

Research Article

Studies on Nanocomposites of Polyaniline and Zinc Oxide Nanoparticles with Supporting Matrix of Polycarbonate

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Nanocomposites of polyaniline and zinc oxide nanoparticles using polycarbonate as supporting matrix were prepared by direct mixing process. These nanocomposites were studied for their DC electrical conductivity using four-in-line probe technique. Stability of DC electrical conductivity in terms of electrical conductivity retention was also studied using two slightly different techniques. The nanocomposites were also characterized using FTIR, SEM, TEM, and XRD. It was found that the electrical conductivity of the nanocomposites first increased with the increase in concentration of ZnO nanoparticles content, but then decreased on further increase in its content. Stability studies showed that the loss in electrical conductivity decreased with increase of ZnO content in nanocomposites. TEM and XRD results showed that nanoparticles are uniformly distributed in polymer matrix and also suggest that the direct solution mixing method may be adopted as an easy and efficient route for the preparation of nanocomposites.

1. Introduction

Polymer-inorganic composites were first prepared by Blumstein in 1960s by polymerizing methyl methacrylate in presence of clay and found unusual properties in the composites he prepared. In early 1990s, polymerization of caprolactam in presence of montmorillonite clay by Toyota researchers improved several properties. This report encouraged the research in the field of polymer nanocomposites as reported by Zhang et al. [1]. There are three main approaches to prepare polymer-inorganic nanocomposites which include direct mixing of two or more components in a common solvent, *in situ* polymerization of monomer units in presence of inorganic nanoparticles and melt mixing of polymer with inorganic nanoparticles, in a mixer as suggested by Wu et al. [2]. Lei and Su [3] report about many studies on conducting polymer nanocomposites in view to find their applications in advanced techniques.

Among the conducting polymers, polyaniline (PANI) is one of the most studied intrinsically conducting polymers. PANI obtained high value in scientific community owing

to its easy preparation, better environmental stability, tuneable electrical conductivity, easy acid/base doping/dedoping behavior, and so forth. The preparation of nanocomposites of PANI with inorganic nanoparticles is thought to be a potential route to improve the performance of PANI aiming to obtain the materials with synergetic or complementary behaviour between PANI and inorganic nanoparticles. Among the inorganic nanoparticles, zinc oxide (ZnO) has received great attention because of its unique catalytic, electrical, electronic, and optical properties, as well as their low cost and extensive applications in diverse areas as discussed by He [4]. We believe that incorporation of ZnO nanoparticles in PANI may result in new material with useful properties.

2. Experimental

2.1. Materials. The materials used include acetone, ammonia, aniline, HCl, potassium persulphate, N-methyl-2-pyrrolidone, and zinc oxide nanoparticles (avg. particles

size 50 nm) that were purchased by the store keeper of the department and provided for the research.

2.2. Preparation of Polyaniline Nanoparticles. Polyaniline (PANI) nanoparticles were obtained by our patented route which simply involves oxidative polymerization of aniline in aqueous acidic solution with little modification (Ansari and Mohammad, [5]). In the typical procedure, the oxidative polymerization of aniline in aqueous HCl was carried out in presence of potassium persulphate ($K_2S_2O_8$) as oxidant in aqueous HCl. The optimum ratio of aniline, oxidant (2 : 1), was kept constant during the reaction. PANI (emeraldine salt) obtained was filtered and washed with double distilled water till filtrate was neutral to pH paper followed by its dedoping using aqueous ammonia solution. It was again washed with double distilled water to get emeraldine base form of PANI which, after drying at 60°C in air oven for 2 days, was kept in dessicator for further studies.

2.3. Preparation of Nanocomposites. Firstly, zinc oxide nanoparticles (ZnO) were dispersed in N-methyl-2-pyrrolidone (NMP) in round bottom flasks for 12 h with continuous stirring at room temperature. In other flasks, polycarbonate (PC) and polyaniline (PANI) nanoparticles base form (EB) were dissolved in NMP with continuous stirring. Dispersion of ZnO nanoparticles were then added to PANI:PC solution at a rate of 1 mL/min. The films of the nanocomposites were obtained by solvent evaporation method at 100°C in an air oven.

Thus, prepared films were cut into small pieces of rectangular shape and subjected to a pressure of 10 tons using electrically operated hydraulic press machine at 150°C to get smooth films. Finally, we prepared films of pure PANI and nanocomposites containing different compositions of PANI, PC, and ZnO (Table 1). These films were then treated with 1M HCl for 24 hrs, washed with double distilled water repeatedly to remove traces of acid, dried at 60°C for 12 h, and were used for electrical studies as per our previous reports [5].

3. Characterization

The pure PANI and nanocomposites of different compositions of PANI, PC, and ZnO nanoparticles were characterized by FTIR, electron microscopy (SEM & TEM), DC electrical conductivity, and XRD techniques.

4. Results and Discussion

4.1. FTIR Studies. FTIR spectroscopy is a very useful and convenient technique to detect the interaction developed between two or more components of a composite material. FTIR spectra of selected samples are shown in Figure 1. The broad peak ranging between 440 cm^{-1} and 550 cm^{-1} (Figure 1(a)) can be assigned to ZnO group [5]. FTIR spectrum of prepared PANI (EB) form is presented in Figure 1(b). The band corresponding to out-of-plane bending vibration of C–H bond of *p*-disubstituted benzene rings appears at

824 cm^{-1} . The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C–N bond appear at 1150 cm^{-1} and 1307 cm^{-1} , respectively. Band at 1582 cm^{-1} and 1496 cm^{-1} are assigned to C=C stretching of quinoid and benzenoid rings, respectively. FTIR spectrum of polycarbonate is described in Figure 1(c). The peaks at 832, 1018, 1082, 1165, 1236, 1367, 1506, 1775, 2874, and 2973 cm^{-1} may be assigned to *p* out-of-plane aromatic CH wagging, *p* in-plane aromatic CH bending, C–C stretching, carbonate C–O stretching, carbonate aryl-O-aryl C–O stretching, CH_3 symmetric deformation, *p*-aromatic ring semicircle stretching, carbonate C=O stretching, CH_3 symmetric stretching and CH_3 asymmetric stretching, respectively, as supported by Madkaur [6]. In case of nanocomposite PANI:PC:Z5 (Figure 1(d)) peaks obtained for individual components have been shifted slightly from their original position. For example, the peaks of pure PANI, shifted to lower wave number in nanocomposites.

4.2. DC Electrical Conductivity Study. The DC electrical conductivity of HCl doped PANI and composite films were measured with increasing temperature (40°C – 150°C) by using four-in-line probe DC electrical conductivity-measuring instrument (Scientific Equipment, Roorkee, India). DC electrical conductivity (σ) was calculated using the following equations:

$$\rho = \frac{\rho^o}{[G_7(W/S)]},$$

$$G_7\left(\frac{W}{S}\right) = \left(\frac{2S}{W}\right) \ln(2),$$

$$\rho^o = \left(\frac{V}{I}\right) (2\pi S),$$

$$\sigma = \frac{1}{\rho},$$
(1)

where $G_7(W/S)$ is a correction divisor which is a function of thickness of the sample as well as probe spacing while I , V , W , and S are current (A), voltage (V), thickness of the film (cm), and probe spacing (cm), respectively.

The electrical conductivity behaviour of the doped PANI and nanocomposites are presented in Figure 2. The addition of zinc oxide nanoparticles into polyaniline results into the decrease in electrical conductivity of nanocomposites. The decrease in electrical conductivity at content of inorganic fillers is also supported in case of TiO_2 and Fe_2O_3 as discussed by Ansari [7]. The decrease in the electrical conductivity of doped polyaniline (as-prepared emeraldine salt, $\sigma(40^\circ\text{C}) = 1.3 \times 10^{-1}\text{ Scm}^{-1}$) on mixing with supporting polymer matrix (due to insulating component for imparting mechanical strength to the nanocomposites) is normal and expected behaviour from the nanocomposites. The behaviour on incorporation of different zinc oxide nanoparticles contents into the composite formulations may be explained in the light of following lines.

The decrease in electrical conductivity on incorporation of zinc oxide nanoparticles into the polyaniline (emeraldine salt) may be attributed to the presence of zinc oxide

TABLE 1: Preparation of PANI:PC:ZnO nanocomposites.

Sample ID	Amount of PANI in 50 mL of NMP (mg)	Amount of ZnO in 50 mL of NMP (mg)	Amount of PC in 50 mL of NMP (mg)
PANI:PC:Z0	950	0	50
PANI:PC:Z1	940	10	50
PANI:PC:Z2	930	20	50
PANI:PC:Z3	920	30	50
PANI:PC:Z4	910	40	50
PANI:PC:Z5	900	50	50

PANI: emeraldine base, ZnO: zinc oxide nanoparticles (~50 nm), PC: polycarbonate, and NMP: N-methyl-2-pyrrolidone.

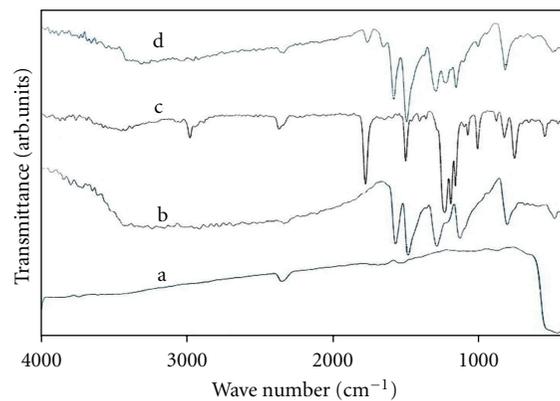
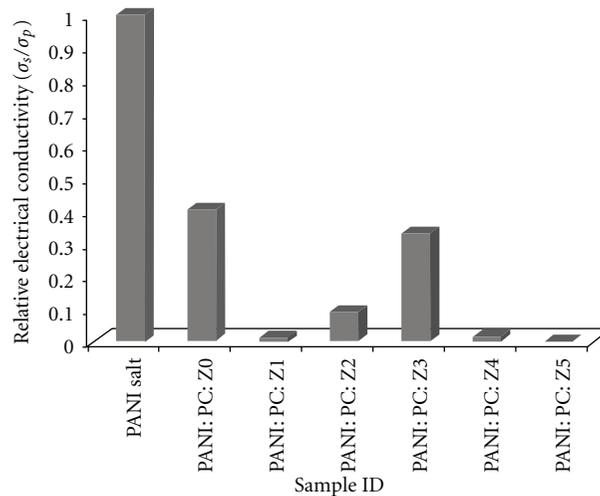


FIGURE 1: FTIR spectra of (a) zinc oxide nanoparticles purchased from MKnano (Canada), (b) emeraldine base nanoparticles, (c) polycarbonate, and (d) PANI:PC:Z5 nanocomposite.



σ_s = Sample

σ_p = Polyaniline salt

σ = Initial electrical conductivity (Scm^{-1}) of polyaniline salt and nanocomposites containing polyaniline, polycarbonate and zinc oxide nanoparticles at 40°C .

FIGURE 2: Schematic diagram of relative electrical conductivity of nanocomposite films containing polyaniline, polycarbonate, and zinc oxide nanoparticles with respect to HCl (1 M) doped polyaniline film.

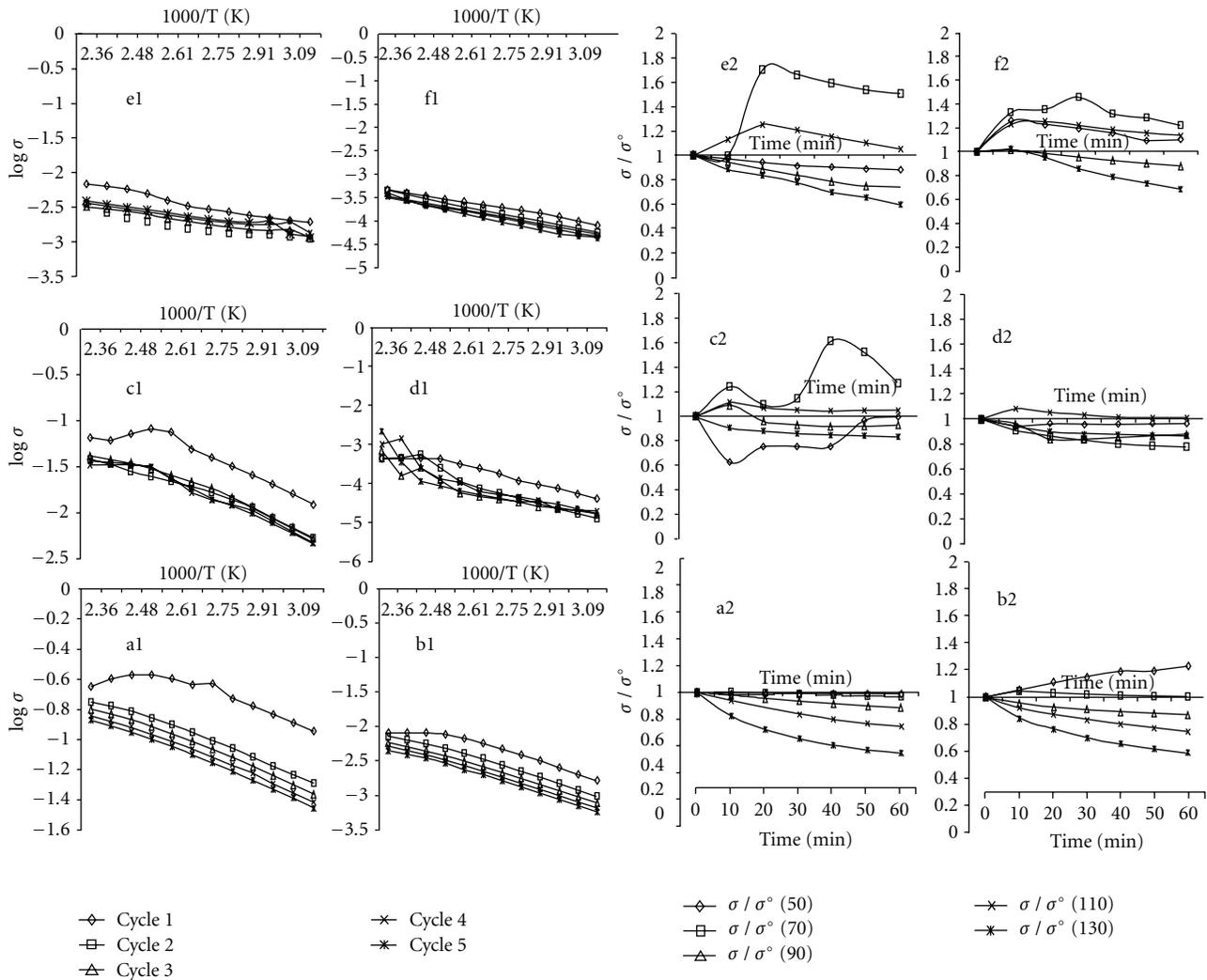


FIGURE 3: Electrical conductivity retention under cyclic/isothermal conditions of (a1/a2) PANI:PC:ZnO, (b1/b2) PANI:PC:ZnO, (c1/c2) PANI:PC:ZnO, (d1/d2) PANI:PC:ZnO, (e1/e2) PANI:PC:ZnO, and (f1/f2) PANI:PC:ZnO under cyclic ageing conditions.

nanoparticles (of relatively lower conductivity) which may also be expected to act as dedoping agent ([7] Ansari 2010) as may be represented by Scheme 1.

However, the increase in electrical conductivity on further increase in the nanoparticles content may be attributed to the combination of PANI and Zn^{2+} present in the matrix as a result of Scheme 1 giving a hole-type conduction as represented in Scheme 2.

At higher zinc oxide contents (in case of 40 mg and 50 mg) in the nanocomposites, again the decrease in electrical conductivity was observed. It seems that there is competition between dedoping shown in Scheme 1 and doping shown in Scheme 2 leading to a maximum followed by the lowering of electrical conductivity.

4.3. DC Electrical Conductivity Stability in Terms of Electrical Conductivity Retention. The stability of electrical conductivity in terms of DC electrical conductivity retention of the nanocomposite samples, along with the polyaniline, was

studied with two slightly different techniques. It was found that the electrical conductivity stability increases with the increase in concentration of zinc oxide nanoparticles.

Electrical Conductivity Retention under Cyclic Ageing Conditions. In this process, the sample is subjected to repeated measurement of electrical conductivity in the defined temperature range after a definite period. In the typical procedure, electrical conductivity of all sample films was obtained after an interval of 45 min for 5 cycles in the temperature range 40°C – 150°C . The sample films in the four-probe instrument were kept undisturbed throughout the experiment. The electrical conductivity behaviours obtained for cyclic study are given in Figure 3. The electrical conductivity data were plotted as log of electrical conductivity ($\log \sigma$) versus $1000/T$ (K).

Electrical Conductivity Retention under Isothermal Ageing Conditions. The stability of electrical conductivity in terms of

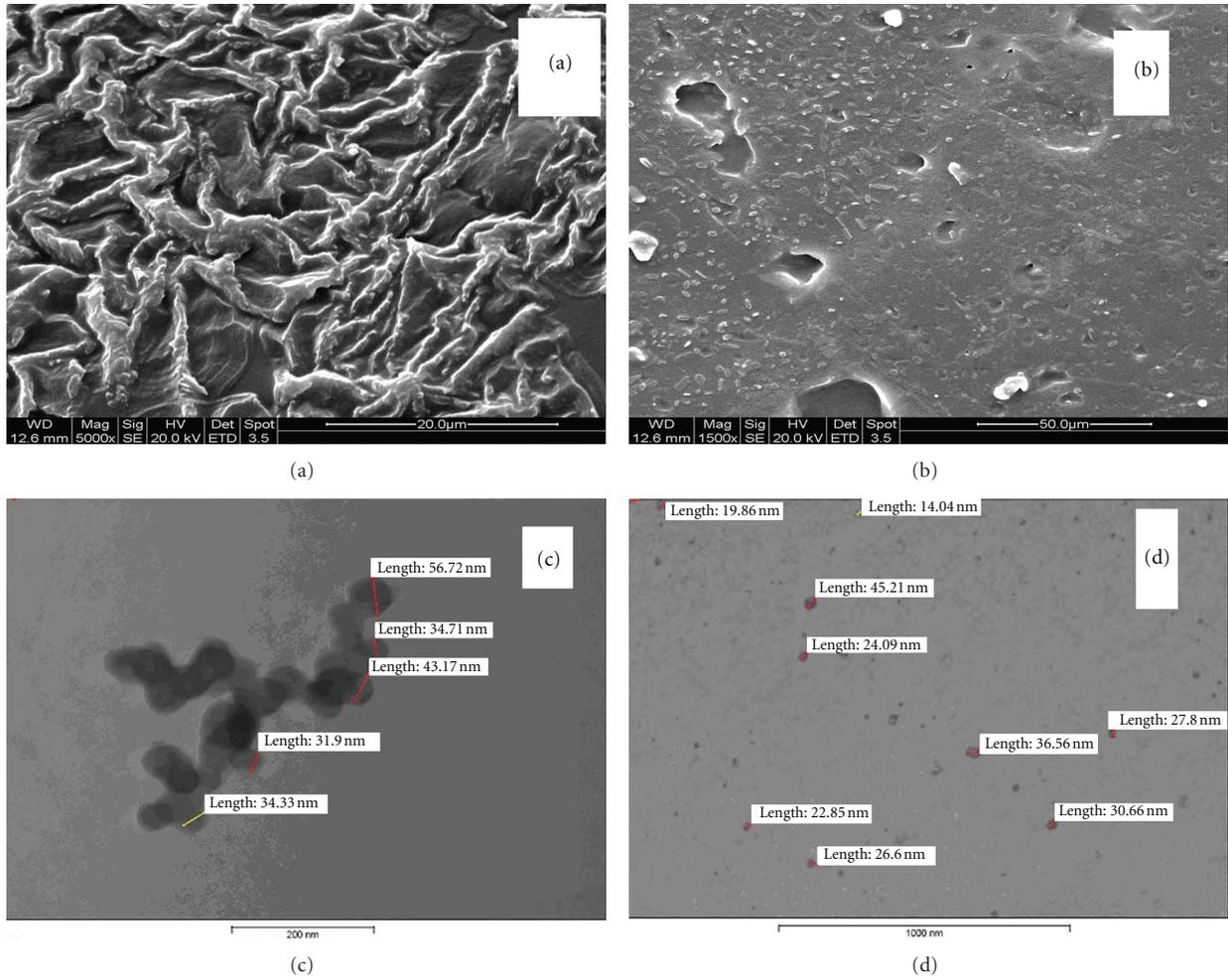


FIGURE 4: (a) SEM image of surface of undoped polyaniline (emeraldine base) film, (b) SEM image of surface of doped PANI:PC:Z5, (c) TEM image of emeraldine base, and (d) TEM image of PANI:PC:Z5.

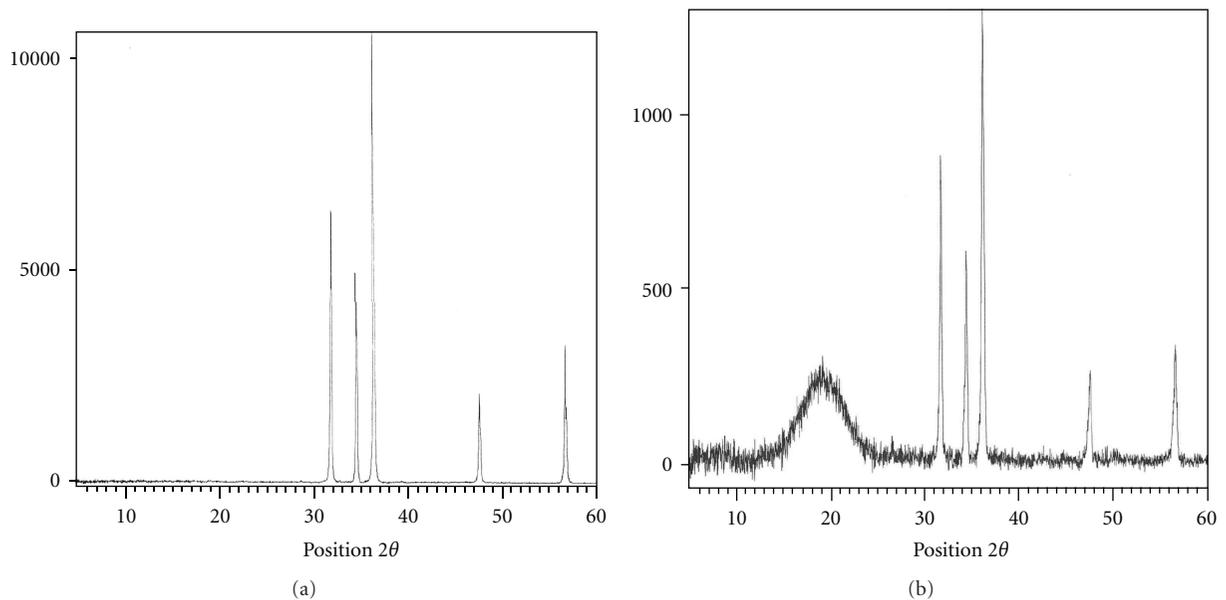
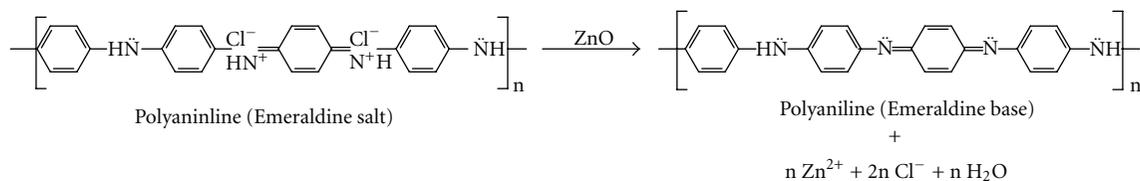
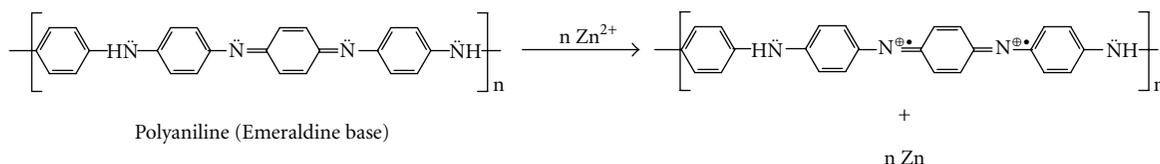


FIGURE 5: XRD pattern of (a) zinc oxide nanoparticles (purchased sample) and (b) PANI:PC:Z5 nanocomposite particles.



SCHEME 1



SCHEME 2

DC electrical conductivity retention was also studied under isothermal condition by using four-in-line DC electrical conductivity measuring instrument. In simple procedure, the electrical conductivity of all the samples were measured at a constant temperature 50°C, 70°C, 90°C, 110°C, and 130°C. Isothermal study of the nanocomposites suggests that the electrical conductivity retention is much better in the nanocomposites having higher content of zinc oxide nanoparticles than those without or having lower content of zinc oxide nanoparticles. The isothermal stability behaviour of electrical conductivity, plots of σ/σ° versus time is given in Figure 3. In general, it may be observed that the electrical conductivity of the polyaniline and nanocomposites containing different polymer matrices and zinc oxide nanoparticles concentration showed good stability in terms of electrical conductivity retention up to 90°C.

4.4. Electron Microscopy Studies (SEM & TEM). Scanning electron microscope (SEM) images of selected samples were obtained using SEM-JEOL 840 A. The SEM images of surface of polyaniline (emeraldine base) and HCl (1 M doped) nanocomposite PANI:PC:Z5 films are given in Figure 4. The surface of undoped polyaniline (PANI) film shows a specific pattern of wave. However, surface morphology of nanocomposite PANI:PC:Z5 totally changed into flaky on doping with HCl (1 M). Transmission electron microscope (TEM) images (Figures 4(c) and 4(d)) of polyaniline (emeraldine base) and PANI:PC:Z5 nanocomposite were obtained using Phillips CM-10. TEM images suggest that the particles of polyaniline (emeraldine base) and that of nanocomposites are in nanometer range.

4.5. X-Ray Diffraction (XRD) Studies. The powder method of X-ray diffraction, basically this method, involves the diffraction of monochromatic X-rays by a powder specimen. X-rays diffractions were carried out using an X'pert Pro XRD X-ray diffractometer and filtered $\text{CuK}\alpha$ radiations. The diffraction patterns of the selected sample powders ZnO nanoparticles and PANI:PC:Z5 were obtained by scanning the samples at an interval of $2\theta = 0 - 60^\circ$ at a rate of $2^\circ/\text{min}$.

The average particles size (D) may be calculated for the selected samples by using Scherrer equation given below:

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (2)$$

where K is the shape factor for the average crystallite (expected shape factor is 0.9), λ is X-ray's wavelength for $\text{K}\alpha$, β is full width at half maximum of the diffraction line, and θ is Bragg's angle.

The XRD patterns of selected samples are given in Figure 5. Peaks obtained in case of pure zinc oxide nanoparticles ($2\theta = 31.8340, 34.4853, 36.3303, \text{ and } 47.6017$ and $2\theta = 56.6575$) are also present in PANI:PC:Z5 ($2\theta = 31.8251, 34.4851, 36.2975, \text{ and } 47.5955$ and $2\theta = 56.6283$) nanocomposites.

XRD pattern of zinc oxide nanoparticles and that of various nanocomposites showed similar peak patterns; therefore, it may be assumed that presence of polyaniline did not cause any change in crystal structure of zinc oxide or negligible change which may be ignored. These results also indicate that the polyaniline present in nanocomposites is amorphous, supporting the previous reports. Moreover, above discussion also supports that the incorporation of supporting polymer into polyaniline does not affect the crystal structure of zinc oxide nanoparticles as reported in work of Ansari [7].

5. Conclusions

FTIR spectra of the samples support the interaction of PANI chains with ZnO which imparts the thermal stability to the nanocomposites. Electrical conductivity study of the samples favours that PANI is mainly responsible for the electrical conduction; however, a little increase in conductivity was observed with the increase in ZnO content. Cyclic and isothermal study reveals that the electrical conductivity of the nanocomposites is more stabilized with increased ZnO concentration in nanocomposites. The TEM and XRD results suggest the uniform distribution of zinc oxide nanoparticles in the nanocomposites. Therefore, it may be inferred that the solution mixing process to produce

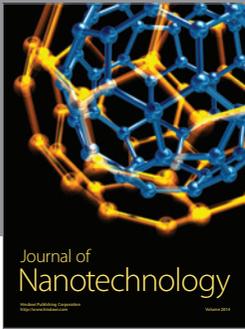
nanocomposites has promising future if handled carefully and these nanocomposites may be used for various electrical and electronic applications.

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