

Preparation and Characterization of Polymer Composites Based on Charge-transfer Complex: O-tolidine-iodine in Polystyrene

R.K. Gupta and R.A. Singh

Molecular Electronics Laboratory, Department of Chemistry, Faculty of Science,
Banaras Hindu University, Varanasi-221005, India

Abstract: Polymer composites of o-tolidine-iodine (1:0.75 molar ratio) charge-transfer complex with polystyrene have been prepared in different weight ratios and characterized by the spectral, structural, thermal and electrical methods. The polymer composites exhibit semiconducting behaviour, having the thermal activation energies in the range of 0.18 to 0.49 eV. The current-voltage characteristics, frequency dependence of conductivities of these composites have been determined. The frequency dependence of ac conductivity of these composites showed contribution from grain, grain boundary and electrode as a function of charge-transfer content. At low charge-transfer content, all the three contributions were present but at high content, only grain contribution was observed.

Key words: Charge-transfer complexes, semiconductor, o-tolidine-iodine, electrical conductivity

INTRODUCTION

Charge-transfer materials have been extensively studied in recent years due to their unusual electrical, magnetic and optical properties^[1,2]. However, the commercial exploitation of these materials is very limited due to their low mechanical strengths and thermal and atmospheric instabilities^[3]. The mechanical strengths of these materials can be improved by preparing their composites with insulating polymers in optimized amount of charge-transfer materials^[4]. Reticulate doping is the excellent technique of preparing polymer composites^[5]. In this technique the charge-transfer complexes are grown in processable polymer matrices.

Reticulate doping of TTT-TCNQ charge-transfer complex in poly (bis phenol A carbonate) yielded dark conductivity of $3 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature at 1 wt% of the complex. It was found that the existence of dendrite like network of microcrystallites in the composite resulting into conducting channels was a prerequisite for high conductivity in these materials. These conducting channels resulted in very low percolation threshold of 0.3 wt% in some systems^[6], otherwise in the systems with no channel growth the percolation threshold was found to be more than 20 wt%^[7]. The formation of conductive network has been confirmed by impedance analyses^[8]. The connectivity of conducting crystalline network has also been demonstrated by measuring the temperature dependence of conductivity for morphologically different samples^[9]. A comprehensive analysis of the parameters controlling the crystallization of charge-transfer

complexes in reticulate doping of polymers has been presented by Tracz *et al.*^[10]. Scanning electron microscopy of reticulate doped TTT-TCNQ complex in polycarbonate and poly (methylmetacrylate) showed conductive network in these materials^[11].

These studies showed that a number of composites based on TTF and its analogues and TCNQ have been prepared. But the preparation of charge-transfer composites based on iodine as acceptors was not studied extensively. In this communication, the preparation and characterization of o-tolidine-iodine-polystyrene composite system are presented. The detailed study of the electrical properties of these composites has been carried out. Apart from electrical properties IR, XRD, microstructure, mechanical properties have also been studied for proper characterization of these materials.

MATERIALS AND METHODS

O-Tolidine (CDH) was purified by recrystallization in benzene. The iodine (S.D.fine- chem. Ltd) was used after purification by sublimation from KI+I₂ mixture (1:1.25). The polystyrene (PS) (G.S.C.India) was used as received. All other chemicals were of A.R. grade. The charge-transfer complex (CTC) of o-tolidine-iodine was prepared by mixing the hot solutions of the required amount of donor and acceptor in benzene^[4]. The stoichiometry of the charge-transfer complex prepared was confirmed by elemental analyses, which agree, well with the overall stoichiometric ratios.

For preparation of composites, the required amount of charge-transfer complex and polystyrene were dissolved in excess of benzene separately and then mixed together. The solvent was evaporated at room temperature with constant stirring. Then the composite were pressed in pellets form under 8 tones load using a hydraulic press.

The current-voltage characteristics were done with the help of a Source-Measure-Unit (Keithely, model-236) and a Picoammeter (Keithely, model-485). The temperature dependence measurements were done using temperature controller (Century, CT-810). The alternating current (ac) measurements were done on LCZ meter (Keithely, model 3330). All the measurements were done using platinum as contacts. The compressive strengths were determined by Amsler Universal Testing machine. The XRD patterns were recorded using CuK_α radiation with the help of X-ray diffractometer. IR spectra were recorded on FTIR machine (Jasco-5300). The microphotographs were taken with the help of Lietz Laborlux-D optical microscope. Elemental analyses were done on Carlo Erba 1108 Heraeus.

RESULTS AND DISCUSSION

Infra-red characterization: The IR spectra of o-tolidine-iodine and its composites have been recorded in KBr medium. The two sharp peaks due to primary amines in the pure o-tolidine at 3465 and 3417 cm^{-1} were totally replaced by the broad bands at 3435 and 3312 cm^{-1} in their complexes. The broad bands at -NH positions indicates the formation of quaternary amine species i.e., $\text{-N}^+\text{-H}$, from which a labile proton is expected. Similarly β (NH_2) for pure o-tolidine at 1604 cm^{-1} changes to 1608 for o-tolidine-iodine complex. The polystyrene has characteristics peaks at 2850 cm^{-1} corresponding to C-H stretching and 1607 cm^{-1} corresponding to C=C in plane of C_6H_5 . It has been observed that the IR spectra of the composites were superimposition on the parent materials. These results revealed that the composites were just a physical mixture of its constituents and no chemical interactions were present in the constituents.

X-ray diffraction data: The powder X-ray diffraction data, indexed by Ito's method^[12] showed that charge-transfer complex had orthorhombic crystal structure with the following lattice parameters:

$$a=9.969 \text{ \AA} \quad b=6.689 \text{ \AA} \quad c=5.028 \text{ \AA}$$

The diffraction patterns were observed only in the pure charge-transfer complex and in the composites having high charge-transfer contents, whereas no good

XRD patterns in the lower composition composites and in pure polystyrene were found (Fig. 1). The lattice parameters for the composites were as follows:

$$\begin{array}{llll} 80\% \text{ CTC} & a=9.987 \text{ \AA} & b=6.689 \text{ \AA} & c=5.001 \text{ \AA} \\ 60\% \text{ CTC} & a=10.052 \text{ \AA} & b=6.702 \text{ \AA} & c=5.049 \text{ \AA} \end{array}$$

The lattice parameters were almost comparable to the pure charge-transfer material. This also confirmed that these polymer composites were just physical mixture of two components.

Micro- structural characterization: The microstructures of the pure components and the composites have been shown in Fig. 2. The polystyrene was transparent, whereas the charge-transfer complex showed dense structure. Such types of structure for different charge-transfer complexes have been reported earlier^[13]. The composites having higher amount of charge-transfer complex were dense and continuous. As the amount of charge-transfer complex decreases in the composites the connectivity of filler is also decreased. These microstructures have a lot of impact on the electrical properties of these materials, which has been discussed along with the electrical characterization of these materials.

Mechanical characterization: The mechanical strength is an important consideration in the polymer composites. The charge-transfer materials are generally fragile and have low mechanical strengths. The mechanical strengths of the pure polymers and its composites have been measured and reported in Table 1. The compressive strengths of these materials have been measured on a

Table 1: Mechanical strength of the composites of o-tolidine-iodine with polystyrene

% Composition of CTC	Compressive strength (kg cm ⁻²)
100	245.1
80	320.1
60	384.7
40	447.9
20	472.1
Pure polymer	567.8

Table 2: DC electrical properties of o-tolidine-iodine- polystyrene composites

Percentage of CTC (% wt.)	Specific conductance (S cm ⁻¹)	Energy of activation (eV)	
		I	II
100	2.85×10^{-5}	0.300	0.183
80	1.31×10^{-5}	0.426	0.306
60	1.07×10^{-5}	0.388	0.259
40	9.63×10^{-6}	0.494	0.413
20	2.33×10^{-6}	0.465	0.443
10	1.23×10^{-6}	0.348	0.275
7	6.71×10^{-10}	0.384	0.217
4	2.42×10^{-12}	0.312	0.312

Table 3: AC electrical properties of o-tolidine-iodine- polystyrene composites

Percentage of CTC (% wt.)	Electrical properties								
	Grain			Electrode			Grain boundary		
	R (Ohms)	Q (Mho)/C (Farad)	n	R (Ohms)	Q (Mho)/C (Farad)	n	R (Ohms)	Q (Mho)/C (Farad)	n
100	7.50×10^3	7.72×10^{-11}	-	-	-	-	-	-	-
80	1.41×10^4	2.53×10^{-10}	0.88	-	-	-	-	-	-
60	2.64×10^4	9.21×10^{-9}	0.65	-	-	-	-	-	-
40	1.37×10^5	4.01×10^{-10}	0.81	6.04×10^4	1.14×10^{-6}	0.48	-	-	-
20	9.36×10^6	4.14×10^{-10}	0.81	9.95×10^5	8.22×10^{-11}	0.93	-	-	-
10	8.18×10^6	2.09×10^{-9}	0.67	4.41×10^6	4.93×10^{-11}	0.95	-	-	-
7	1.70×10^7	6.35×10^{-11}	1.00	2.89×10^6	5.01×10^{-11}	0.94	2.83×10^6	5.20×10^{-11}	0.94
4	1.30×10^7	1.18×10^{-10}	1.00	1.30×10^7	1.08×10^{-10}	1.00	7.07×10^6	4.00×10^{-11}	0.86

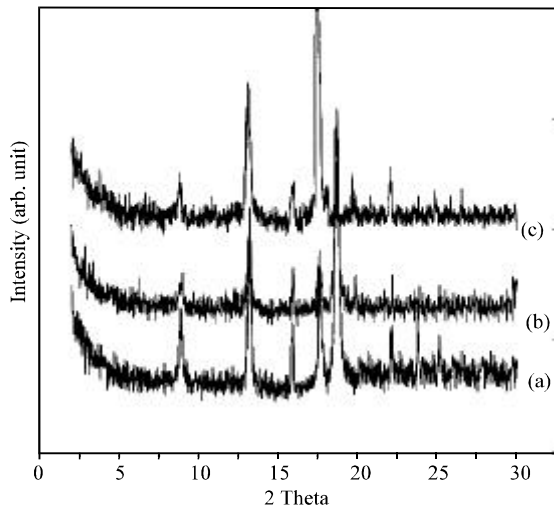


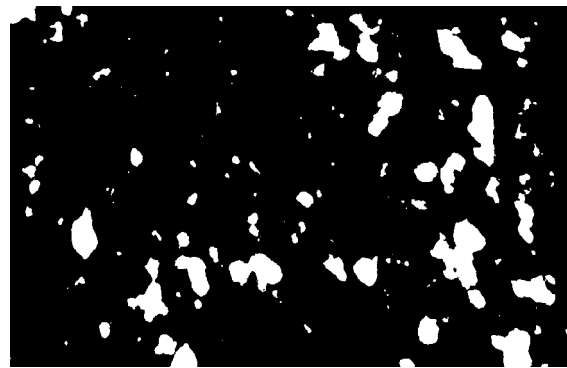
Fig. 1: XRD pattern for o-tolidine-iodine-polystyrene composite. (a) Pure CTC, (b) 80% CTC, (c) 60% CTC

pellet of uniform dimension (1.5 ± 0.2 cm) having fixed weight of the materials. These studies reveal that the mechanical strengths of the composites increase with the increases of insulating polymers.

Thermal characterization: The pure charge-transfer complex decomposed in two steps. About 47% weight loss took place in first step with maximum loss at 208°C . This was due to loss of 0.75 mole of iodine in the range of $150\text{-}350^\circ\text{C}$. Rest of the material was lost between $350\text{-}600^\circ\text{C}$, with maximum loss at 575°C . The polystyrene decomposed in the range of $135\text{-}450^\circ\text{C}$. Whereas, the composite materials showed a mixed nature of thermal degradation.

Electrical characterization

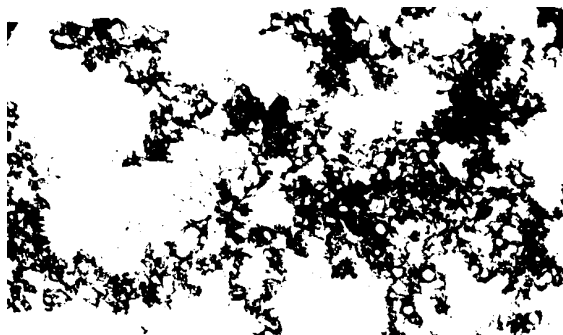
Direct current studies: Current-voltage (I-V) characteristics of the charge-transfer complex and its composites have been studied at room temperature using platinum as contacts. It has been found that the I-V



(a)

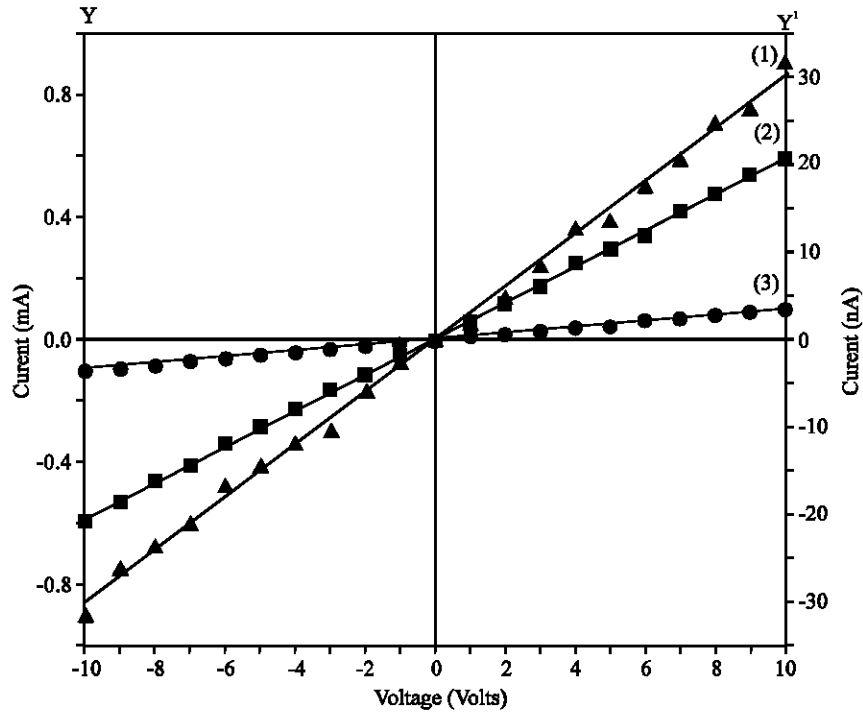


(b)



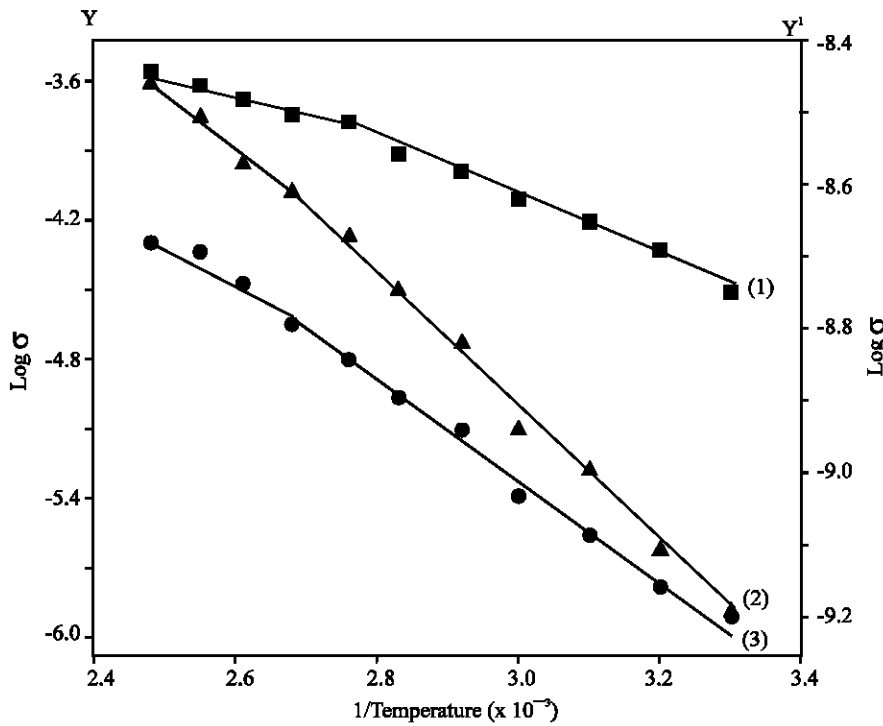
(c)

Fig. 2: Optical microphotographs ($\times 250$) for (a) Pure CTC, (b) 20% CTC, (c) 7% CTC



Y-axis (2) 60% CTC Y¹-axis (1) 7% CTC
 (3) 20% CTC

Fig. 3: Current-Voltage characteristics of o-tolidine-iodine-polystyrene composite



Y-axis (1) Pure CTC Y¹-axis (2) 7% CTC
 (3) 10% CTC

Fig. 4: Arrhenius plot for o-tolidine-iodine-polystyrene composite

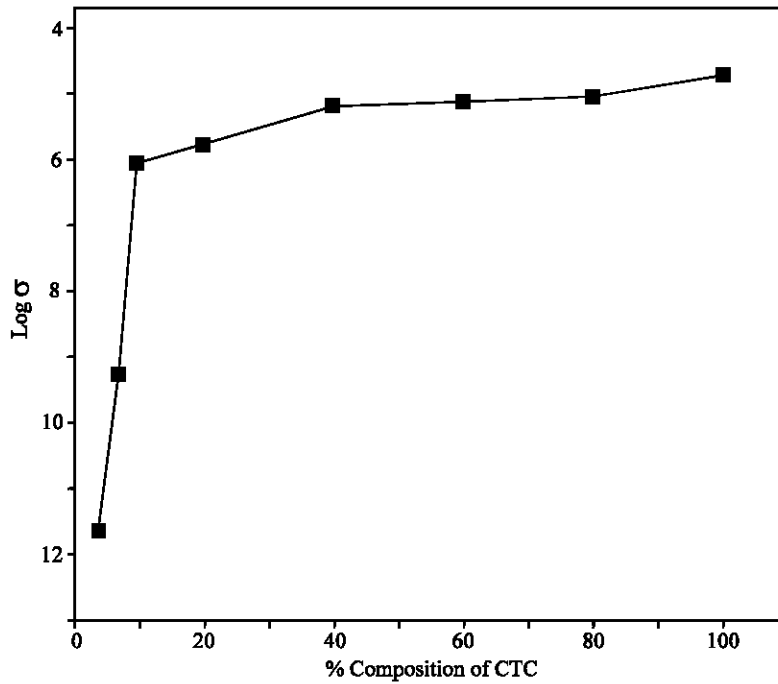


Fig. 5: Plot of Sp. Conductivity vs % composition of CTC in polystyrene

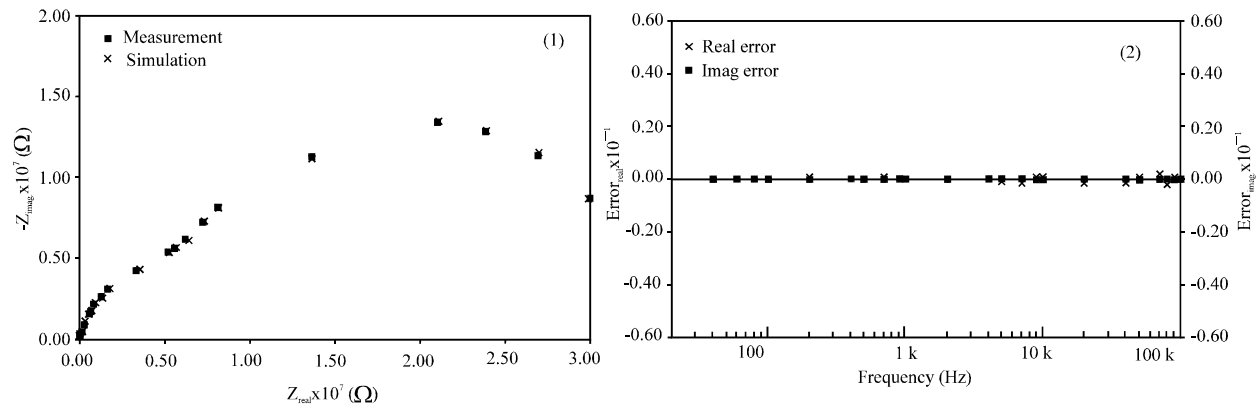


Fig. 6: Real and imaginary plots for o-tolidine-iodine -polystyrene (7% CTC) composite. (1) Impedance plot (2) Error plot

characteristics of these materials were ohmic in the range of ± 10 volts. The I-V characteristics of these materials have shown in Fig. 3. The conductivities were also studied as a function of temperature. In all the systems the conductivity increased with temperature indicating that these materials are semiconductor in nature. The Arrhenius plots of these materials have been shown in Fig. 4. Two clear-cut slopes were observed in the Arrhenius plots, indicating two different types of conduction mechanism in the temperature range studied^[14]. The conductivity and the thermal activation energies of these composites have been reported in Table 2. The plot of conductivity verses composition for

different compositions of charge-transfer complex has been shown in Fig. 5. Very low percolation threshold (~ 7 wt% of CTC) has been observed which can be explained on the basis of the continuous structure of the composites at and above this percentage composition.

Alternating current studies: The impedance analyses of the charge-transfer complex and its composites have been done in the frequency ranges of 40 Hz-100 kHz. It has been observed that these systems exhibit frequency dependence of the electrical conductivities. A possible equivalent circuit is given to the system by feeding the frequency, real and imaginary impedance in the CNLS

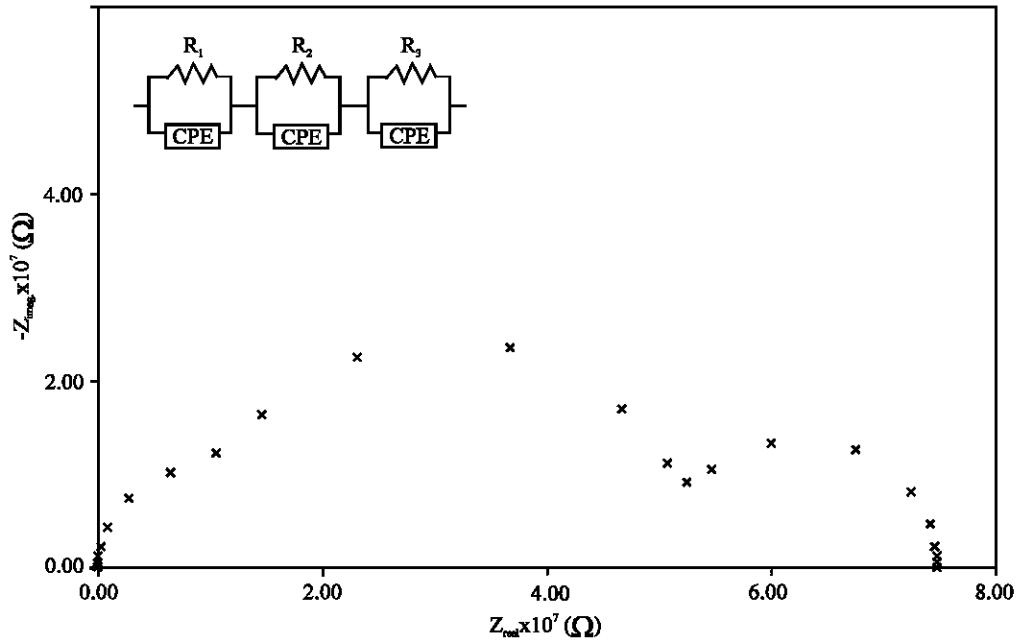


Fig. 7: Complex impedance plot for o-tolidine-iodine-polystyrene (7% CTC) composite

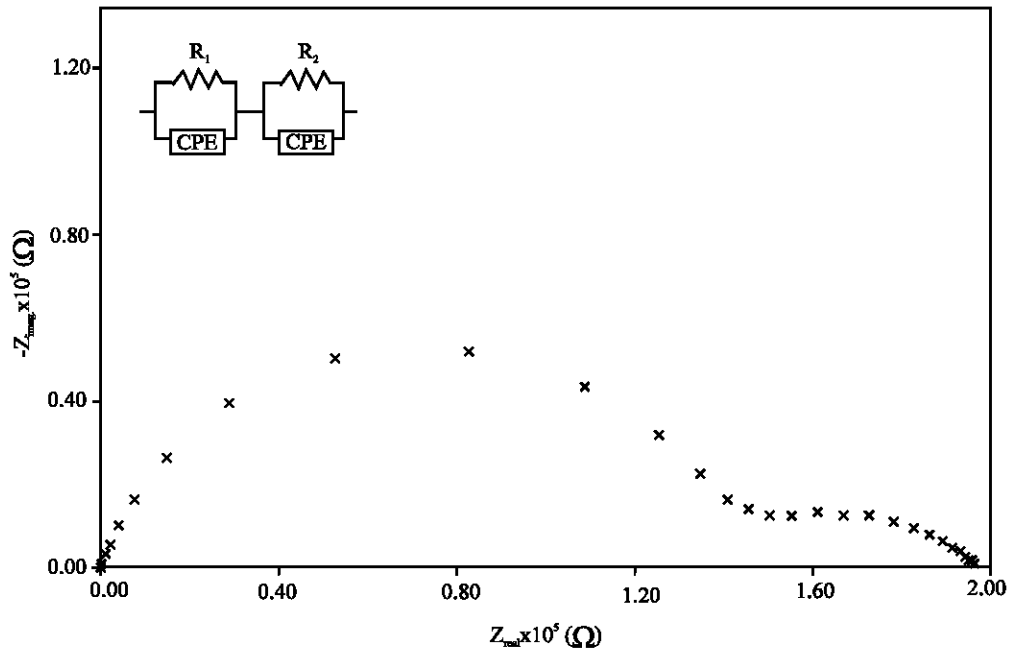


Fig. 8: Complex impedance plot for o-tolidine-iodine-polystyrene (40% CTC) composite

software. The best-fitted circuit of the system has been determined by observing the coherence between the experimental and the simulated data in complex impedance and modulus plots, as well as the minimum real and imaginary errors. Some representative plots have been given in Fig. 6. It has been observed that there was strong coherence in the measured data and simulated data in the

measured frequency range. Then the data were simulated in the frequency range required for the best resolution (10^{-3} to 10^{11} Hz) using the parameters of the equivalent circuit.

The overall measured electrical properties of the materials generally contains grain, grain boundary and electrode contributions. So, in general it is expected the

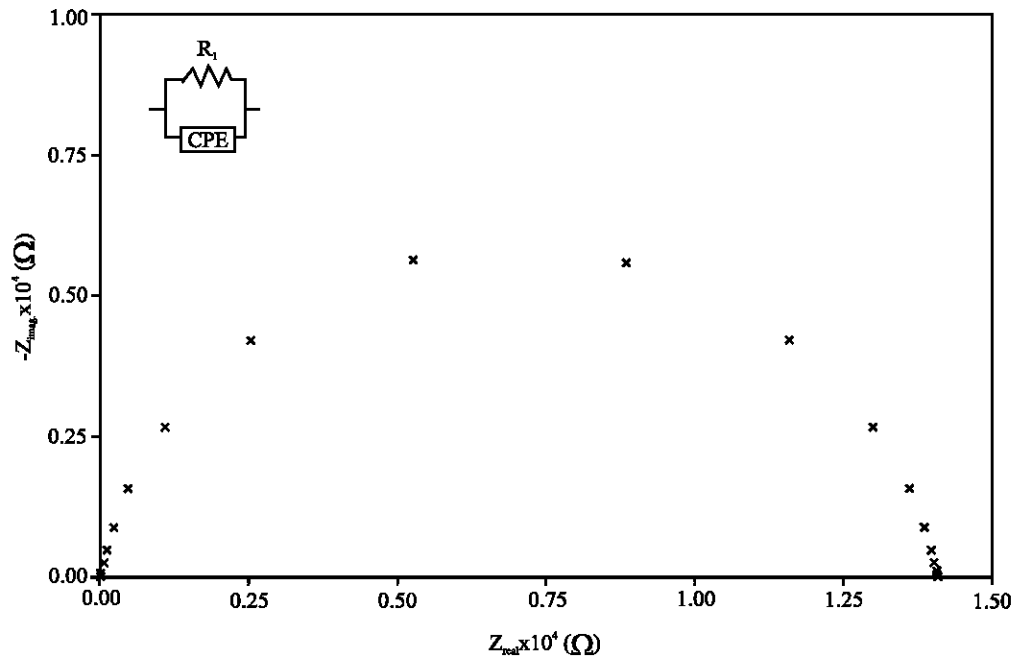


Fig. 9: Complex impedance plot for o-tolidine-iodine-polystyrene (80% CTC) composite

presence of three arcs. The arc with lowest frequency range corresponds to the electrode contribution and arc with highest frequency range passing through origin represents the bulk resistance, whereas the arc in between the two corresponds to the grain boundary contribution. We have found all the three expected contributions to the total ac electrical conductivities in the composites having lower amount of conducting polymers (Fig. 7). As the concentration of charge-transfer complex increases, there will be a continuity of conducting polymer in the polystyrene matrix and the grain contribution will be lost (Fig. 8) and finally when the conducting polymer concentration is very high the electrode conductance will be masked with the bulk conductance and we find only the grain contribution (Fig. 9). It has been observed that the pure charge-transfer complex have (RC) equivalent circuit whereas, composites have combinations of (RQ) equivalent circuits. Since the composites have good elastic properties, it is not possible to make the powder of these materials, thus pellets are not expected to be very smooth at microscopic level^[15]. So. It is better to represent the data as RQ circuit instead of RC circuit^[16]. The values of the resistance (R) and capacitance (C)/constant phase elements (Q) obtained from the above analysis were given in Table 3.

CONCLUSION

Polymer composites of o-tolidine-iodine with polystyrene have been characterized. These materials have been by spectral, structural, thermal, mechanical and

electrical methods. These composites have improved mechanical properties, while retaining their electrical properties to a large extent. A correlation between microstructure and ac electrical properties has been given.

ACKNOWLEDGMENT

R.K. Gupta would like to thanks Banaras Hindu University, Varanasi, India for awarding a research fellowship.

REFERENCES

1. Ulanski, J., 1990. Conductivity of organic composites with 3- and 2- dimensional crystalline networks I. Continuity of the conducting phase. *Synth. Met.*, 39: 13-24.
2. Tracz, A., 2002. The microcrystals of BEDT-TTF and BEDO-TTF polyiodides forming the conducting networks within polymer film surface and their transformations. *Pol. J. Chem.*, 76: 457-470.
3. Ashwell, G.J., 1992. *Molecular Electronics*. John Wiley and Sons Inc., New York.
4. Srivastava, D.N. and R.A. Singh, 2000. Molecularly dispersed polymer composites of charge-transfer materials: morphology and physical properties. *Synth. Met.*, 114: 361-364.
5. Tracz, A., J.K. Jeszka, E. El. Shafee, J. Ulanski and M. Kryszewski, 1986. Stoichiometry of the CT complex crystallites in polymer films. *J. Phys. D: Appl. Phys.*, 19: 1047-1055.

6. Ulanski, J., A. Tracz and M. Kryszewski, 1985. Is a percolation threshold in conductive systems below 0.003 possible. *J. Phys. D: Appl. Phys.*, 18: 451-459.
7. Banerjee, P. and B.M. Mandal, 1995. Blends of HCl-doped polyaniline nanoparticles and poly (vinyl chloride) with extremely low percolation threshold-a morphology study. *Synth. Met.*, 75: 257-261.
8. Ulanski, J., M. Kryszewski, A. Tracz and F. Kremer, 1988. Temperature dependence of ac conductivity in polymer/organic metal systems. *Synth. Met.*, 24: 89-94.
9. Ulanski, J., A. Tracz, G. Debrue and R. Deltour, 1987. Connectivity of conducting crystalline networks in reticulate doped polymers. *J. Phys. D: Appl. Phys.*, 20: 1512-1518.
10. Tracz, A. and M. Kryszewski, 1988. Analysis of the main parameters controlling the charge-transfer complex crystallization in the reticulate doped process. *Makromol. Chem. Suppl.*, 15: 219-231.
11. Jeszka, J.K., A. Tracz, M. Kryszewski, J. Ulanski, T. Kobayashi and N. Yamamoto, 1990. Submicroscopic structure of the TTT-TCNQ conductive network in reticulate-doped polymers revealed by SEM. *Synth. Met.*, 35: 215-220.
12. Azaroff, L.J. and B.J. Buerger, 1958. *The Powder Method in X-ray Crystallography*. McGraw-Hill, New York.
13. Singh, R.A. and R. Singh, 1996. Microstructural and thermal studies on charge-transfer materials. *Mol. Cryst. Liq. Cryst.*, 75: 195-210.
14. Singh, R. and R.A. Singh, 1997. Semiconducting charge-transfer materials based on phenothiazines. *Mol. Mater.*, 8: 187-219.
15. Srivastava, D.N. and R.A. Singh, 2000. Preparation and characterization of polymer composites based on charge-transfer complexes: Phenothiazine-iodine (2:3) in poly (vinylacetate). *Indian J. Phys.*, 74: 335-338.
16. Ulanski, J., G. Boiteux-Steffan, G. Seyter, A. Tracz, J.K. Jeszka, G. Vallet and M. Kryszewski, 1987. Ac conductivity of polymers reticulate-doped with charge-transfer complexes. *J. Phys. D: Appl. Phys.*, 18: L-5-L-7.