

Studies of AC Conductivity and Dielectric Relaxation Behavior of CdO-Doped Nanometric Polyaniline

Aashis S. Roy, Koppalkar R. Anilkumar, M. V. N. Ambika Prasad

Department of Materials Science, Gulbarga University, Gulbarga, Karnataka, India

Received 5 May 2010; accepted 12 April 2011

DOI 10.1002/app.34696

Published online 22 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The Cadmium oxide doped in nanocrystalline polyaniline (CdO/PANI) composite were prepared with various weight percentages by *in situ* polymerization method using aniline, ammonium per sulfate, and CdO as starting materials. The frequency dependent conductivity and dielectric behavior of PANI/CdO composites have been studied. The formation of nano PANI and PANI/CdO composites with regards to the structural and microstructural properties of the materials were investigated by XRD, FTIR, and SEM techniques. The variation of σ_{ac} with frequency obeys Jonscher power law except a small deviation in the low frequency region and is due to dipole polarization effect. The σ_{ac} increases with increase in CdO concen-

tration. Studies of dielectric properties at lower frequencies show that the relaxation behavior is superimposed by dipole polarization effect. The appearance of peak for each concentration in the loss tangent suggests the presence of relaxing dipoles in the PANI/CdO composite. On addition of CdO, the peak shifts toward higher frequency side indicating the speed up of the relaxation time. Analysis of frequency dependent dielectric suggests that the electronic and polymer segmental motions are strongly coupled. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1928–1934, 2012

Key words: nanocomposites; polyaniline; dielectric constant; AC conductivity

INTRODUCTION

Building the new supramolecular architectures with the desired structures and properties with greater ease of applications has been of great interest in recent years.¹ Polymers have traditionally been considered as a good electrical insulators and a variety of their applications have relied on their insulating property.² The discovery of doping has led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 S cm^{-1} . The presence of an extended π conjugation in polymers, however, confers the required mobility to charges that are created on the polymer backbone (by the process of doping) and make them electrically conducting.³

The conducting polymer/inorganic nanoparticles composites having unique physical properties that have attracted more and more attention. Because they combine the merits of conducting polymers and inorganic nanoparticles, they have wide potential applications in diverse areas such as chemistry,

physics, electronic, optics, materials, and biomedical science.^{4–9} Among all polymers, polyaniline (PANI) is an air-stable conducting polymer and has attracted considerable attention because of its moderate electrical conductivity. PANI is unique as its electronic properties can be controlled both by varying the oxidation state of the main chain and by protonation.¹⁰ Recent investigations have shown that PANI can be an excellent matrix for forming polymer-nanomaterials composites.^{11–14} Enhancement in CdS photoluminescence has been observed by Xi et al. on incorporation of CdS nanowires in nonconducting PANI matrix. A mechanism wherein photo-generated charge carrier transfer from PANI to CdS has been suggested.¹⁵ Similar effects have been observed in PANI-ZnO nanocomposites.¹⁶

Rashid and Suhail reported the variation of the photoluminescence intensity of the CdO and ZrO₂ nanocrystals with respect to the molar fraction of PANI in the composite.¹⁷

Salunkhe et al. reported that cadmium oxide itself is active and responds to LPG gas, the principle on which it relies is the change in conductivity on exposure to a target gas and its gas-sensing performance can be enhanced by doping of impurities and/or using a small amount of a noble metal catalyst, such as palladium (Pd) and platinum (Pt), which not only promotes gas sensitivity but also improves the response time.¹⁸

To the best of our knowledge, this is the first attempt by the authors reporting the synthesis, characterization,

Correspondence to: M. V. N. A. Prasad (prasad1_amb@rediffmail.com).

Contract grant sponsor: Department of Science and Technology (DST), New Delhi, Govt. of India; contract grant number: SR/S2/CMP-20/2007.

ac conductivity, and dielectric relaxation behavior of nanostructured polyaniline and polyaniline/Cadmium oxide (PANI/CdO) composites.

EXPERIMENTAL

Materials and methods

All chemicals used were analytical grade (AR). The monomer aniline was doubly distilled prior to use. Ammonium persulphate ((NH₄)₂S₂O₈), hydrochloric acid (HCl), and cadmium oxide (CdO), were procured and were used as received. Synthesis of polyaniline/cadmium oxide (CdO) composites has been carried out by *in situ* polymerization. Aniline (0.1 mol) was dissolved in 1M HCl to form aniline hydrochloride. Cadmium oxide is added in the weight percent to the above solution with vigorous stirring to keep the cadmium oxide suspended in the solution. To this above reaction mixture, 0.1M of ammonium persulphate [(NH₄)₂S₂O₈] which acts as the oxidant was added drop wise slowly with continuous stirring for 4–6 h at 0–5°C to polymerize. The precipitate was filtered and washed with deionized water. Finally the resultant precipitate was dried in an oven for 24 h to achieve a constant weight. In this way five different polyaniline/CdO composites with different wt % of CdO (10, 20, 30, 40, and 50) in polyaniline have been synthesized.^{19,20} The pellets of 10-mm diameter are prepared with thickness varying up to 2 mm by applying pressure of 10 Tons in a UTM - 40 (40 Ton Universal testing machine). For temperature-dependent conductivity and sensor studies, the pellets are coated with silver paste on either side of the surfaces. The copper electrodes are placed on each of the surface to obtain better contacts.

The X-ray diffraction (XRD) pattern of the PANI/CdO composites was recorded at room temperature by employing an X-ray powder diffractometer (Rigaku Miniflex) with Cu K α radiation ($\alpha = 1.5405$ Å) in the 2θ (Bragg angles) range ($2^\circ = 2\theta \leq 10^\circ$) at a scan speed of $0.5^\circ \text{ min}^{-1}$. Optical micrographs of the films were made through a polarizing microscope (Nikon Eclipse E 400 POL) equipped with a digital camera.

The IR spectra of the samples are recorded on Perkin-Elmer (Model 783) IR spectrometer in KBr medium at room temperature. For recording IR spectra, powders are mixed with KBr in the ratio 1 : 25 by weight to ensure uniform dispersion in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of ~ 1 mm thickness. The percentage transmittances for the entire sample are measured from 300 to 4000 cm^{-1} . The SEM images of polyaniline cadmium oxide composites were recorded using Philips XL-30 (ESEM) scanning elec-

tron microscopy. The set up used for measuring ac conductivity is Hioki 3050 impedance analyzer, which is in turn interfaced to the computer.

Analysis of the dielectric properties of the PANI/CdO composites has been carried out using impedance spectroscopy on application of a small ac signal across the sample cell with blocking electrode (stainless steel). Complex impedance parameters (i.e., capacitance, dissipation factor, impedance, phase angles parameters) were measured with a computer-controlled impedance analyzer (HIOKI LCR Hi-Tester, Model: 3532, Japan). σ_{ac} has been evaluated from dielectric data in accordance with the relation:

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta, \quad (1)$$

where ϵ_0 permittivity of the free space, ϵ' real part of dielectric constant, and $\tan \delta$ is tangent loss. The real and imaginary part of permittivity was calculated from the relation

$$\epsilon^* = \epsilon' - j\epsilon'', \quad (2)$$

where $\epsilon' = -Z''/\omega C_0 (Z'^2 + Z''^2)$ and $\epsilon'' = -Z'/\omega C_0 (Z'^2 + Z''^2)$

RESULTS AND DISCUSSION

Figure 1(a–c) shows the X-ray diffraction pattern of nanostructured pure PANI, CdO, and polyaniline/CdO composite with 50 wt % of CdO in polyaniline. It is seen from figure that the monoclinic peaks of CdO indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of CdO, the prominent peaks corresponding to $2\theta = 44.61^\circ$, 50.12° , and 67.35° are due to, (111), (200), and (222) planes which indicates the presence of CdO in PANI. By comparing the XRD patterns of pure polyaniline with its composites, it is observed that there is homogenous distribution of CdO in polyaniline and also confirmed that CdO has retained its structure even though dispersed in PANI during polymerization reaction.

The FTIR spectra measurement was carried out to study the molecular bonding of the PANI and PANI/CdO composites (CdO 50 wt % in PANI). Figure 2(a,b) shows the FTIR spectra of the pure PANI and PANI/CdO composites. For the pure PANI [Fig. 2(a)], the characteristic peaks appear at 1564 cm^{-1} due to C=C stretching of quinoid rings, 1475 cm^{-1} due to stretching of the benzenoid ring, which conforms the formation of polyaniline.

In the FTIR spectrum of PANI/CdO composite [Fig. 2(b)], some other important peaks are observed such as 3431 and 2968 cm^{-1} due to N–H bending,

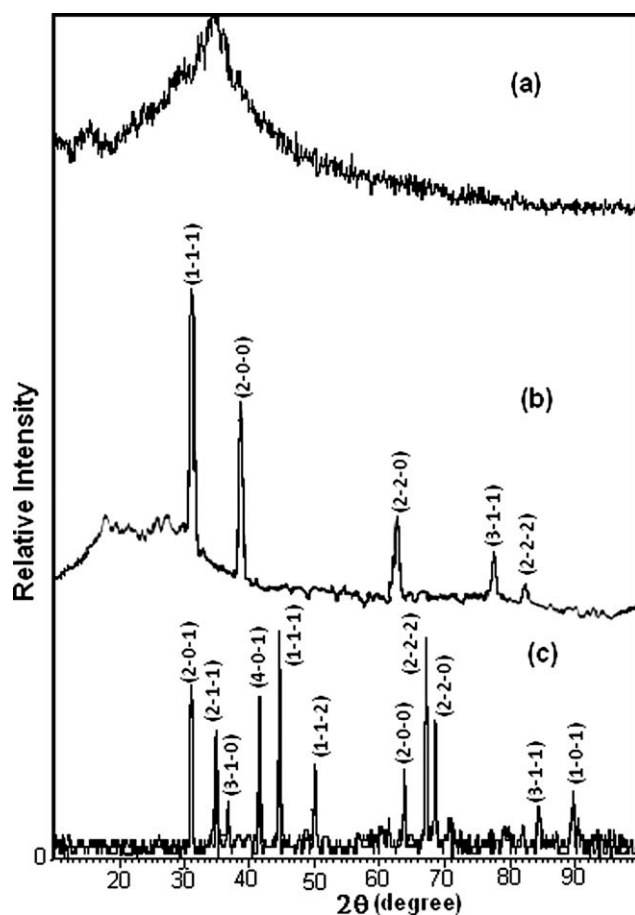


Figure 1 (a–c) show the X-ray diffraction pattern of pure PANI, CdO, and polyaniline/CdO composite with 50 wt % of CdO in polyaniline.

2922 and 2849 cm^{-1} due to C–H stretching, 1483 cm^{-1} due to CH_2 bending, and 626 and 711 cm^{-1} due to the metal oxygen vibration of CdO. By comparing the FTIR spectra of PANI and PANI/CdO composites, it is observed that in the composite the characteristic stretching frequency are shifted toward lower frequency side which may be due to the Van der Waal's interaction between CdO and PANI chains and thus FTIR spectra conforms the formation of PANI/CdO composites.

Figure 3(a–c) shows the scanning electron micrograph (SEM) of polyaniline, cadmium oxide, and PANI/CdO composites (CdO 50 wt % in PANI). The SEM performed on these samples indicate that the transformation of highly branched-like polyaniline of size 60–80 nm to granular-like structure were CdO particle is highly agglomerated with the PANI of size around 450 nm. The increase of CdO in PANI (10, 20, 30, 40, and 50 wt % of CdO in PANI), increases the granular size and decreases the porosity. The SEM image also reveals the presence of CdO in polyaniline which is homogeneously distributed throughout the polymer sample.

Transport properties

Figure 4(a) shows the variation of dielectric constant (ϵ') with frequency for different wt % of CdO in nanostructured PANI at room temperature. In all the cases, a strong frequency dispersion of permittivity is observed in the low frequency region followed by a near frequency-independent behavior above 10 kHz.

The decrease of ϵ' with increase in frequency may be attributed to the electrical relaxation processes and this behavior is conformed by eq. (2). At lower frequencies, there is significant change in dielectric constant that is noticeable and is attributed to dipolar contribution from the hopping of electrons between isolated polarons and bipolarons states. It is seen that with addition of CdO, the ϵ' value gradually decreases in lower frequency and remains constant in higher frequency region. The CdO addition may result in more localization of charge carriers along with polarons causing higher DC conductivity. This may be the reason for higher ϵ' and strong low frequency dispersion on addition of CdO in nanostructured PANI.^{21,22}

Figure 4(b) shows the variation of dielectric constant (ϵ') with various wt % of CdO in nanostructured PANI at room temperature. It is found that the value of (ϵ') approaches to 10^6 for 50 wt % at 10 KHz and further, it decreases for 10 wt % and PANI where as it remains constant for 30 and 40 wt % of CdO in PANI. The same behavior is observed even at 100 and 1000 KHz frequencies.

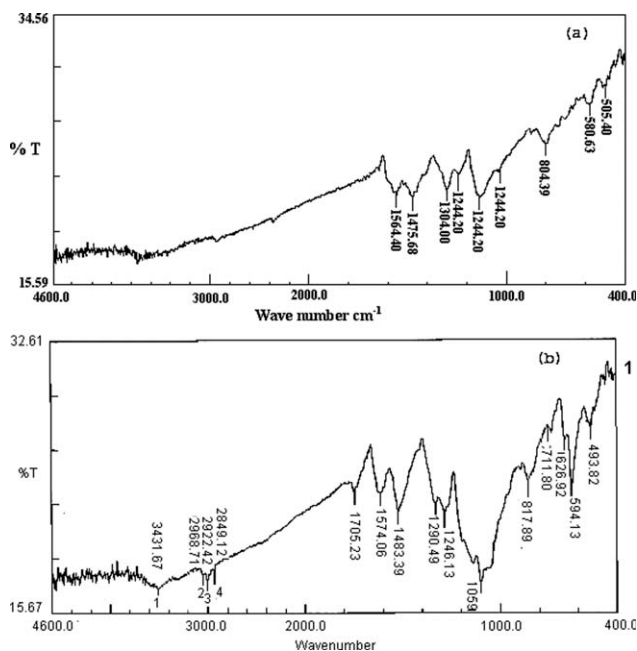


Figure 2 (a) shows the Fourier Transform Infra Red (FTIR) spectra of the pure PANI. (b) shows the Fourier Transform Infra Red spectra (FTIR) of the PANI/CdO composites.

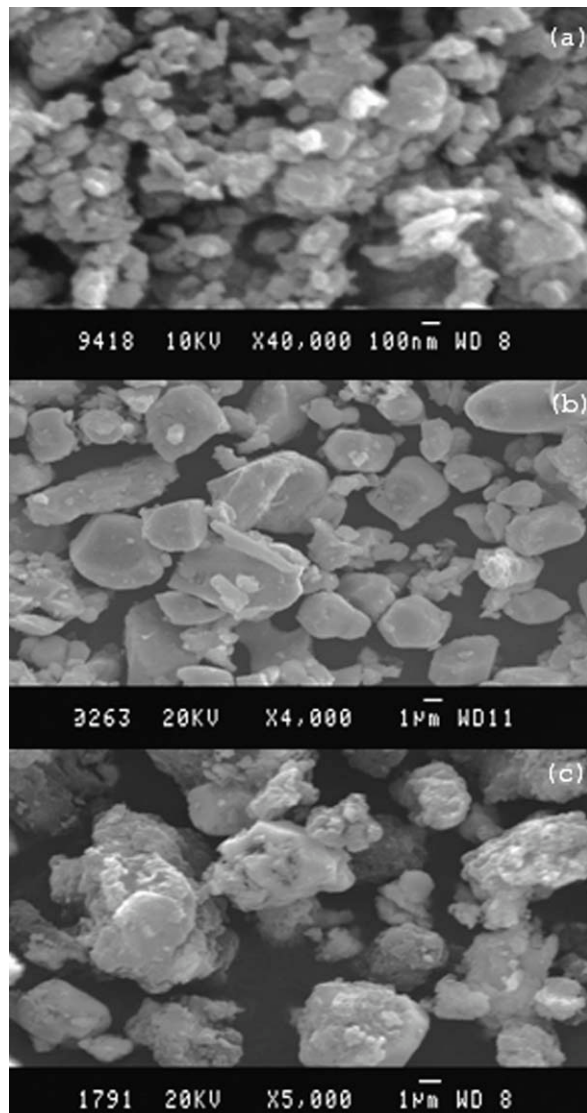


Figure 3 (a–c) shows the scanning electron micrograph (SEM) of polyaniline, cadmium oxide, and PANI/CdO composites.

Figure 5(a) shows the variation of imaginary part of dielectric constant (ϵ'') with frequency for different wt % of CdO in PANI at room temperature. At room temperature, ϵ'' decreases with increasing frequency. The higher value of imaginary part of dielectric (ϵ'') at low frequency is due to the free charge motion within the materials. Further addition of CdO in PANI, ϵ'' remains almost constant in the entire frequency region.²³

Figure 5(b) shows the variation of imaginary part of dielectric constant (ϵ'') as a function of wt % of CdO in PANI. It is observed that imaginary dielectric constant changes for PANI and remains constant on introduction of CdO in PANI matrix. This confirms the enhancement of mobility of charge carries in the composites is due to CdO in PANI.

It is generally believed that dielectric data is characterized by superposition of two processes: a conductivity contribution that produces an increase of both real part ϵ' and the imaginary part ϵ'' of the dielectric function on decreasing frequency and a relaxation process exhibiting a minimum in ϵ'' that shifts higher frequency side with increase in concentration of CdO. The measured imaginary dielectric constant (ϵ'') spectrum contains contribution from two sources: dipolar orientation and diffusion of charge carrier. When interfacial polarization occurs it can be written²⁴ as

$$\epsilon''_{\text{meas}}(\omega, T) = \epsilon''_{\text{pol}}(\omega, T) + \epsilon''_{\text{inter}}(\omega, T) + \epsilon''_{\text{dc}}(\omega, T), \quad (3)$$

with $\epsilon''_{\text{dc}}(\omega, T) = \epsilon''_{\text{dc}}(T)/(\epsilon_0''\omega^{1-k})$ where $k = 0 \leq k \leq 1$

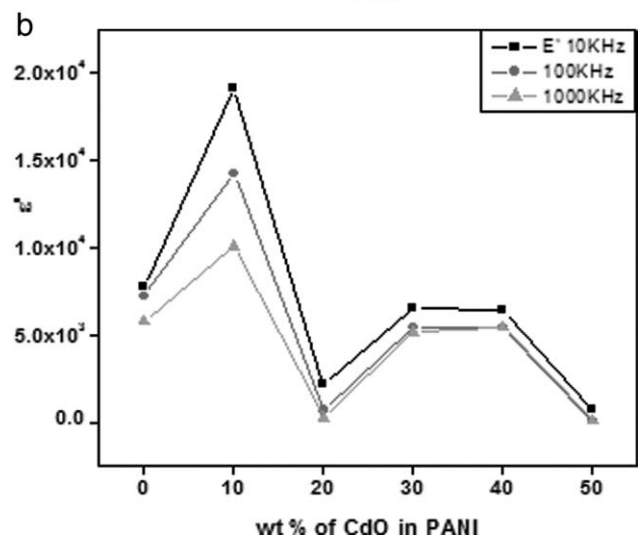
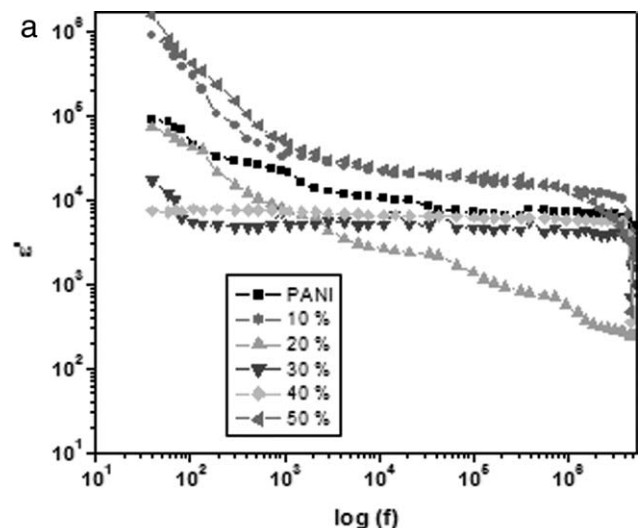


Figure 4 (a) shows the variation of dielectric constant (ϵ') with frequency for different wt % of CdO in PANI at room temperature. (b) shows the variation of dielectric constant (ϵ') with various wt % of CdO in PANI at room temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

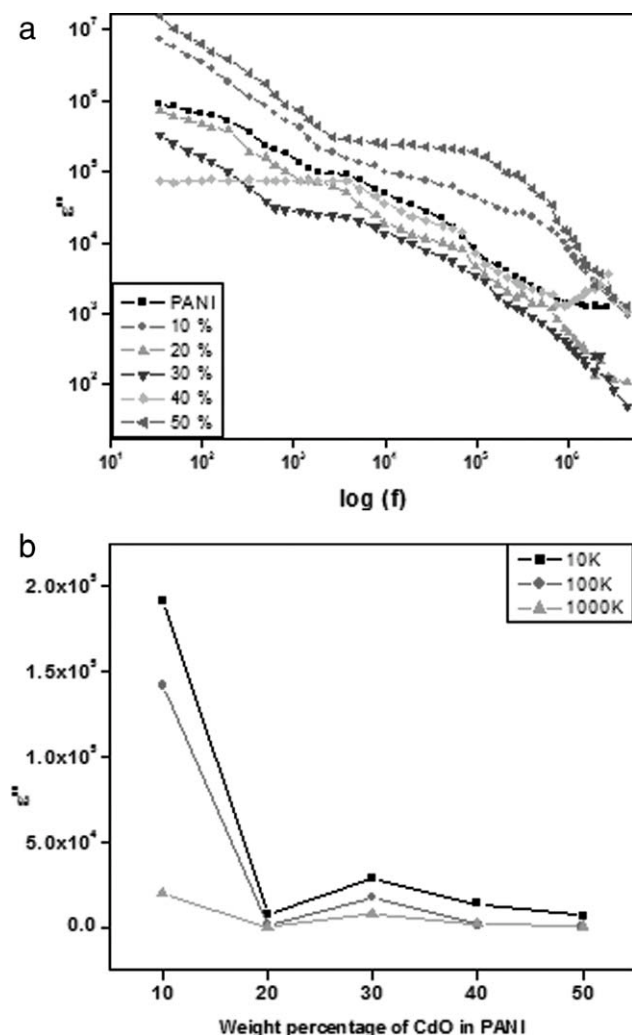


Figure 5 (a) shows the variation of imaginary part of dielectric constant (ϵ'') with frequency for different wt % of CdO in PANI at room temperature. (b) show the variation of imaginary part of dielectric constant (ϵ'') as a function of wt % of CdO in PANI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

When the loss is due to Ohmic electrical conduction where ϵ''_{dc} dominates and then addition of CdO resulted in overall decrease of ϵ' and ϵ'' due to both dipolar and free charge contributions. The overall result is enhancement of conductivity on addition of CdO in PANI matrix.

$$\epsilon''_{\text{meas}}(\omega, T) = \sigma_{dc}(\omega, T) / (\epsilon_0'' \omega^{1-k}) \quad (4)$$

Figure 6 shows the variation of tangent loss with frequency for different wt % of CdO in PANI at room temperatures. The loss spectra characterized by peak appearing at a characteristic frequency for both PANI and PANI/CdO composites suggest the presence of relaxing dipoles in PANI and nonrelaxing dipole in composites.

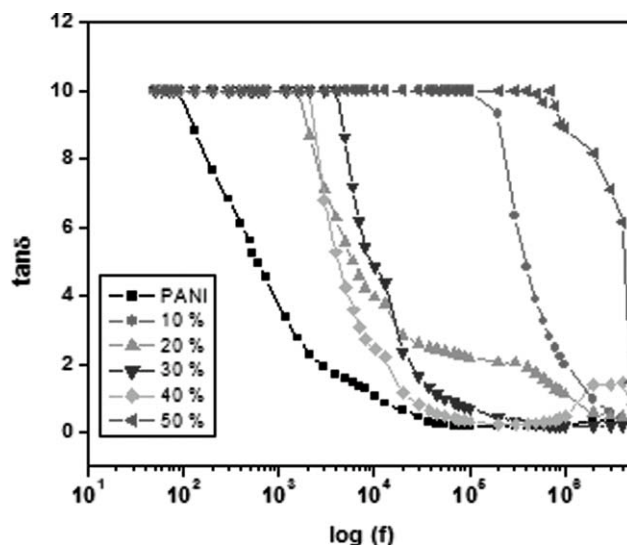


Figure 6 It shows the variation of tangent loss with frequency for different wt % of CdO in PANI at room temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The strength and frequency of relaxation depend on characteristic property of dipolar relaxation. The tangent loss remains constant for all the frequencies side on increase in CdO in PANI. On addition of CdO, it is believed that there is an increase in the crystallinity content in the materials.

Figure 7 shows the variation of σ_{ac} with frequency for different weight percentages of CdO in PANI at room temperature. The ac conductivity values decrease with decrease in frequency at very low frequency. These drops in σ_{ac} indicate dipole polarization where the rotation of dipoles between two

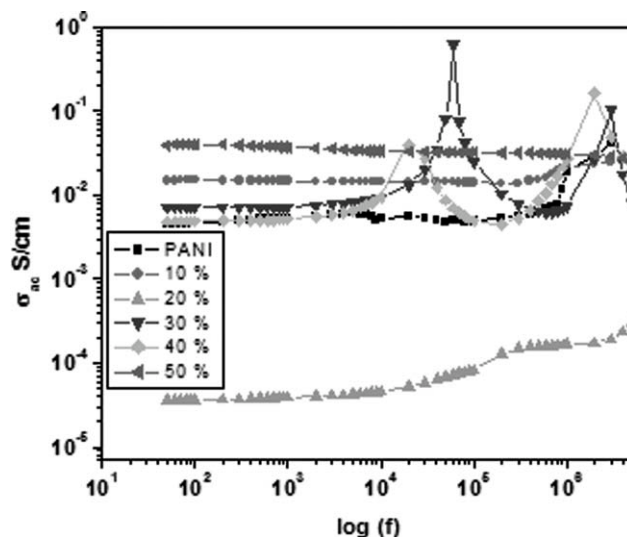


Figure 7 It shows the variation of σ_{ac} with frequency for different weight percentages of CdO in PANI at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

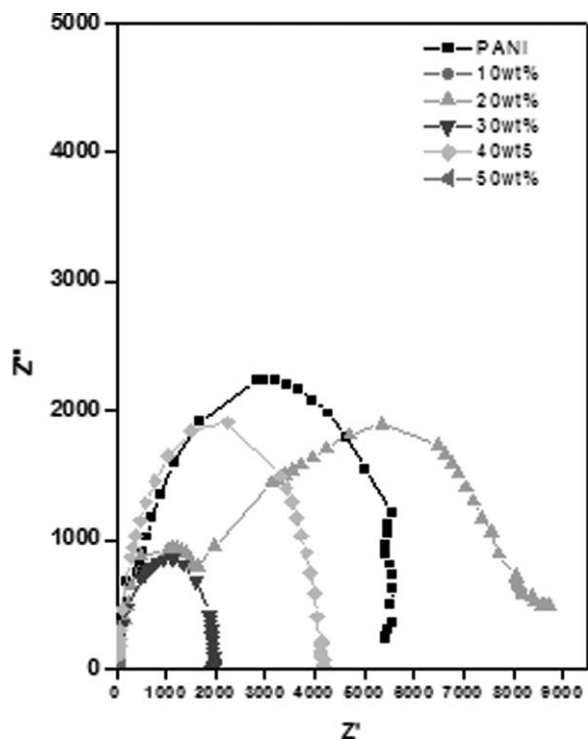


Figure 8 It shows the frequency dependence of the real and imaginary part of the impedance of pure polyaniline and polyaniline composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

equivalent equilibrium positions is involved. It is the spontaneous alignment of dipoles in one of the equilibrium positions that gives rise to the nonlinear polarization behavior of these composites. The data analysis σ_{ac} , $\epsilon'(\omega)$ for this composites shows that the charge transport does not occurs via the usual mechanism.

This behavior obeys the universal power law,²⁵ $\sigma(\omega) = \sigma_0 + A\omega^n$, (the solid line is the fit to the expression) where σ_0 is the dc conductivity (frequency independent plateau in the low frequency region), A is the pre-exponential factor, and n is the fractional exponent between 0 and 1. On crystallization the conduc-

tivity spectrum remains similar as that of the PANI except dispersion in the low frequency region, where the deviation from σ_{dc} (plateau region) is more prominent. The deviation from σ_{dc} (plateau region) value in the conductivity spectrum (in the low frequency region) is due to the electrode polarization effect. The values of σ_0 , A and n were obtained by fitting the $\sigma(\omega)$ to $\sigma(\omega) = \sigma_0 + A\omega^n$. The overall behavior of σ_{ac} follows the universal dynamic response,¹⁴ which has widely been observed in disordered materials like ionically conducting glasses,²⁶ conducting polymers, and also doped crystalline solids^{27,28} and is generally believed to be reflected in the mechanism of charge transport behavior of charge carriers.

Figure 8 shows the frequency dependence of the real part of the sample impedance, which is governed by the resistance of pure polyaniline and polyaniline composites. It is observed that the real part of the impedance is starting to decrease even from low frequencies and reaches an asymptotic value in the high frequency range and that the HCl doping is decreasing the impedance of the sample.

It is observed that resistance of the composites decreases as the doping level is increased. The increase in resistance suggests that the effect is eventually determined by the capacitance component of the equivalent electric circuit.²⁹ The simple equivalent circuit of impedance spectroscopy can be represented as shown in Figure 9(a,b) The projection on the real axis of the center of the circle in the representation imaginary impedance versus real impedance, defined by R_0 , has a smooth decrease as the doping level is increased were R_0 is radius of curvature.^{30,31}

CONCLUSIONS

The effect of CdO on dielectric and electrical properties of conducting polyaniline composite has been studied. At low frequency, the variation of real part of dielectric constant with frequency shows the presence of dipole polarization processes. The loss

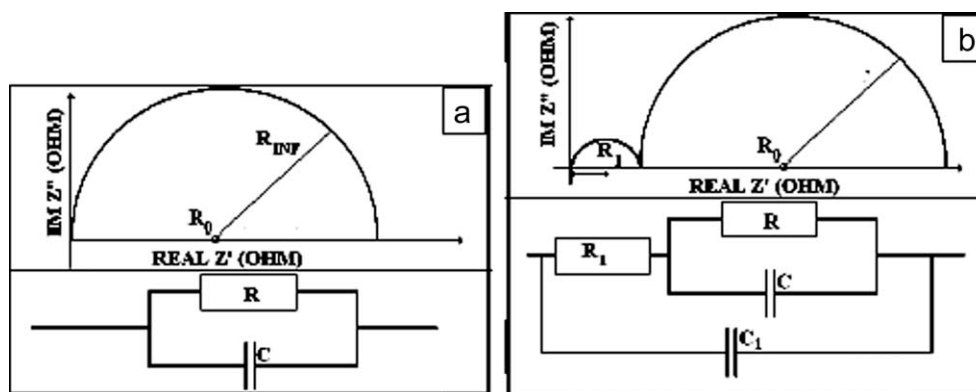


Figure 9 Simple equivalent circuits in impedance spectroscopy.

tangent peaks appearing at a characteristic frequency suggest the presence of relaxing dipoles in all the samples. The frequency dependence of ac conductivity follows the universal power law with a small deviation in the low frequency region due to the dipole polarization effect. The conductivity increases with increase in wt % of CdO in PANI which results in variation of the size of conducting islands and was confirmed by the SEM micrograph.

References

- Ianabe, T.; Annewurf, C. R.; Lyding, J. W.; Mogual, M. K.; Marks, T. J. *Mol Cryst Liq Cryst* 1983, 93, 355.
- Gowrikar, V. R.; Vishwnathan, N. V.; Jayadev, S. *Polymer Science*; Wiley Eastern: New Delhi, 1986.
- Diaz, A. F.; Hall, B. *J Rev Dev* 1983, 27, 342.
- Nazar, L. F.; Zang, Z.; Zinkweg, D. *J Am Chem Soc* 1992, 114, 6239.
- Cao, G.; Garcia, M. E.; Aleala, M.; Burgess, L. F.; Mallouk, T. E. *J Am Chem Soc* 1992, 114, 7574.
- Becreft, L. L.; Ober, C. K. *Chem Mater* 1999, 9, 1302.
- Somani, P. R.; Marimuthu, R.; Mulik, U. P.; Sainkar, S. R.; Amalnerkar, D. P. *Synth Met* 1999, 106, 45.
- Kim, B. H.; Jung, J. H.; Hong, S. H. *CurrAppl Phys* 2001, 1, 112.
- Schnitzler, D. C.; Meruvia, M. S.; Hummelgen, I. A.; Zarbin, A. J. G. *Chem Mater* 2003, 15, 4658.
- Bredas, J. L.; Silbey, R., Eds. *Conjugate Polymers*; Kluwer Academic: London, 1991.
- Godovsky, D. Y.; Varfolomeev, A. E.; Zaretsky, D. F.; Chandrakanthi, R. L. N.; Kundig, A.; Weder, C.; Caseri, W. *J Mater Chem* 2001, 11, 2465.
- Chandrakanthi, R. L. N.; Careem, M. A. *Thin Solid Films* 2002, 417, 51.
- Khanna, P. K.; Kulkarni, M. V.; Singh, N.; Lonkar, S. P.; Subbarao, V. V. V. S.; Viswanath, A. K. *Mater Chem Phys* 2006, 95, 24.
- Vivekchand, S. R. C.; Kam, K. C.; Gundiah, G.; Govindaraj, A.; Cheetham, A. K.; Rao, C. N. R. *J Mater Chem* 2005, 15, 4922.
- Xi, Y.; Zhou, J.; Guo, H.; Cai, C.; Lin, Z. *Chem Phys Lett* 2005, 412, 60.
- Zheng, Z. X.; Xi, Y. Y.; Dong, P.; Huang, H. G.; Zhou, J. Z.; Wu, L. L.; Lin, Z. H. *Phys Chem Commun* 2002, 5, 63.
- Rashid, M.; Suhail, S. *J Dispersion Sci Technol* 2009, 30, 613.
- Salunkhe, R. R.; Shinde, V. R.; Lokhande, C. D. *Sens Actuators B* 2008, 133, 296.
- Narshima Parvatikar, M. V. N.; Prasad, A. *J Appl Polym Sci* 2006, 100, 1403.
- Garnier, F.; Tourillon, G. *J Electroanal Chem* 1983, 52, 135.
- Mellander, B. E.; Albinsson, I. In *Solid State Ionics: New Developments*, Proceeding of 5th Asian Conference; Chowdari, B. V. R., Dissanayake, M. A. K. L., Careem, M. A., Eds.; World Scientific Publishing Co Pte Ltd: Kandy, Sri Lanka, 1996; p83.
- Baskran, R.; Selvasekarapandian, S.; Hirankumar, G.; Bhuvaneshwari, M. S. *J Power Source* 2004, 134, 235.
- Lestreiz, B.; Maazouz, A.; Gerard, J. F.; Sautereau, H.; Boiteux, G.; Seytre, G.; Kranbuehl, D. E. *Polymer* 1998, 39, 6733.
- Jonscher, A. K. *Dielectric Relaxation in Solids*; Chelsea Dielectric Press: London, 1983; Vol.131, p 390.
- Elliott, S. R. *Solid State Ionics* 1988, 27, 131.
- Leon, C.; Lucia, M. L.; Santamaria, J. *Phys Rev B* 1997, 55, 882.
- Leon, C.; Lucia, M. L.; Santamaria, J.; Parsi, M. A.; Sanz, J.; Varez, A. *Phys Rev B* 1996, 54, 184.
- Dyre, J. C. *J Appl Phys* 1988, 64, 2456.
- Doblhofere, K.; Rajeshwar, K. In *Handbook of Conducting Polymers*, 2nd ed.; Elsenbaumer, R., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1988; p531 (Revised and Expanded T. A. Skotheim).
- Bisquert, J.; Garcia-Belmonte, G.; Bueno, P.; Longo, E.; Bulhoes, L. O. S. *J Electroanalytical Chem* 1998, 452, 229.
- Mulder, W. H.; Sluyters, J. H. *Electrochem Acta* 1988, 33, 30.