

Studies on conductivity and dielectric properties of polyaniline–zinc sulphide composites

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Abstract. In the present paper, we report electrical conductivity and dielectric studies on the composites of conducting polyaniline (PANI) with crystalline semiconducting ZnS powder, wherein PANI has been taken as inclusion and ZnS crystallites as the host matrix. From the studies, it has been observed that the value of room temperature d.c. conductivity of the composites with volume fraction of PANI > 0.65 shows an unusual behaviour wherein, conductivity values of the composites exceed that of PANI itself with maximum value as high as 6 times that of PANI at the volume fraction of 0.85. A similar trend has also been observed for the real and imaginary parts of complex dielectric constant values of the composites. This unusual behaviour in the d.c. conductivity and dielectric properties has been attributed to the enhancement in the degree of crystallinity of PANI as a consequence of its interfacial interaction with ZnS matrix. The results of optical microscopy show coating of PANI all around the ZnS particles. The temperature dependent conductivity studies suggest the quasi one-dimensional VRH conduction in PANI as well as its composites with ZnS. FTIR and XRD studies have also been reported.

Keywords. Complex dielectric constant; percolation threshold; interfacial interaction; degree of crystallinity; characteristic temperature.

1. Introduction

Conducting polymers have emerged as a very important class of materials because of their unique electrical, optical and chemical properties leading to the wide range of technological applications. This class of materials provide tremendous scope for tuning of their electrical conductivity from semiconducting to metallic regime by way of doping (MacDiarmid and Epstein 1994; Wessling 1999). The unique properties of conducting polymers not only provide great scope for their applications but also have led to the development of new models to explain their observed properties, particularly various mechanisms of charge transport (Kaiser *et al* 1995, 1997). Among different conducting polymers, conducting polyanilines are the most extensively studied materials due to the ease of synthesis, better environmental and thermal stabilities and greater scope of playing with chemistry to tailor their properties (Kumar *et al* 1996). However, when they are taken in the composite form their electrical as well as dielectric properties are altered from those of basic materials. A number of groups have reported studies on the electrical conductivity and dielectric properties of composites of a variety of conducting polymers (Yoon *et al* 1995; Yang *et al* 1996; Gangopadhyay *et al* 2001; Muru-

gesan and Subramanian 2003). It has been shown that the conductivity of these heterogeneous systems depends on a number of factors such as the concentration of conducting fillers, their shape, size, orientation and interfacial interaction between filler molecules and host matrix (Krysze-waski 1991; Brosseau *et al* 2001). The geometrical shape of the dispersant governs the ability of conductive network formation which results in large increase in the conductivity (Truong *et al* 1994). Also, dispersant/matrix interactions and physical properties of the matrix influence the agglomeration of the dispersant phase which, in turn, affects the dielectric properties of the composites. In case of conducting polymers as fillers, the degree of cross-linking between the polymeric chains also affects the electrical properties in these composites (MacDiarmid and Epstein 1995).

Although the percolation theory has been generally used to explain the behaviour of electrical conductivity and dielectric properties of conducting polymer composites (Tuncer *et al* 2002), but it could not explain very low values of percolation threshold observed in many of the composite systems of conducting polymers. Wessling (1998) proposed a non-equilibrium theory for the composites of conducting polymers. This theory while accounting for the interfacial interactions between conducting polymers and host matrix could explain the observations of low percolation threshold.

In the present paper, we report XRD, IR, optical microscopy, electrical conductivity studies and microwave

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measurements on the polyaniline–ZnS composite systems to explain the unusual behaviour.

2. Experimental

2.1 Sample preparation

The samples of conducting polymer–semiconductor composites were prepared by thorough mixing of zinc sulfide powder with conducting HCl-doped emeraldine salt by mechanically grinding them in a pestle mortar while taking weight percentage of conducting polyaniline with an increment of 20%. The composite with 20% weight fraction of PANI was named as sample, S1 and subsequent composites with concentration of PANI at 40, 60 and 80% as S2, S3 and S4, respectively. Precise filling factor or volume fraction was calculated by using the following formula

$$f = \frac{\text{vol. inclusion powder}}{\text{vol. inclusion powder} + \text{vol. host powder}} \quad (\text{Bober } et al)$$

$$= \frac{(M_i/\rho_i)}{[(M_i/\rho_i) + (M_h/\rho_h)]},$$

where M_i , ρ_i ($= 1.52 \text{ g cm}^{-3}$) are the mass and density of the inclusion and M_h , ρ_h ($= 1.96 \text{ g cm}^{-3}$) are of host material, respectively.

2.2 Measurements

An HP8510C Network Analyser was used to perform transmission and reflection measurements on these samples in X-band (8.2–12.4 GHz) of MW frequency. The values of complex permittivity ($\epsilon_r = \epsilon'_r - j\epsilon''_r$) and permeability ($\mu_r = \mu'_r - j\mu''_r$) along with loss tangent ($\tan \delta = \epsilon''_r/\epsilon'_r$) of the composite materials were calculated from measured values of S-parameters using Nicolson–Ross algorithm (Chen *et al* 2004). The room temperature d.c. conductivity measurements were performed by using four-point resistivity probe. The variable temperature d.c. conductivity measurements were carried out in the temperature range 20–300 K by using four-point resistivity probe placed in Janis Model CCS-850 closed cycle refrigerator system. The XRD spectra of the composites were obtained by using powder XRD system Model PANalytical X'Pert Pro having $\text{CuK}\alpha_1$ X-ray source of wavelength, 1.5406 Å. The FTIR spectra were recorded in KBr by using SHIMADZU Model 8101A FTIR spectrometer. The optical microscopic studies were carried out by using optical microscope Model Nikon Eclipse E600.

3. Results and discussion

3.1 FTIR studies

The FTIR spectra of the pure materials and their composites are shown in figure 1. It can be seen from the figure that

in case of ZnS no absorption peaks are observed in the region 4600–400 cm^{-1} . Whereas for pure PANI two prominent absorption peaks are observed at 1713 cm^{-1} and 1006 cm^{-1} due to C=NH stretching (Lide *et al* 1993) and terminal monosubstituted benzenes vibration (Harada *et al* 1989), respectively. Other absorption peaks are observed at 1374 cm^{-1} due to benzene nitrogen stretching (Lide *et al* 1993). The absorption peak around 3426 cm^{-1} are attributed to N H stretching (Harada *et al* 1989).

Further, it is also observed from the figure that on mixing PANI with ZnS, the IR absorption peak of PANI at 1713 cm^{-1} due to C=NH stretching vibration reduces in intensity as well as broadens showing multiple peaks of weak intensity in the composites, S2, S3 and S4. Furthermore, the intensity of peak around 1006 cm^{-1} reduces and shifts to higher wave number. The observed changes in the IR spectra of composites are mostly around C=NH and terminal monosubstituted benzene sites thereby suggesting strong coupling/interaction of ZnS crystallites with the imine nitrogen in the conducting polymer.

3.2 Optical microscopic studies

The optical microscopic photographs of pure conducting polyaniline, ZnS sample and their composites, S1, S2, S3 and S4, are shown in figure 2. From this figure it can be seen that the optical micrograph of pure conducting polyaniline shows independent fine black coloured particles whereas ZnS particles can be seen as optically transparent particles. Further, it can be seen that in composite S1, where the concentration of PANI is 20%, we observe very thin black layer of PANI around the transparent particles of ZnS. As we increase the concentration of PANI to 40%, the black coating becomes thicker around these particles. On further increasing the concentration of PANI to 80%, we observe that PANI almost completely overcoats the ZnS particles and they are seen as completely black. The studies, therefore, suggest almost complete and thick coating of PANI around the ZnS particles at higher concentration of PANI (>60%).

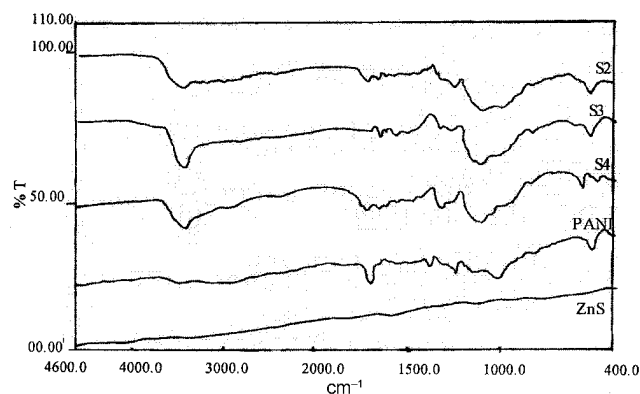


Figure 1. FTIR spectra of PANI, ZnS and their composites.

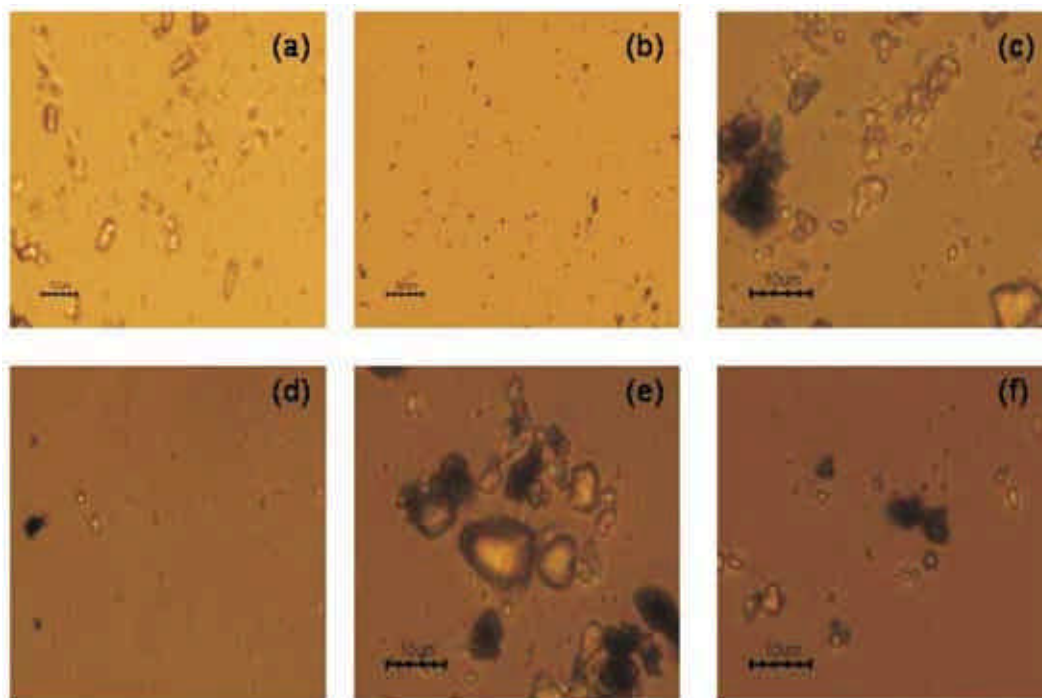


Figure 2. Optical microscopic photographs of (a) ZnS, (b) PANI, (c) S1 (20% PANI + 80% ZnS), (d) S2 (40% PANI + 60% ZnS), (e) S3 (60% PANI + 40% ZnS) and (f) S4 (80% PANI + 20% ZnS).

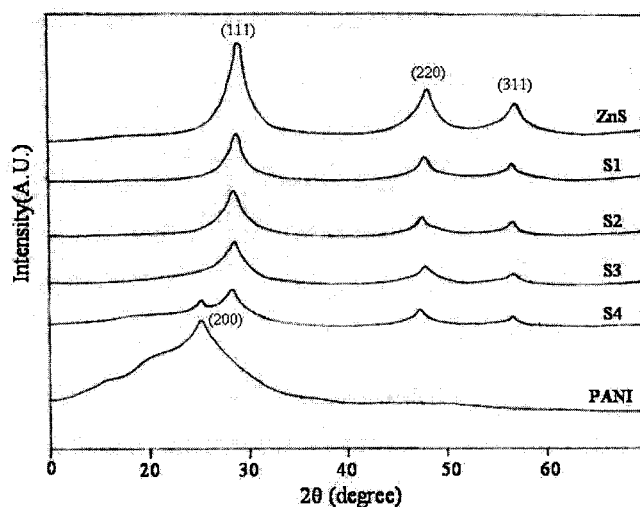


Figure 3. XRD spectra of PANI, ZnS and their composites.

3.3 XRD studies

The powder XRD spectra of pure PANI, pure ZnS and their composites with different volume fractions are shown in figure 3. From this figure, in the XRD spectra of pure PANI, we observe a broad reflection at lower Bragg angle 2θ value of $25\text{--}38^\circ$ corresponding to (200) diffraction plane of ES-I structure of HCl doped PANI (Joo *et al* 1998). In XRD spectra of ZnS, we observe three reflection peaks at 2θ value of 28.858° , 47.515° and 56.289° corres-

ponding to (111), (220) and (311) set of diffraction planes, respectively of the cubic crystalline structure.

However, in the XRD spectra of the composites we observe that at 20% concentration of ZnS in PANI (sample, S4) intensity of XRD peak due to PANI has been reduced significantly and XRD pattern of ZnS starts dominating. It is interesting to note that on further increasing the concentration of ZnS to 40% (sample, S3) we find peaks due to ZnS only, even though the composite contains 60% of PANI. All other samples (samples, S1 and S2) with higher concentration of ZnS also show XRD patterns due to ZnS only. XRD study thus suggests that during the mechanical grinding of PANI with ZnS, PANI undergoes interfacial interactions with ZnS crystallites and loses its own morphology by its coating over ZnS crystallites.

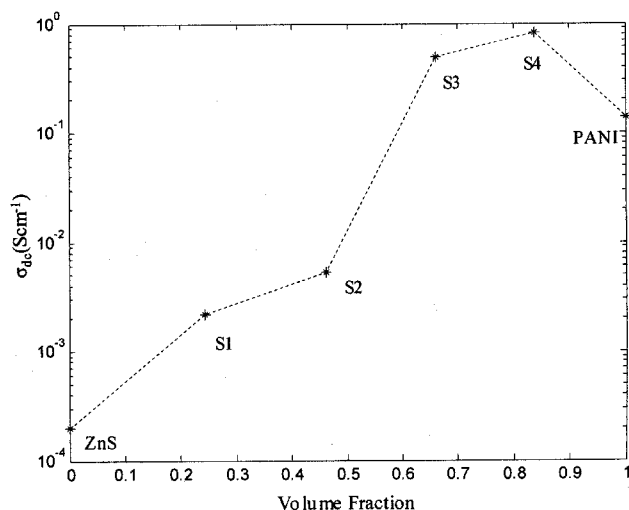
3.4 Room temperature d.c. conductivity studies

The plot of room temperature d.c. conductivity vs volume fraction of PANI–ZnS composites are given in figure 4. It is quite interesting to note that although the conductivity of ZnS is almost three orders of magnitude lower than that of pure PANI, however, the conductivity values of its composites with PANI above volume fraction, 0.65, are significantly higher than PANI itself (table 1).

In general, percolation theory is used to describe the conductivity behaviour of conducting metal particle filled insulating polymeric composites, wherein, sudden increase in the conductivity of composite is observed above certain

Table 1. Compositions and d.c. conductivity of PANI–ZnS composites.

Sl no.	Description of sample	Weight percentage of constituents	Volume fraction of PANI	DC conductivity (S/cm)	VRH exponent (γ)	T_0 (°K)
1.	Pure ZnS	100% ZnS	0.00	0.0002	–	–
2.	Composite, S1	20% PANI + 80% ZnS	0.25	0.0022	0.40	4929.5
3.	Composite, S2	40% PANI + 60% ZnS	0.45	0.0053	0.41	4512.5
4.	Composite, S3	60% PANI + 40% ZnS	0.65	0.4954	0.47	2562.0
5.	Composite, S4	80% PANI + 20% ZnS	0.85	0.8088	0.50	1600.6
6.	Pure PANI	100% PANI	1.00	0.1367	0.52	2712.0

**Figure 4.** Plot of d.c. conductivity vs volume fraction in PANI–ZnS composites.

concentration of conducting fillers which is called ‘percolation threshold’. On further increasing the concentration of conducting filler above percolation threshold, the conductivity values gradually increase and attain the value of filler at volume fraction of unity. The classical percolation theory has successfully explained the conductivity behaviour of conducting polymer filled insulating polymeric composites having higher values of percolation threshold, >0.16 . However, it alone could not explain the conductivity behaviour at very low values of percolation threshold observed in a number of conducting polymers based systems (Fizazi *et al* 1990; Suzuki *et al* 1990; Blaszkiewicz *et al* 1992). This is due to the fact that the percolation theory is purely statistical in nature and does not account for the interfacial interactions of conducting polymers with their matrices. Wessling (1998) carried out extensive studies on the conductivity behaviour of dispersions of different types of conducting polymers in a variety of polymeric matrices and attributed the lower values of percolation threshold of these composites to the interfacial interactions between the filler and host matrix. From their studies, they proposed a non-equilibrium theory based on the thermodynamics of interfacial interactions to explain the conductivity behaviour of heterogeneous conducting polymer

composites. In all such studies the conductivity is maximum for conducting filler. However, in the present studies, the conductivity values of the composites have been found to be greater than pure PANI and the same cannot be explained on the basis of non-equilibrium theory.

The mechanisms of electrical conductivity in conducting polymers are well studied. It has been reported in the literature that the d.c. conductivity of conducting polymers depend on their morphology and certain other factors such as type of monomer, doping level, degree of crystallinity etc (MacDiarmid and Epstein 1994). It has been reported that the large increase in conductivity originates from the fact that doped (protonated) polyaniline is a polyelectrolyte, i.e. a macromolecule bearing a large number of ionizable groups. MacDiarmid and Epstein (1995) reported that its molecular conformation upon reaction with the vapour of appropriate substance changes the compact coil structure to an expanded coil like structure. The attainment of expanded molecular conformation acts to reduce π -conjugation defects in the polymer backbone and the opening up of coil tends to promote linear conformation necessary for crystallization, thus increasing the crystallinity of the polymer with enhancement of the intermolecular component of the bulk conductivity.

In the present composite systems we feel that the mechanical grinding of PANI with ZnS causes strong interfacial interactions between PANI and ZnS crystallites, as suggested by the FTIR and XRD studies, thereby changing the molecular conformation of PANI from compact coil structure to an expanded coil like structure. As a consequence there may be an enhancement in the conductivity of composites of PANI and ZnS. Further, at higher volume fractions of PANI, it fully overcoats ZnS particles and the conductivity of composites attains values greater than pure PANI, as has been observed in the optical microscopic photographs of composites, S3 and S4.

3.5 Temperature dependent d.c. conductivity studies

The plot of d.c. conductivity, $\sigma_{d.c.}$ of conducting PANI and its composites with temperature is shown in figure 5. From this figure we observe the exponential increase in $\sigma_{d.c.}$ with temperature from 20–300 K in pure PANI and its composites, thereby indicating the behaviour of disordered

semiconductor. Further, composites, S3 and S4, maintain their higher $\sigma_{d.c.}$ values than pure PANI over the entire temperature range 20–300 K.

The analysis of temperature dependent conductivity data suggests that the charge transport mechanism in PANI as well as all its composites can be explained by the variable range hopping (VRH) model where dependence of d.c. conductivity is governed by the following relation (Dutta *et al* 2001),

$$\sigma_{d.c.}(T) = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^\gamma,$$

where T_0 is the characteristic temperature evaluated from linear slope of $\ln(\sigma_{d.c.})$ vs $T^{-\gamma}$ as shown in figure 6 (table 1), σ_0 the d.c. conductivity at absolute zero temperature, and γ the VRH exponent which depends upon the dimension

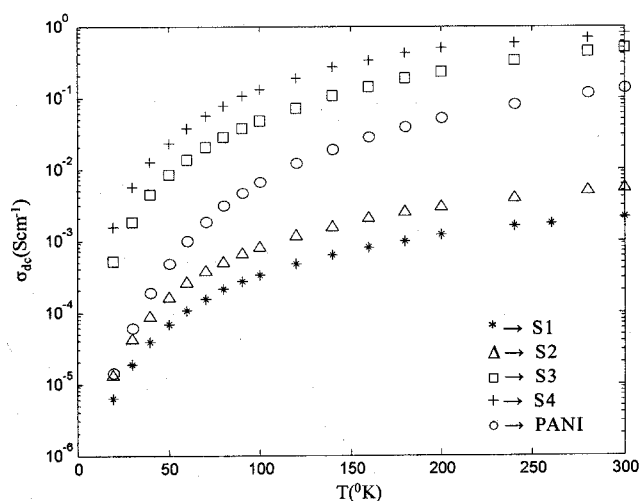


Figure 5. Plot of d.c. conductivity vs temperature of PANI-ZnS composites.

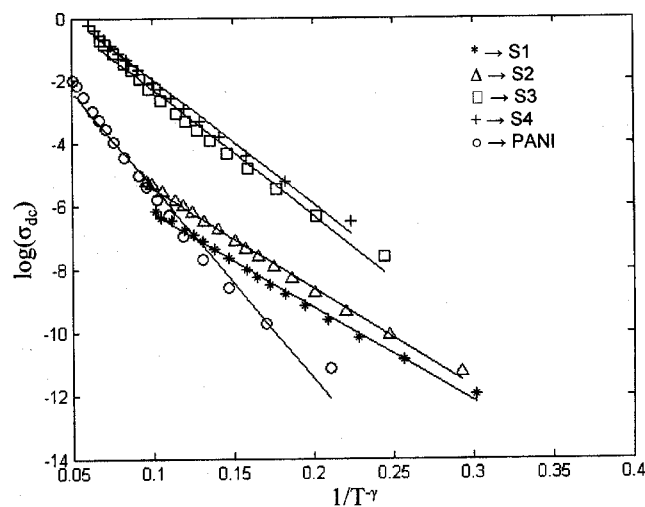


Figure 6. Plot of $\log(\sigma_{d.c.})$ vs $T^{-\gamma}$ of PANI-ZnS composites.

of the system. The value of VRH exponent, γ , has been determined from the reduced activation energy (W),

$$W = \frac{d \ln \sigma}{d \ln T},$$

and it has been found to lie between 0.40 and 0.51 (table 1), which indicates the presence of quasi one-dimensional hopping structure in all the composites similar to that of pure PANI (Epstein *et al* 1994). Hence, these studies show that although the composites, S3 and S4, having higher values of $\sigma_{d.c.}$ as compared to pure PANI but formation of 3-dimensional conducting network is not likely and thus such enhancement of $\sigma_{d.c.}$ values can be attributed to the uncoiling of polymeric chains due to strong interfacial interactions between ZnS crystallites and PANI caused by mechanical grinding.

3.6 Microwave characterization

The plots of complex permittivity and loss tangent vs volume fraction of PANI-ZnS composites at 10.3 GHz are given in figure 7. From the figure it is observed that these composites show high values of both real (ϵ_r') and imaginary (ϵ_r'') parts of dielectric constant. Moreover, the values of loss tangent ($\tan \delta$) are quite high, suggesting that they are highly lossy materials. Further, it is observed that the values of dielectric constant follow the trend almost similar to the one in the case of d.c. conductivity wherein the values of dielectric constant of composites, S3 and S4, are higher as compared to pure PANI, which can be attributed to the higher values of electrical conductivity of these composites.

In general, in case of heterogeneous mixtures, the behaviour of dielectric properties is governed by Maxwell-

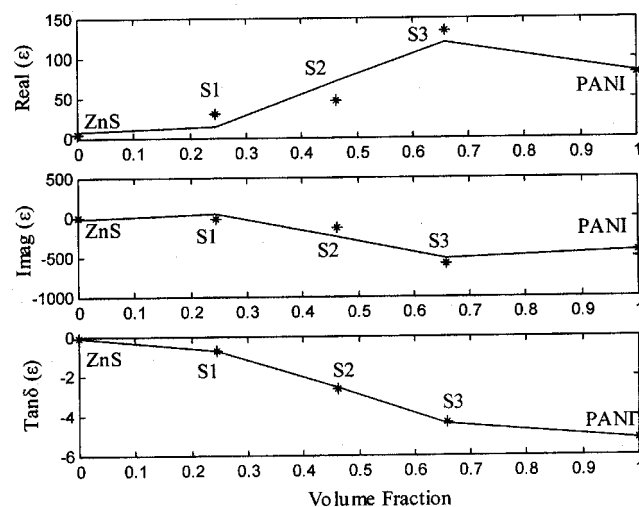


Figure 7. Plots of complex permittivity and $\tan \delta$ vs volume fraction of PANI-ZnS composites at 10.3 GHz.

Wagner–Sillier model (Hedying 1977). As per this model, it is predicted that the values of dielectric constant increase with the increase in the concentration as well as conductivity of the inclusion. Although, this model takes into consideration the interfacial polarization between the inclusion and the host particles, but the results of present study could not be explained by it. Also, effective medium theory (EMT) (Merrill *et al* 1999) has also been mostly used to explain the effective dielectric properties of composites, but the results of our studies could not be explained by the same, as our system has been rendered complex due to interactions between PANI and ZnS resulting into modification in morphology of PANI.

4. Conclusions

From the above studies, we have observed that the values of d.c. conductivity and dielectric constant of PANI have unusually enhanced by simply mechanically grinding it with crystalline ZnS powder. The FTIR studies suggest the occurrence of chemical interaction between PANI and ZnS crystallites, while the optical microscopic studies indicate complete overcoating of PANI on ZnS crystallites at volume fraction >0.65. The XRD study suggests modification in the structure of PANI due to its interfacial interactions with ZnS crystallites. The enhancement in the conductivity has been attributed to the increase in the degree of crystallinity of PANI due to uncoiling/stretching of polymeric chain caused due to the strong interfacial interactions with ZnS crystallites. The temperature dependent conductivity studies suggest the quasi one-dimensional VRH conduction in pure PANI and its composites. These composites have been found to show high values of both real and imaginary parts of dielectric constant and loss tangent, thus having good microwave lossy behaviour.

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