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Preparation and characterization of polymer composites based on charge-transfer complex of phenothiazine–iodine in polystyrene

R A SINGH*, R K GUPTA and S K SINGH

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, India

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Abstract. **Polymer composites based on charge-transfer complex of phenothiazine and iodine with polystyrene have been prepared in different weight ratios and characterized by FTIR, XRD, mechanical, microstructure and electrical properties (d.c. as well as a.c.). These composites show semiconducting behaviour as the conductivity increases with increasing temperature. Low percolation threshold (10% wt CTC) has been found indicating that processable conducting polymers with improved mechanical properties can be prepared by this method.**

Keywords. **Phenothiazine–iodine; polymer composite; charge-transfer complex; polystyrene.**

1. Introduction

Molecular electronic materials based on charge-transfer complexes have attracted considerable attention in recent years (Foster 1969; Singh *et al* 1991; Ashwell 1992). They have unusual electrical, magnetic and optical properties, which could be used in fabrication of devices (Ulanski 1990). However, the mechanical strengths of these materials are very low, which restrict their application (Ashwell 1992). Mechanical strength of these charge-transfer complexes can be improved by preparing their composites with insulating materials (Margolis 1989). Such composite materials have improved mechanical strengths, while retaining their other properties e.g. electrical conductivity, optical and magnetic properties. Such electrically conductive polymer composites have been prepared by using graphite, carbon black, metal powders and flakes as filler into insulating polymer materials (Skotheim 1986). Polymer composites of conductive polymers such as polyacetylene, polypyrrole, polythiophene and polyaniline have also been reported (Yoon *et al* 1994; Benerjee and Mandal 1995; Omartova *et al* 1996; Yigit *et al* 1996).

Highly conductive polymer composites have been prepared by reticulate doping of poly (bisphenyl A carbonate/propylene carbonate) with micro crystals of charge-transfer materials (Jeszka *et al* 1981). The room temperature conductivity of this system was found to be 3×10^{-2} S/cm at 1 wt% of the complex. High conductivity in these materials was related to the existence of conducting path due to microcrystallization of the complex in the polymer matrix. Nano-structured conducting polymer composites of super paramagnetic particles in conducting polymer were studied (Kryszewski and Jeszka 1998). Highly conductive films of poly (vinylidine fluoride) reticulately doped with 2 wt% of TTF–TCNQ complex having electrical conductivity of about 1 S/cm were reported (Choi *et al* 1990). Generally reticulate growths are obtained at elevated temperature (Srivastava and Singh 2000). So the composite of charge-transfer complexes with iodine as acceptor cannot be made by this method, because iodine may start liberating at high temperature. So, the composite of charge-transfer materials in which iodine is used as acceptor are generally made by two-step reticulate doping (Jeszka and Tracz 1992; Tracz *et al* 1996) or by solution evaporation or diffusion method at lower temperature, resulting in dispersion type of composite (Kang *et al* 1994).

We have prepared the composites of phenothiazine–iodine with poly (vinyl chloride) (Singh and Srivastava 1999) and poly (vinylacetate) (Srivastava and Singh 2000). It is well established that the properties of a composite are highly dependant on the morphology of the system (Carmono *et al* 1980). In this paper, we report the morphological dependence of the physical properties of the phenothiazine–iodine charge-transfer complex in polystyrene. The detailed electrical properties of these composites have been studied. Apart from electrical characterization, IR, XRD, microstructure and mechanical properties have also been reported.

2. Experimental

Phenothiazine (Aldrich) was used after recrystallization in ethanol and iodine (S.D. Fine-Chem. Ltd.) was used after purification by sublimation from $KI + I_2$ mixture (1 : 1·25). The polystyrene (GSC) was used as received. All other

*Author for correspondence
(rasingh@bhu.ac.in; rasinghbhu@yahoo.com)

chemicals used were of AR grade. The phenothiazine–iodine (Ptz–I_2) complex was prepared by mixing the hot solutions of phenothiazine and iodine (in 1 : 2 molar ratio) in diethyl ether (Singh *et al* 1991). For preparation of composites, the required amount of charge-transfer complex (CTC) and polystyrene (PS) was dissolved in benzene separately and mixed together. The solvent was evaporated at room temperature. The fine powders of the composites were pressed in pellets in a hydraulic press under 8 tonnes load.

The d.c. measurements were done with the help of a Source-Measure Unit (Keithley model-236). The a.c. measurements were done on LCZ meter (Keithley model-3330). Platinum was used as contact for all the measurements. The microstructures were obtained from Lietz Labour Lux-D, XRD patterns were recorded with the help of diffractional X-ray diffractometer using CuK_a radiation, IR spectra were recorded on FTIR (Jasco-5300) and mechanical strengths by Instron Universal Testing Machine.

3. Results and discussion

3.1 *Physical nature*

The physical nature of the composite was confirmed by IR and XRD studies. The IR spectra of phenothiazine have broad band between 3320 and 3380 cm^{-1} corresponding to weakly acidic N–H in the cation radical of phenothiazine (Singh *et al* 1991). Similarly IR spectra of polystyrene have a characteristic band at 1618 cm^{-1} corresponding to C=C (in plane of C_6H_5). The characteristic band was found at 3320 and 3380 cm^{-1} (Ptz–I_2) and at 1618 cm^{-1} (PS) in the composite. This indicates that no chemical interaction is present in the constituents. Hence

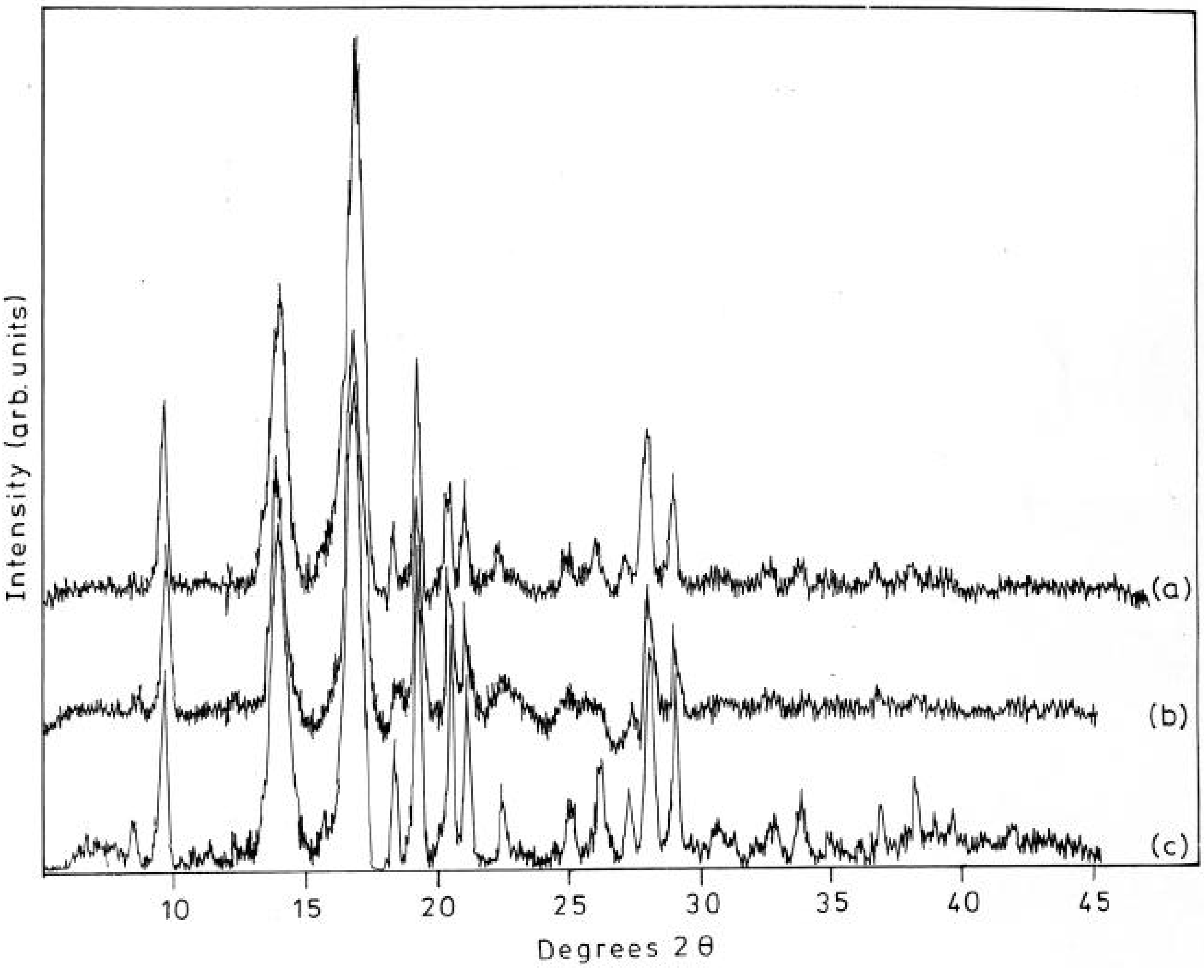

Figure 1. Powder X-ray diffraction pattern of (a) 20% CTC, (b) 60% CTC and (c) pure CTC.

the IR spectra confirm the physical mixture nature of the composites.

The superimposition of the XRD peaks of the composite reveals that the composites are just a physical mixture of their constituent (figure 1), which also confirms that these composites are microcrystals dispersed in the polymer matrix. Polystyrene is amorphous whereas phenothiazine–iodine charge-transfer complex shows good crystallinity (Singh *et al* 1991). The XRD data were analysed by Ito's method (Azaroff and Duerger 1958). The indexing of data shows that phenothiazine–iodine complex has orthorhombic crystal structure, which is retained in the composite as well. The diffraction patterns in composite are due to CTC only, so no diffraction patterns are observed in low percentage compositions. A few of the lattice parameters are given here:

Pure phenothiazine–iodine: $a = 5{\cdot}256$, $b = 5{\cdot}297$, $c = 9{\cdot}172$; 60 wt% CTC: $a = 5{\cdot}189$, $b = 5{\cdot}248$, $c = 9{\cdot}007$; 20 wt% CTC: $a = 5{\cdot}219$, $b = 5{\cdot}270$, $c = 9{\cdot}118$.

These results reveal that the composites are just a physical mixture of the constituents and no chemical interaction is present between them.

3.2 *Mechanical properties*

The compressive strengths of these composites were measured on a pellet of uniform dimensions by taking fixed weight of the materials. The compressive strength of these composites was found to be increasing as the amount of polymer increased (table 1). Pure CTC has a compressive strength of 189·2 kg/cm^2, whereas the 80 wt% CTC has a compressive strength of 315·4 kg/cm^2, which increases to 540·3 kg/cm^2 for 20 wt% CTC, which was almost comparable to the pure polymer.

3.3 *Electrical properties*

3.3a *Direct current studies*: The current and voltage characteristics of these composites were studied in the voltage ranges of ± 10 V and were found to be ohmic in nature (figure 2). The values of conductivity vary from

Table 1. Compressive strength of the composites.

Percentage of CTC (% wt)	Compressive strengths* (kg/cm^2)
Pure PS	571·9
20	540·3
40	526·4
60	447·8
80	315·6
Pure CTC	189·2

*For the sample of dimension, $A = 1{\cdot}32$ cm^2, $l = 2 \pm 0{\cdot}2$ cm.

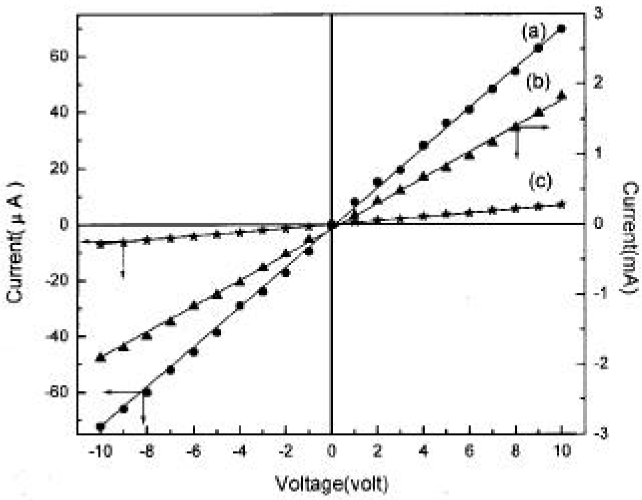

Figure 2. Current–voltage characteristics of phenothiazine–iodine–PS (a) 60% CTC, (b) pure CTC and (c) 20% CTC.

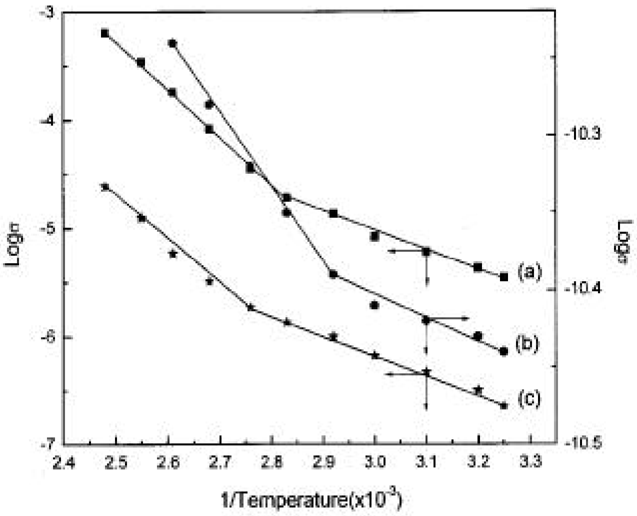

Figure 3. Arrhenius plot for phenothiazine–iodine–PS (a) 80% CTC, (b) 8% CTC and (c) 40% CTC.

Table 2. D.C. electrical properties of phenothiazine–iodine–PS composites.

Percentage of CTC (% wt)	Specific conductance (S/cm)	Energy of activation (eV) I	Energy of activation (eV) II
100	$3{\cdot}19 \times 10^{-5}$	0·49	0·44
80	$2{\cdot}67 \times 10^{-6}$	0·86	0·36
60	$1{\cdot}35 \times 10^{-6}$	0·75	0·38
40	$2{\cdot}38 \times 10^{-7}$	0·81	0·37
20	$1{\cdot}40 \times 10^{-7}$	0·08	0·02
10	$3{\cdot}46 \times 10^{-7}$	0·10	0·03
8	$1{\cdot}00 \times 10^{-11}$	0·09	0·03
6	$2{\cdot}69 \times 10^{-12}$	0·11	0·04
4	$2{\cdot}72 \times 10^{-12}$	0·06	0·03

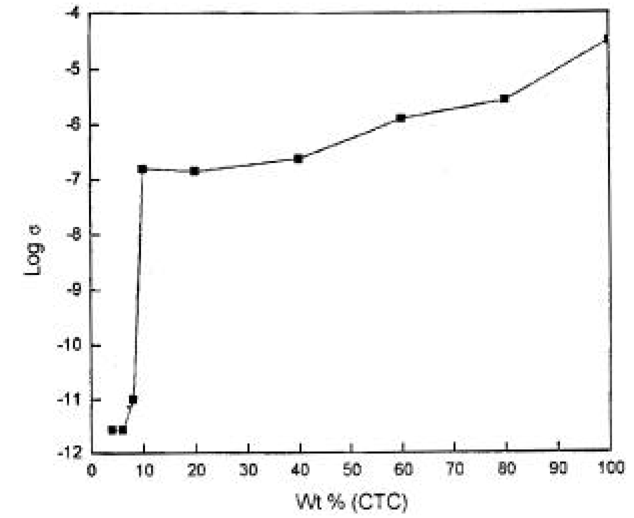

Figure 4. Variation of specific conductance of composite as a function of amount of charge-transfer complex.

$3{\cdot}19 \times 10^{-5}$ S/cm (pure CTC) to $2{\cdot}72 \times 10^{-12}$ S/cm (4% CTC composite). The conductivities were also studied as function of temperature in the range 303–393 K. The increase of conductivity with temperature indicates the semiconductive nature of the pure CTC and its composites (figure 3). Two slopes were observed in the Arrhenius plots of these materials indicating the presence of two different types of conduction mechanism in these systems. Similar results have been reported for pure CTC (Singh and Singh 1997). The values of specific conductivities and energy of activations have been calculated and reported in table 2. The plot of conductivity vs composition (wt% of CTC), as shown in figure 4, indicates low percolation threshold (10 wt%), which is much higher than the same for reticulately doped polymers with CTC (Ulanski *et al* 1985). This may be due to different growth mechanisms and microstructures of these composite materials.

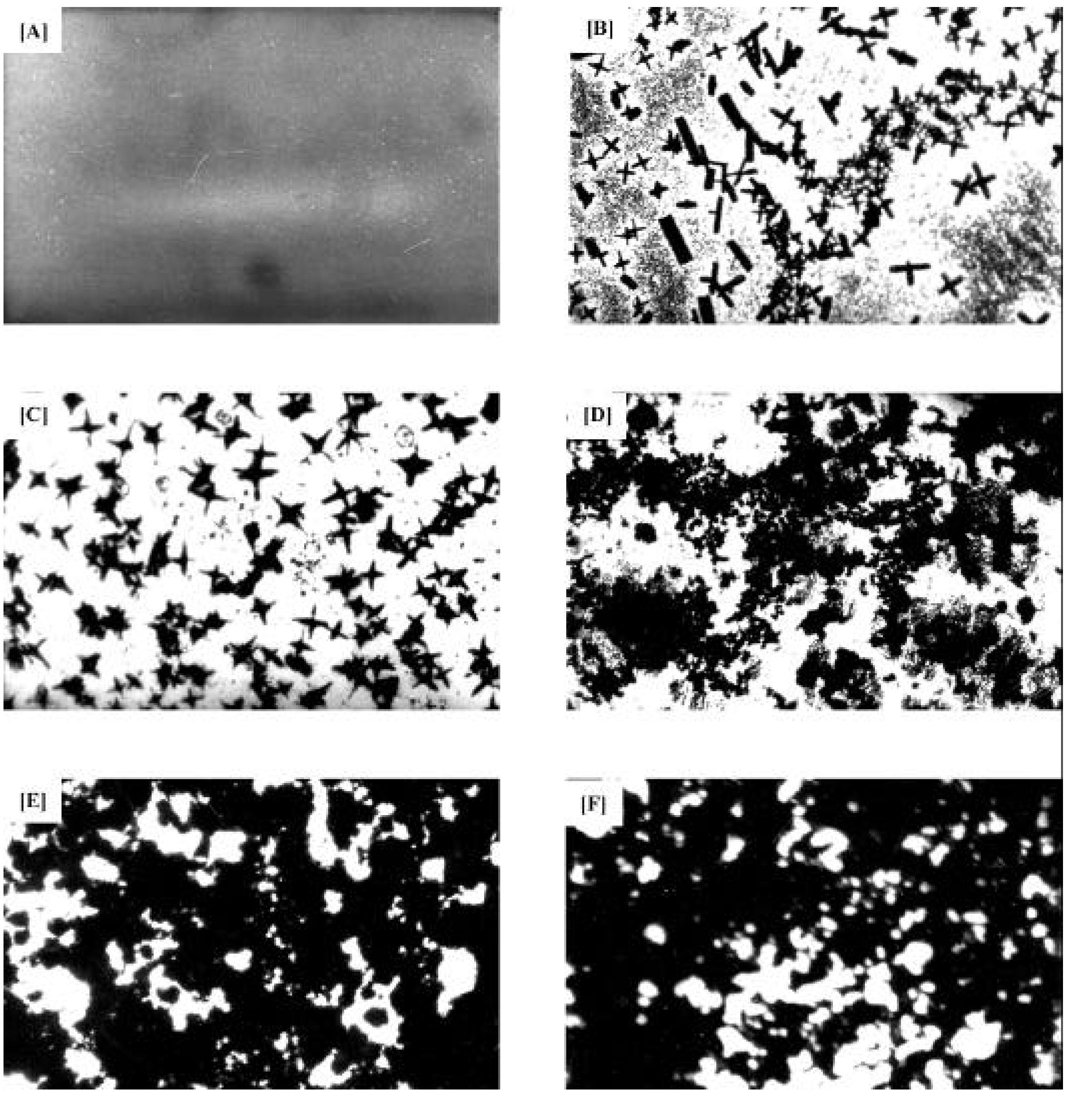

Figure 5. Microphotographs of [**A**] pure PS, [**B**] 2% CTC, [**C**] 4% CTC, [**D**] 10% CTC, [**E**] 40% CTC and [**F**] 60% CTC.

3.3b *Alternative current studies*: It is clearly seen from the micrographs of the composites that there exist discontinuities in the filler (figure 5). So we expect a frequency dependence of conductivity. We measure the a.c. conductivities using compact pellets of these materials in a pellet holder made of brass metal using platinum contact in the range 40–10^5 Hz, and then the data were simulated in the range 10^{-3}–10^{11} Hz using an EG & G CNLS fitting software (Manoharan *et al* 1986). A few representatives of such plots are given in figure 6.

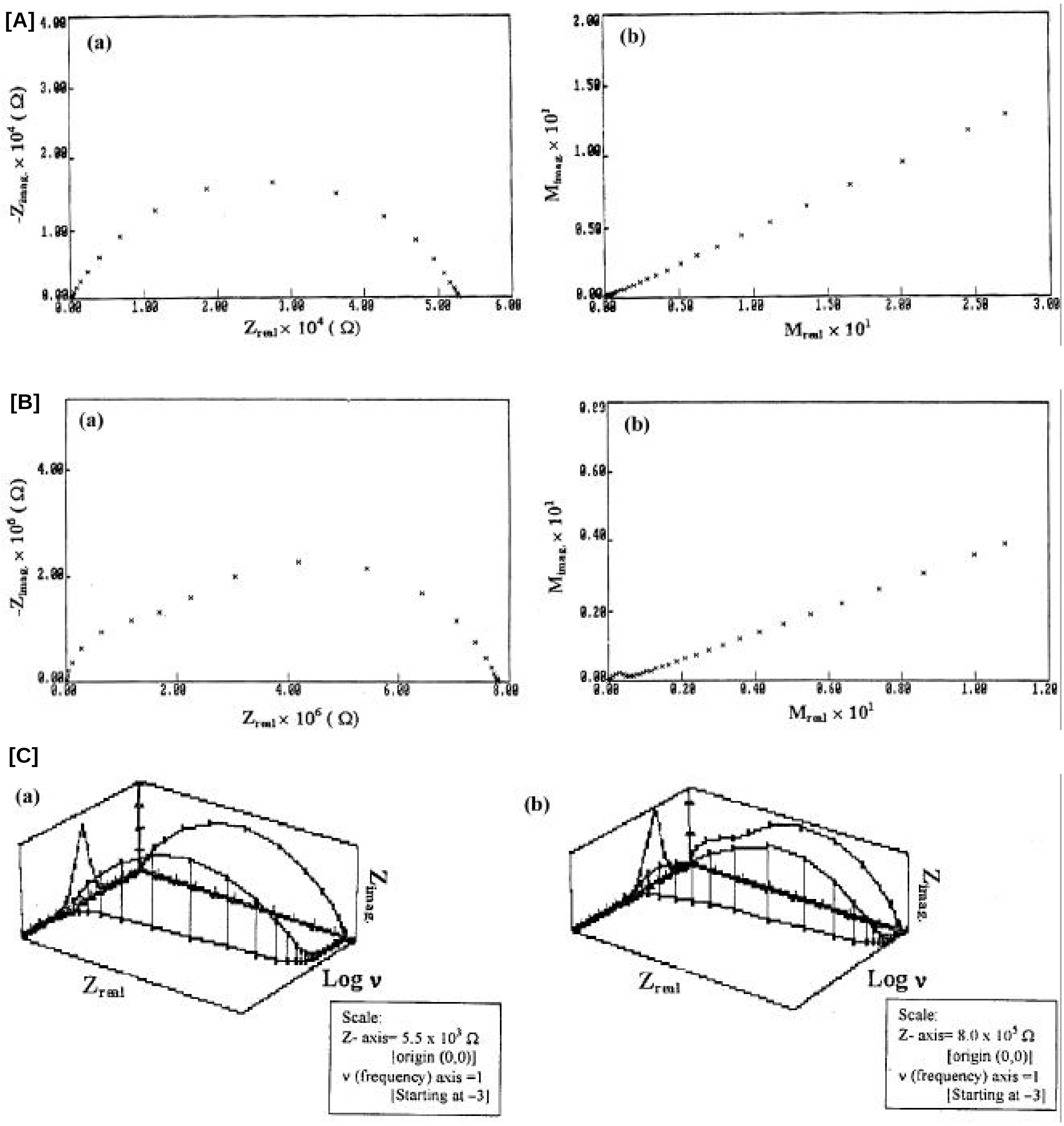

Figure 6. **A**. Complex immittance plots for phenothiazine–iodine–PS for 60 wt% CTC composite: (a) complex impedance plot and (b) complex modulus plot, **B**. complex immittance plots for phenothiazine–iodine–PS for 20 wt% CTC composite: (a) complex impedance plot and (b) complex modulus plot and **C**. three-dimensional perspective plots for phenothiazine–iodine–PS: (a) 60 wt% CTC and (b) 20 wt% CTC.

Table 3. Bulk and contact resistance and capacitance separated by a.c. immittance studies for phenothiazine–iodine–PS composites.

	Electrical properties								
	Grain			Electrode			Grain boundary		
Percentage of CTC (% wt)	R (Ω)	Q (Mho)/ $C(F)$	n	R (Ω)	Q (Mho)/ $C(F)$	n	R(Ω)	Q (Mho)/ $C(F)$	n
100	$1{\cdot}86 \times 10^{3}$	–	–	–	–	–	–	–	–
80	$2{\cdot}39 \times 10^{4}$	$6{\cdot}43 \times 10^{-10}$	0·78	–	–	–	–	–	–
60	$5{\cdot}28 \times 10^{4}$	$1{\cdot}41 \times 10^{-9}$	0·72	–	–	–	–	–	–
40	$2{\cdot}05 \times 10^{5}$	$1{\cdot}23 \times 10^{-10}$	0·91	$1{\cdot}29 \times 10^{5}$	$1{\cdot}65 \times 10^{-7}$	0·47	–	–	–
20	$6{\cdot}44 \times 10^{6}$	$8{\cdot}89 \times 10^{-10}$	0·77	$1{\cdot}35 \times 10^{6}$	$4{\cdot}80 \times 10^{-11}$	0·96	–	–	–
10	$5{\cdot}21 \times 10^{6}$	$5{\cdot}74 \times 10^{-10}$	–	$3{\cdot}84 \times 10^{6}$	$9{\cdot}08 \times 10^{-11}$	–	$1{\cdot}88 \times 10^{6}$	$6{\cdot}69 \times 10^{-11}$	0·91
8	$2{\cdot}63 \times 10^{6}$	$5{\cdot}36 \times 10^{-11}$	–	$6{\cdot}47 \times 10^{6}$	$2{\cdot}69 \times 10^{-10}$	–	$9{\cdot}96 \times 10^{5}$	$1{\cdot}06 \times 10^{-10}$	0·89
6	$2{\cdot}43 \times 10^{6}$	$1{\cdot}54 \times 10^{-10}$	–	$3{\cdot}38 \times 10^{6}$	$1{\cdot}03 \times 10^{-9}$	–	$1{\cdot}32 \times 10^{6}$	$8{\cdot}38 \times 10^{-11}$	0·89
4	$2{\cdot}93 \times 10^{6}$	$1{\cdot}24 \times 10^{-10}$	–	$4{\cdot}31 \times 10^{6}$	$7{\cdot}29 \times 10^{-10}$	–	$1{\cdot}59 \times 10^{6}$	$1{\cdot}08 \times 10^{-10}$	0·87

Generally we expect the grain, grain boundary and electrode contribution to the overall measured electrical properties. The pure phenothiazine–iodine complex does not show any frequency dependence of a.c. conductivity (Srivastava and Singh 2000). We found only resistive component and no capacitive component for 100 wt% CTC. The disappearance of capacitive component is due to the fact that no charge accumulates since the sample is highly conductive (Singh and Srivastava 1999). However, all the three expected contributions to the total a.c. electrical conductivities were present in the lower content charge-transfer composites (≤ 10 wt% CTC). As the amount of CTC increases in the composites, the discontinuities gradually reduce due to increased loading and we observe only two arcs viz. grain and electrode. This was actually observed for the compositions from 20–40 wt% CTC. On further increase of charge-transfer content in the polymer, the electrode contributions were also lost due to large difference in the magnitude of resistances between bulk and electrode. We have found one resistor (R) and one constant phase element (Q) in parallel in 80 and 60 wt% CTC composites corresponding to the bulk materials and one resistor and one constant phase element (CPE) in parallel connected in series with another resistor and CPE in parallel in 40 and 20 wt% CTC composites. The a.c. data for all the systems are given in table 3.

4. Conclusions

We prepared polymer composites of phenothiazine–iodine with polystyrene and characterized by a number of techniques. The above study shows that the composite of charge-transfer complexes with insulating polymers could be prepared, which has both good electrical and mechanical properties. These materials could be used for fabrication of solid-state galvanic cells.

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