are calculated and presented.

Keywords: Polyaniline; Phthalocyanine; Dielectric permittivity; ac and dc conductivity

1. Introduction

Organic and metallo-organic polymers gained importance because of their electrical, electronic, non-linear optical, electrochemical and photochemical applications [1–4]. In order to make use of these polymer compounds for specific applications, they are modified either by co-polymerisation or by making blends with other polymers [5]. Production of blends using organic and metallo-organic polymers is an attempt to derive new polymeric materials by combining the properties of the individual components of the blend [6,7]. The use of blends/composites in various electric and electronic devices attracted attention because of their conducting nature, chemical stability and the economic viability. Among the many conducting polymers, polyaniline seems to be one of the best candidates for preparing conducting polymer composites since it is stable both thermally and environmentally [8–11]. The blends of polyaniline doped with sulphonic acid [12], phosphoric acid in different polymers such as polymethyl methacrylate [13], cellulose [14] and polyurethane [15] have been investigated. Electrical properties of polyaniline blended with other polymers are relatively different from that of pure polyaniline. Along with the incorporation of insulating polymers into conducting polymers, introducing polymeric/oligomeric phthalocyanine into polyaniline matrixes are also investigated [7,16]. Incorporation of oligomeric phthalocyanine onto polypyrrole facilitates electrochemical process involving cation transport. A conductive polymer composite using polyaniline and polymeric phthalocyanine can be potential materials for rechargeable batteries [16].

In this paper, optical and electrical studies on blends of polyaniline–oligomeric cobalt phthalocyanine are discussed. The dielectric and conductivity measurements of polyaniline at different proportions with oligomeric cobalt phthalocyanine are carried out for different temperatures and the conduction mechanism in these composites is explained based on the Mott's variable range hopping model.

2. Experimental

Polyaniline doped with camphor sulphonic acid (PANICSA) [16–18] was blended with tetrameric cobalt phthalocyanine

---

[*] Corresponding author. Present address: Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India. Tel.: +91 80 2293 2263.

[**] Corresponding author.

E-mail addresses: shrisharavanan@yahoo.co.uk (S. Saravanan), mra@cusat.ac.in (M.R. Anantharaman).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.08.048

(CoPc) [19–21] by mixing them homogeneously in an agate mortar for several hours. The materials were prepared in the following volume fractions: 90% PANICSA–10% CoPC, 50% PANICSA–50% CoPC, and 10% PANICSA–90% CoPC.

FTIR spectra of the samples in transmission mode were recorded by using Perkin-Elmer FTIR spectrometer (model spectrum 1000). The conducting polymer composite samples were pressed in the form of pellets of diameter 10 mm and thickness ranging from 1 mm to 3 mm. The permittivity studies were carried out on these pellet samples using a home made dielectric cell and an HP 4285A LCR meter in the frequency range 100 kHz–5 MHz from room temperature (300 K) to 383 K under dynamic vacuum (10^{-2} Torr). The cell was standardised using standard teflon samples where the lead and fringe capacitances were eliminated. The LCR meter was interfaced via a GPIB card to PC. A package based on virtual instrumentation (VI) known as LabVIEW was used for measuring dielectric permittivity from the obtained capacitance values by employing the following relation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{1}$$

where C is the capacitance of the sample, A the surface area of the sample, ε_0 the permittivity of air and ε_r is the dielectric permittivity of the sample. ac conductivity of the sample was calculated by using the empirical relation:

$$\sigma_{ac} = 2\pi \varepsilon_0 \varepsilon_r f \tan\delta \tag{2}$$

where ε_0 is the permittivity of air, ε_r the dielectric permittivity of the sample, f the frequency and $\tan\delta$ is the dielectric loss.

Electrical conductivity measurements was carried out on the pellets of conducting polymer composites using Keithley source measuring unit (SMU 236) and a home made conductivity cell under high vacuum (10^{-5} Torr) in the temperature range, 70–300 K by employing a two-probe technique.

3. Results and discussions

3.1. FTIR studies

The FTIR spectrum of tetrameric cobalt phthalocyanine and PANICSA/CoPC composites are as shown in Figs. 1 and 2, respectively. In Fig. 1, the peak at 721 cm^{-1} is attributed to non-polar deformation vibrations of the CH bonds of benzene ring [22]. The peaks at 1460 cm^{-1}, 1307 cm^{-1} are indicative of skeletal stretching vibrations of C–C in benzene ring. The characteristic peak for C=N skeletal stretching vibration is also noted at 1517 cm^{-1} [23]. Metal–ligand vibration band is observed at 904 cm^{-1} for tetrameric cobalt phthalocyanine proclaiming the stability of the metal phthalocyanine, which is due to the strong bonding between the metal ion and four surrounding nitrogen atoms [24]. The CO stretching and OH deformation confirm the presence of COOH, which is characterised by the band at 1696 cm^{-1}. Moskalev and Kirin found an intense band at 1006–1008 cm^{-1} and Stymne observed at 1539 cm^{-1} for NH vibration in metal free phthalocyanine [25,26]. The absence of these peaks in Fig. 1 suggests that the sample does not have any metal free phthalocyanine.

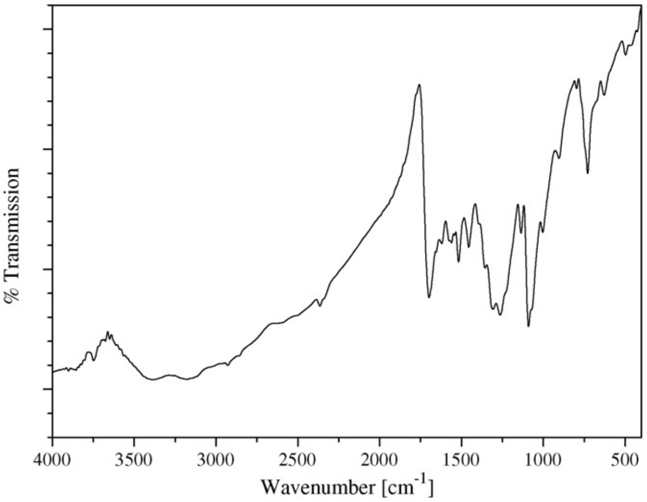

Fig. 1. FTIR spectrum of tetrameric cobalt phthalocyanine.

IR spectra of polyaniline with tetrameric cobalt phthalocyanine blends show peaks at 715–733 cm^{-1}, 904–1038 cm^{-1}, 1081–1100 cm^{-1} and 1695–1728 cm^{-1}, which are attributed to phthalocyanine skeleton [27–29]. In addition, bands observed at 1460–1479 cm^{-1}, 1578–1597 cm^{-1}, 1234–1299 cm^{-1} and 1129–1142 cm^{-1}, are due to polyaniline [30], wherein the bands at 1234–1299 cm^{-1} and 1129–1142 cm^{-1} show that the incorporated polyaniline in composites is camphor sulphonic acid doped polyaniline. Apart from these, the peaks at 1695–1728 cm^{-1} in the blends correspond to –COOH group.

3.2. Dielectric studies

A typical set of graphs depicting the dielectric behaviour of the conducting polymer composites of polyaniline with tetrameric cobalt phthalocyanine over the frequency range 100 kHz–5 MHz at different temperatures is shown in Fig. 3.

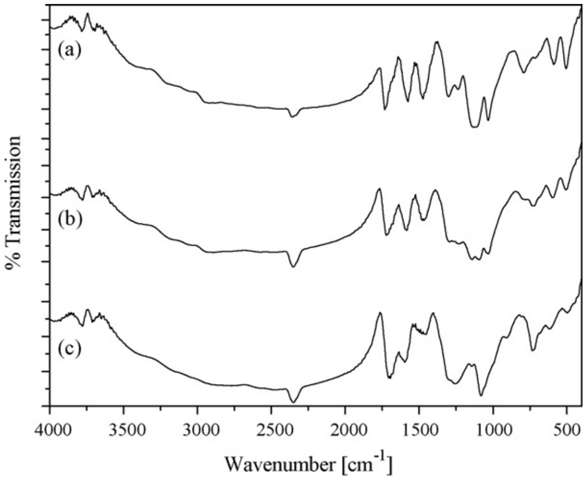

Fig. 2. FTIR spectra of conducting polymer composites: (a) PANICSA90 CoPc10, (b) PANICSA50 CoPc50, and (c) PANICSA10 CoPc90.

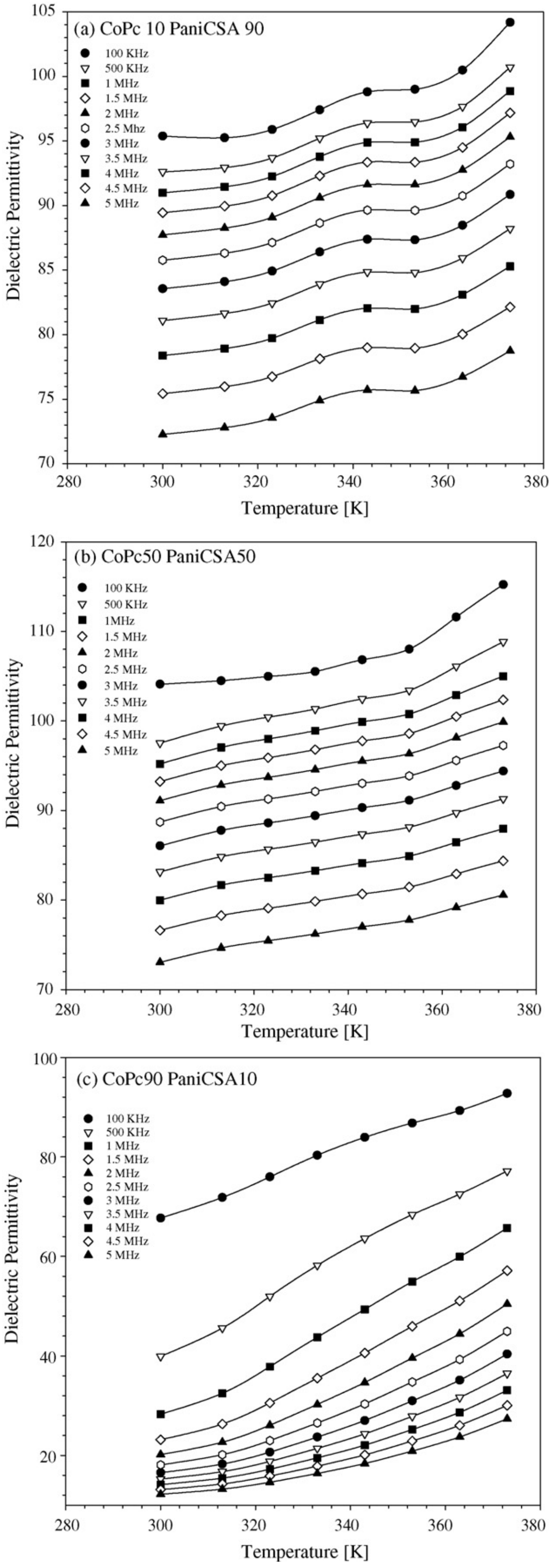

Fig. 3. Variation of dielectric permittivity of conducting polymer composites at different frequencies.

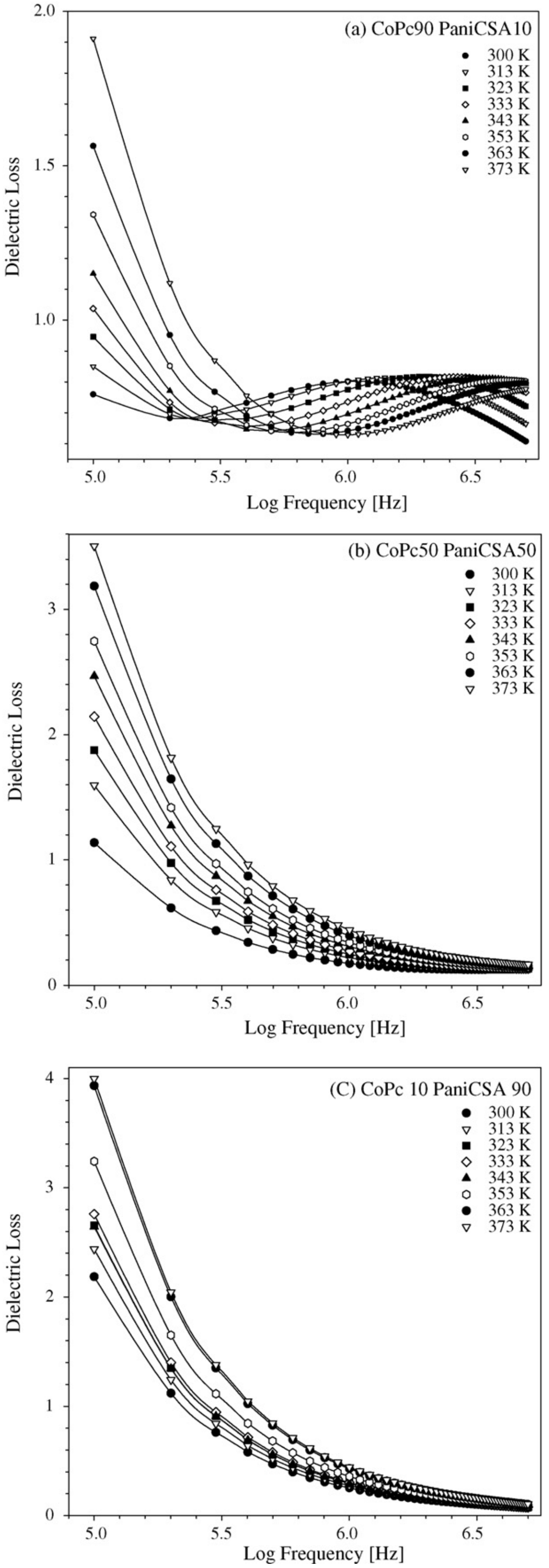

Fig. 4. Variation of dielectric loss of conducting polymer composites at different temperatures.

The variation pattern of dielectric permittivity for all compositions is almost similar and the typical values at 373 K for 1 MHz are compared. The value of dielectric permittivity at 1 MHz of oligomeric cobalt phthalocyanine at 373 K is 50.78 and it increases with increase of polyaniline concentration till both PANICSA and CoPc are at equal proportions, and after which it decreases. The dielectric permittivity value of CoPc90 PANICSA10 at 373 K at 1 MHz is about 65.71, which is higher than that of CoPc. Also the dielectric permittivity value of CoPc10 PANICSA90 is 98.86. But the value of PANICSA at the same condition is 105.26, which does not show much variation like CoPc and CoPc90 PANICSA10. However, the value of dielectric permittivity of CoPc50 PANICSA50 approaches (104.99) towards the PANICSA value but not CoPc. This shows that the tetrameric cobalt phthalocyanine does not show much influence on the dielectric permittivity of composites.

The dielectric permittivity increases with increase of temperature and at a particular temperature it decreases monotonically with increasing frequency. This may be due to the tendency of induced dipoles in macromolecules to orient themselves in the direction of the applied field when the frequency of alternation is low. However, at high frequencies the induced dipoles will hardly be able to orient themselves in the direction of the applied field and hence the dielectric permittivity decreases [31]. Frequency dependence of the dielectric permittivity in these composites is more pronounced at lower frequencies. This is because the interfacial polarisation plays an important role in these composites at lower frequencies. This polarisation will arise only when the phases with different conductivities are present [32]. Conducting polymers and its composites show high dielectric permittivity due to the large effective size of metallic islands in these compounds and easy charge transfer through well-ordered chains in disordered regions.

The dielectric loss *versus* frequency curves for composites are presented in Fig. 4. The loss factor decreases with increase of frequency and increases with temperature. This is usually associated with ion drift, dipole polarisation or interfacial polarisation [33]. The increase of dielectric loss with decreasing frequency is very rapid at low frequencies. Also the study of miscibility in blends/composites by dielectric relaxation involves the assessment of one or more loss peaks. In binary blends, one or multiple loss peaks will occur [34]. These blends do not exhibit peaks except in the case of CoPc90 PANICSA10 composition.

In the case of CoPc90 PANICSA10 mixture, there appears a peak in the dielectric loss curve at higher frequencies. Also the loss peak is shifted towards the higher frequency as the temperature increases. This shift in the loss peak is in accordance with the Debye theory of dipole orientation [35], i.e., at high temperatures and for a given frequency, a maximum of $\tan\delta$ will occur such that $2\pi f_{\text{relax}} = 1/\tau$, where τ is relaxation time. Accordingly f_{relax} will be greater when τ is less. The rise in temperature cause a reduction in the mean time of stay of ionic dipoles which in turn change τ to decrease and f_{relax} to occur in higher temperatures. The appearance of a peak only in this composition is because of the extended conjugated structure of CoPc tetramer, which causes delocalisation of the charge and hence the peak shift towards higher frequency. As polyaniline

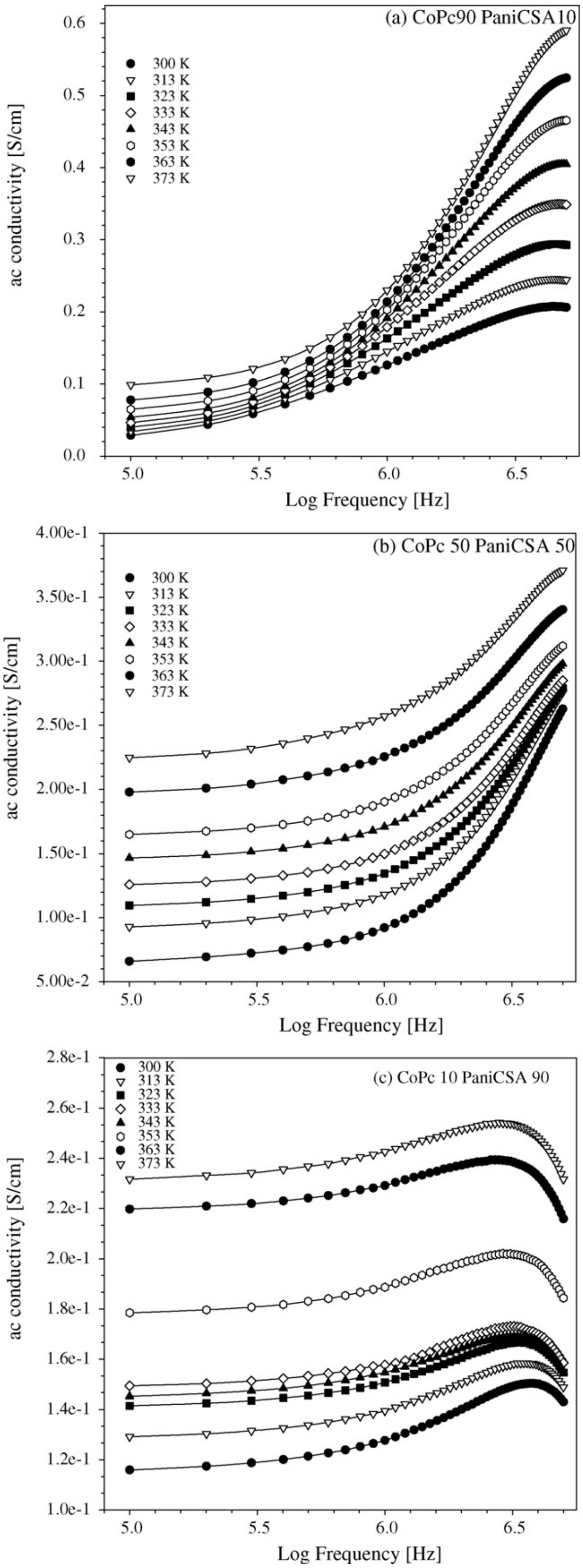

Fig. 5. Variation of ac conductivity of conducting polymers composites at different temperatures.

content increases in the mixture, the mixture exhibits the characteristic of polyaniline itself because of very high conductivity of polyaniline there by leading to loss peak at lower frequency. This dielectric loss behaviour is in accordance with the dielectric permittivity behaviour observed for the same blends.

3.3. ac conductivity

ac conductivity of the composite samples is calculated from the measured dielectric permittivity and dielectric loss. Variation of ac conductivity of conducting polymer composites with frequency for different temperatures is shown in Fig. 5.

From Fig. 5, it can be seen that in samples with high concentration of CoPc, the frequency dependence is predominant whereas samples with high concentration of PANICSA show less frequency dependence. This is because of the incorporation of phthalocyanine materials in conducting polymers improving the charge storage capacity of the blends [16]. The ac conductivity obeyed the empirical relation of the form [36]:

$$\sigma_{\mathrm{ac}}(w) = A\omega^{s} \tag{3}$$

where σ_{ac} is the ac conductivity, ω the angular frequency, A the proportionality constant and s is the index which is characteristic of the type of conduction mechanism/relaxation mechanism dominant in amorphous materials.

The variation of exponent s with temperature gives information about the conduction mechanism involved. The value of s is less than 1 for all samples. An increase in ac conductivity with frequency and temperature dependence indicates that there may be charge carriers, which are transported by hopping through the defect sites along the polymer chain [37]. Also the increase in electrical conduction with increasing temperatures is due to the build up of ordered polycondensed rings, which allow charge transport. This temperature dependence of conductivity at higher temperatures suggests that the variable range hopping of charge carriers may occur in these composites.

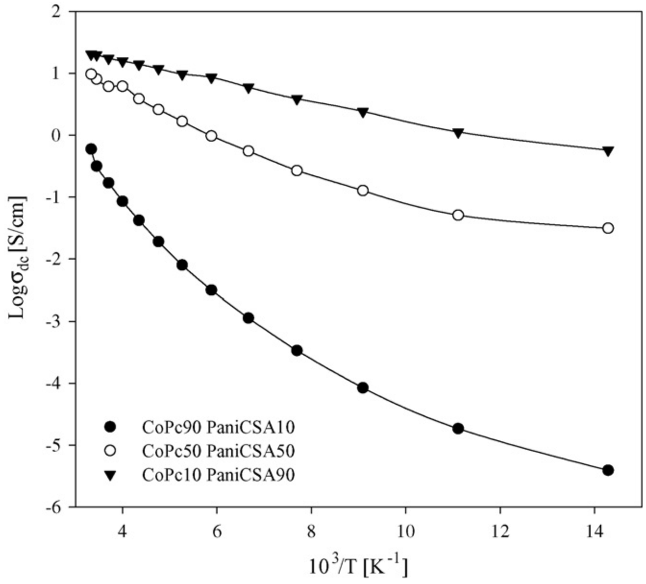

Fig. 6. Temperature dependence of dc conductivity of composites.

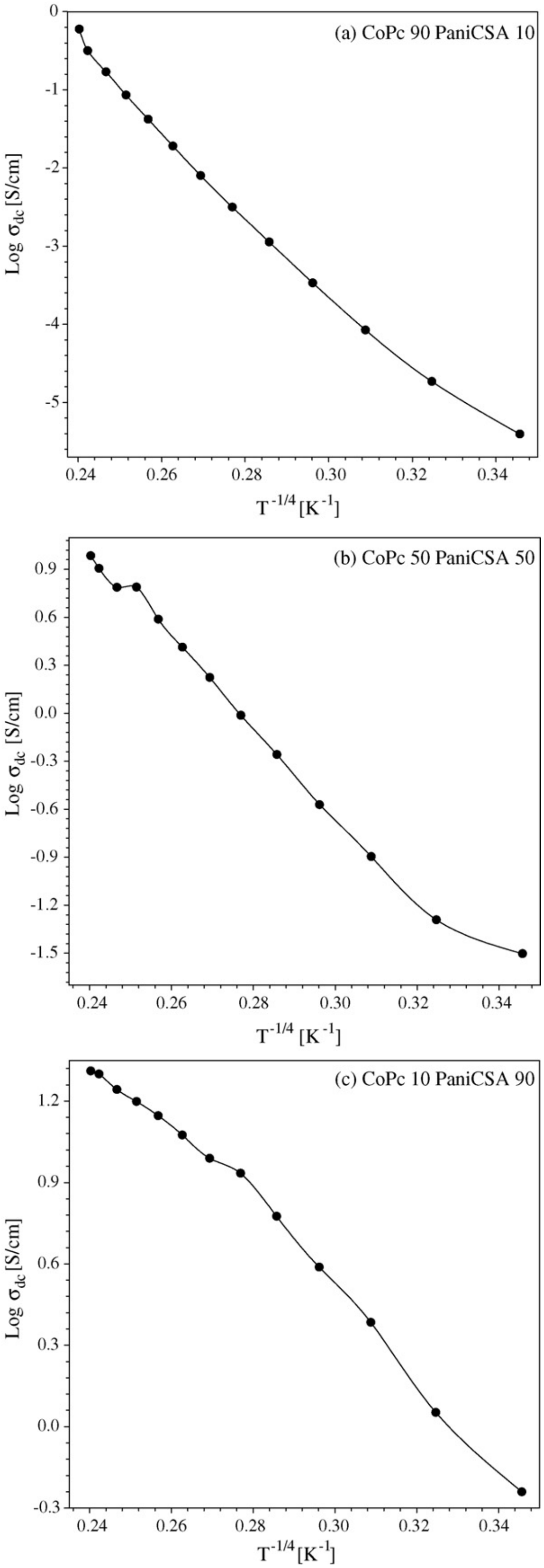

Fig. 7. $\log \sigma_{\mathrm{dc}}$ *vs.* $T^{-1/4}$ of composites.

Table 1
Mott's parameters for composites

Sample	Order of conductivity 300 K (S/cm)	Mott temperature	$N(E_F)$ (cm^{-3} eV^{-1})	R_{hop} (Å) 100 K	W_{hop} (eV) 100 K
PANICSA	2.78×10^1	2.50×10^3	8.39×10^{22}	7.99	0.01
CoPc10 PANICSA90	2.04×10^1	1.37×10^6	1.52×10^{23}	5.22	0.05
CoPc50 PANICSA50	9.67	1.19×10^7	1.76×10^{22}	3.04	0.16
CoPc90 PANICSA10	5.98×10^{-1}	1.71×10^8	1.22×10^{21}	1.56	0.31
CoPc[38]	4.11×10^{-3}	9.68×10^6	2.17×10^{22}	3.20	0.15

3.4. dc conductivity

To investigate the charge transport mechanism in composites, the temperature dependence of the electrical conductivity is studied in the temperature range 70–300 K for all compositions. The temperature dependence of dc conductivity for different volume fractions of polyaniline doped with camphor sulphonic acid in the blends is shown in Fig. 6.

In semiconductors, if the main conduction mechanism is due to the carriers excited beyond the mobility edge into non-localised or extended states, then the dc conductivity is expressed as [36]:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{4}$$

where σ_0 is the proportionality constant, E_a the activation energy, k the Boltzmann constant and T is the temperature.

Conductivity increases with increase of temperature for all compositions and it increases with increase of volume fraction of polyaniline doped with camphor sulphonic acid (PANICSA). The increase of conductivity with increasing temperature indicates the semi conducting behaviour of the composites. The activation energy values are calculated from Fig. 6 and it is found that the activation energy decreases with increase of volume fraction of polyaniline doped with camphor sulphonic acid. The low values of activation energy implies that the conduction is due to the excitation of carriers into mobility edge and/or to the localised states at the band edges which is inadequate to explain the conduction mechanism.

Thus the conductivity data are analysed with the help of Mott's variable range hopping (VRH) model. This mechanism is very often used to explain the dc conductivity of disordered and amorphous materials. In polymers with non-degenerate ground states, the charge transport is due to polarons and bipolarons [38,39]. This is consistent with the existence of high-density states in the band gap. Charge carrier localisation may give rise to the formation of polarons and the charge transport may be considered due to the variable range hopping. Basic theory and mechanism of the Mott's variable range hopping model has been already reported in detail [40,41,20]. According to Mott's theory, the conductivity is expressed as:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^N\right] \tag{5}$$

In this equation, if $N = 1/2$ or $1/4$ corresponds to the VRH conduction in one dimension or in three dimensions, respectively. $\log\sigma$ *versus* $T^{-1/4}$ gives best fit as seen in Fig. 7. But $\log\sigma$ *versus* $T^{-1/2}$ is not resulting in a perfect fit. The value of Mott's characteristic temperature T_0 and Mott's parameters for CoPc tetramers [20], PANICSA and the blends are given in Table 1. From Table 1, it is found that typical values of T_0 are low for PANICSA and it increases with increase of CoPc percentage. The value of T_0 implies an effective energy separation between localised states. If the value of T_0 decreases, the system becomes highly conducting and the value of T_0 contains the geometrical parameters of the system like size and distance between the grains and columbic interaction energy [14]. The conduction mechanism of unblended polyaniline is characteristic of three-dimensional variable range hopping (3D VRH) instead of one-dimensional variable range hopping (1D VRH), which is normally found in doped polyaniline. This may be due to the better inter-chain coupling in PANICSA and also due to the more sites are available for hopping in 3D [15]. Tetrameric cobalt phthalocyanine also follows the three-dimensional hopping conduction [20].

The dc conductivity of CoPC–PANICSA blends is compared with other conducting polymer composites. Reports exist on conductivity studies carried out in PANI–PVC blends. These composites exhibit a temperature dependence of conductivity that is quite different that of doped PANI [42]. As the temperature is decreased, the blends showed a much smaller decrease of conductivity than the unblended PANI [42]. It is found that the decrease of conductivity even more pronounced in the case of polyaniline (PANI)–poly methyl methacrylate (PMMA) blends than in PANI–PVC blends. The blends of PANI with copolyester of polyethylene terephthalate (PETG) show a flattening in σ at high temperatures in a manner similar to PANI–PMMA blend, and the decrease in conductivity as the temperature is reduced. The value of σ for PANICSA–CoPC blends is found to be decreased from that of unblended PANICSA like PANI–PVC [42] and PANI–PMMA [43]. The conducting polymer composites mentioned above follow either 1D VRH or 3D VRH conduction mechanism.

From our observations and the comparison of PANICSA–CoPC blends with the available data of conducting polymer composites, it is clearly seen that both tetrameric cobalt phthalocyanine and polyaniline contribute to the conduction process depending on the volume fraction.

4. Conclusions

Blends of polyaniline and tetrameric cobalt phthalocyanine are prepared and characterised by FTIR spectrum. The dielectric permittivity studies of these blends are carried out in the frequency range 100 kHz–5 MHz in the temperature range of 300–373 K, and the corresponding dielectric losses are compared. From *I–V* studies it is clear that variable range hopping conduction is the dominant conduction mechanism in the blends, which obeys 3D type mechanism. The conduction mechanism is explained with the help of Mott's theory and the Mott's parameters are determined.

Acknowledgment

MRA and SS thank the Department of Space for financial assistance received in the form of a project under ISRO-RESPOND, Government of India (file no. 10/03/354 dtd.23-02-1999).

References

[1] J.L. Bredas, R.R. Chance (Eds.), Conjugated Polymeric Materials-Opportunities in Optoelectronics and Molecular Electronics, NATO Advanced Study Series, Kluwer, Dordrecht, 1990.
[2] T.A. Skotheim (Ed.), Handbook of Conducting Polymers, vol. 1/2, Marcel Dekker, New York, 1986.
[3] D.R. Ulrich, in: R.A. Hann, D. Bloor (Eds.), Organic Materials for Non-Linear Optics, Royal Society Chemistry, London, 1989.
[4] J. Simon, J.J. Andre (Eds.), Molecular Semiconductors—Photoelectrical Properties and Solar Cells, Springer–Verlag, Heidelberg, 1985.
[5] W.A. Gazotti Jr., G. Gasalbore-Miceli, S. Mitzakoff, A. Geri, M.C. Gallazzi, M.A. De Paoli, Electrochem. Acta 44 (1999) 1965.
[6] S. Venkatachalam, P.V. Prabhakaran, Eur. Poly. J. 29 (5) (1993) 711.
[7] V. Vijayanathan, S. Venkatachalam, V.N. Krishnamurthy, Synth. Met. 114 (2000) 273.
[8] P. Dutta, S. Biswas, M. Ghosh, S.K. De, S. Chatterjee, Synth. Met. 122 (2002) 455.
[9] N.J. Pinto, A.A. Acosta, G.P. Sinha, F.M. Aliev, Synth. Met. 113 (2000) 77.
[10] C.K. Jeong, J.H. Jung, B.H. Kim, S.Y. Lee, D.E. Lee, S.H. Jang, K.S. Ryu, J. Joo, Synth. Met. 117 (2001) 99.
[11] M.G. Han, S.S. Im, J. Appl. Polym. Sci. 82 (2001) 2760.
[12] W.-J. Lee, Y.-J. Kim, S. Kaang, Synth. Met. 113 (2000) 237.
[13] M. Reghu, C.O. Yoon, D. Moses, P. Smith, A.J. Heeger, Y. Cao, Phys. Rev. B 50 (1994) 13931.
[14] J. Planes, A. Wolter, Y. Cheguettine, A. Pron, F. Genoud, M. Nechtschein, Phys. Rev. B 58 (12) (1998) 7774.
[15] B. Sanjai, A. Raghunathan, T.S. Natarajan, G. Rangarajan, S. Thomas, P.V. Prabhakaran, S. Venkatachalam, Phy. Rev. B 55 (16) (1997) 10734.
[16] S. Venkatachalam, P.V. Prabhakaran, Synth. Met. 97 (1998) 141.
[17] S. Saravanan, C.J. Mathai, M.R. Anantharaman, S. Venkatachalam, P.V. Prabhakaran, J. Phys. Chem. Solids 67 (2006) 1496.
[18] W.S. Huang, B.D. Humphery, A.G. MacDiarmid, J. Chem. Soc. Faraday Trans. 82 (1986) 2385.
[19] S. Venkatachalam, K.V.C. Rao, P.T. Manoharan, Synth. Met. 26 (1988) 237.
[20] S. Saravanan, C.J. Mathai, M.R. Anantharaman, S. Venkatachalam, P.V. Prabhakaran, J. Appl. Polym. Sci. 91 (2004) 2529.
[21] S. Sagar, S. Saravanan, S. Sureshkumar, S. Venkatachalam, M.R. Anantharaman, J. Phys. D: Appl. Phys. 39 (2006) 1678.
[22] A. Ahmad, R.A. Collins, J. Phys. D: Appl. Phys. 24 (1991) 1894.
[23] W.J. Kroenke, M.E. Kenney, Inorg. Chem. 3 (1964) 696.
[24] T. Kobayashi, F. Kurokawa, N. Uyeda, E. Suito, Spectrochim. Acta A 26 (1970) 1305.
[25] P.N. Moskalev, I.S. Kirin, Rus. J. Inorg. Chem. 15 (1970) 7.
[26] B. Stymne, F.X. Sauvage, G. Wettermark, Spectrochim. Acta A 35 (1979) 1195.
[27] A.B.P. Lever, Adv. Inorg. Chem. Radiochem. 7 (1965) 44.
[28] S. Venkatachalam, K.V.C. Rao, P.T. Manoharan, Synth. Met. 26 (1988) 237.
[29] B.N. Achar, G.M. Fohlen, J.A. Parker, J. Poly. Sci., Polym. Chem. Ed. 20 (1982) 1785.
[30] L.W. Shacklette, J.F. Wolf, S. Gould, R.H. Baughman, J. Chem. Phys. 88 (1988) 3955.
[31] F.M. Reicha, M. El Hiti, A.Z. El Sonbati, M.A. Diab, J. Phys. D: Appl. Phys. 24 (1991) 369.
[32] O. Prakash, K.D. Mandal, C.C. Christopher, M.S. Sastry, D. Kumar, J. Mater. Sci. 31 (1996) 4705.
[33] H. Birey, J. Appl. Phys. 49 (5) (1978) 2898.
[34] V. Rao, P.V. Asokan, J.V. Amar, J. Appl. Polym. Sci. 86 (2002) 1702.
[35] K.P. Paramasivam, M. Radhakrishnan, C. Balasubramanian, Thin Solid Films 74 (1980) 189.
[36] N.F. Mott, E.A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon, Oxford, 1971.
[37] A.K. Jonscher, Thin Solid Films 1 (1967) 213.
[38] Y. Hirai, H. Tanaka, T. Mishi, Jpn. J. Appl. Phys. 29 (1987) L1401.
[39] P. Kuivalainen, H. Stubb, H. Isotalo, P.Y. Lahti, C. Holmstorm, Phys. Rev. B 31 (1985) 7900.
[40] K. Nair, S.S. Mitra, J. Non-Cryst. Solids 24 (1977) 1.
[41] R. Singh, R.P. Tandon, V.S. Panwar, S. Chandra, J. Appl. Phys. 69 (1991) 2504.
[42] C.K. Subramaniam, A.B. Kaiser, P.W. Gilberd, B. Wessling, J. Polym. Sci. B 31 (1993) 1425.
[43] A.B. Kaiser, C.K. Subramaniam, P.W. Gilberd, B. Wessling, Synth. Met. 69 (1995) 197.