Preparation of Nano-Hybrid Materials Based on Pani/Peg/Zno via Biomimetic Methods

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Research Article

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ABSTRACT

Polyaniline and its composites with PEG, ZnO have been prepared via biomimetic method. The presence of these polymers (PEG) hinders the growth of large particles due to a diffusion-limited process. The particle size decreases from PAni (60.3 nm)>PAni-PEG (42.7 nm)>PAni-ZnO (34.5 nm)>PAni-PEG-ZnO (16.1 nm). These materials have been characterized by FTIR, UV-visible, XRD, SEM, TGA and AC Impedance spectroscopy techniques. The AC Impedance measured data were simulated using CNLS fitting software in the frequency range of 10^{-3} Hz to 10^{11} Hz for best resolution using the parameters of the equivalent circuit. It was found that there was a marked difference in AC impedance spectra, corresponding equivalent circuit elements and relaxation times depending on the particle size of the nanomaterials.

INTRODUCTION

Polyanilines have been studied extensively in recent years due to many advantages over other conducting polymers such as low cost, easy synthesis, range of electrical conductivities and unique reversible proton doping-dedoping processes in these materials. It's the most attractive conducting polymers because of presence of reactive NH-group in polymer chain [1-4]. Semiconducting zinc oxide (ZnO) has attracted lot of attention due to its unique properties such as direct wide band gap (3.37 eV) and large exciting binding energy (60 meV) at room temperature [5]. Synthesis and characterization of conducting polyaniline nanocomposites containing ZnO nanorods were reported [6]. It was prepared by the chemical oxidation methods of aniline in acidic medium with ammonium peroxydisulphate (APS) as oxidant. Chemical vapour sensing properties of electrospum nanofibers of PANI/ZnO nanocomposites was reported earlier [7]. ZnO nanoparticles were synthesized by simple sol-gel methods and nanofibers of polyaniline and PAni/ZnO nanocomposite prepared by using the electrospinning technique. The PAni/ZnO nanocomposites were prepared by co-polymerization method [8]. It was found that the electrical conductivity of composite with 20% weight of ZnO was found to be highest among all other composites and even more than polyaniline. Effect of ZnO particle size on AC electrical properties of polyaniline- ZnO composites was reported [9]. AC conductivity measurements showed that the electrical conductivity of the composites was occurring through the electron charge carriers of ZnO. These studies prompted us prepare and characterize polyaniline nanocomposites by the biomimetic synthesis method which is useful in controlling the size of particles due to diffusion-limited growth. Another purpose of the present work was study the effect of synthetic conditions and particle size on the AC Impedance spectra of these materials. The samples were characterized by TEM, SEM, XRD, TGA, FT-IR, UV–visible and AC impedance spectra. This will, not only, help in preparing materials with desired properties but also, in testing the applicability of this technique in studying inorganic/organic nanocomposites.

MATERIAL AND METHODS

Aniline (Merck, A.R. Grade) was distilled before use. ZnO from Merck, polyethylene glycol (LOBA chemicals, A.R. grade) and acids (HCl) from BDH were used as received. Triple distilled water obtained from a quartz double distillation unit was used for the synthesis. Ammonium peroxodisulphate (Merck) was used as received.

Synthesis

Polyaniline was synthesized by IUPAC protocol [10]. PAni/PEG and PAni/ZnO were synthesized via standard procedure method [6,11-13].

Synthesis of PAni/PEG/ZnO Composites

5 mL aniline was added in 100 mL HCl. In this 2.0 g PEG dissolved in 50 mL H_2O was added. In this solution, ZnO 0.25 g was added. The resulting solution was stirred for about 5 minutes. 14.0 g APS dissolved in 100 mL H_2O was added slowly for about half an hour with continuous stirring. Bluish green solution was obtained. The reaction was done in between 0-5⁰C. The solution was filtered and washed three times with distilled water. The precipitate was dried in oven at 60°C and then over anhydrous $CaCl_2$. Yield in (g) of PAni-PEG-ZnO composites: 3.8 g.

Measurements

The FT-IR spectra of these materials were done in KBr medium in the range of 450-4000 cm^{-1} using Varian 3100 FT-IR Encalibur Series. UV-visible spectroscopy was done by using UV-1700 Pharma. Spec. Simadzu corp. in nujol medium in the range of 300-1000 nm. The powder X-ray diffraction of the polyaniline, polyethylene glycol and ZnO composites were analysed using Rigaku(Model-RINT-2000; Japan) X-ray Diffractometer using Cu Kα radiation (1.542×10^{-10} m) in the 2θ range 5–60°. Scanning electron microscope studies were made using Leica Cambridge 440 microscope. The AC conductance (G), capacitance (C) and resistance(R) of different samples were measured in the range of 40 Hz to 100 kHz using LCZ meter (Keithley, model-3330). The basic accuracy of the L C Z meter used for our measurements was 0.1% for the impedances in the range of 0.1 mΩ to 19.999 MΩ ; capacitances in the range of 0.001 pF to 199.99 mF and for conductance in the range of 0.001 μS to 199.99 S. The measured data were simulated using CNLS (complex non-linear least square fitting) software in the range of 10^{-3}-10^{11} Hz by to determine the equivalent circuits. The relaxation times were evaluated from the products of R and C obtained from the equivalent circuit analysis.

RESULTS AND DISCUSSION

The biomimetic synthesis of PAni-PEG-ZnO involves the controlled growth of materials in the presence of water soluble organic polymer matrix, (PEG). Aniline hydrochloride was distributed uniformly in polyethylene glycol solution to which ammonium peroxodisulphate was added slowly. Polyethylene glycol threads hinder the growth of large particles. The Triple hybrid materials were prepared by adding ZnO in the aniline hydrochloride and polyethylene glycol to which APS was added slowly. The biomimetic method thus ensured the diffusion-limited growth of different components separately for comparison of results [11-13].

UV-Visible Spectroscopy

Electronic spectra of polyaniline and its composites have been taken in nujol medium in the range of 300 to 1000 nm. For polyaniline (bulk polymerization), the peak around 380 nm and 425 nm were attributed to the π-π* and excitonic transitions. The peak around 825 nm was due to polaron formation. The electronic spectra of PAni composite with ZnO bands at 383 nm and 430 nm were due to π-π* and excitonic transition and band at 807 nm was due to polaron transition. In the electronic spectra of PAni/PEG/ZnO, the electronic bands at 344 nm and 441 nm were due to π-π* and exciton band transition. However, band at 796 nm was obtained due to polaron transition. On observing these spectra of composites of PAni with metal oxide (ZnO), it is evident that the shape of UV/visible absorption bands and their position λ_{max} markedly affected indicating that in the presence of ZnO the polymerization occurs at the surface of ZnO and there is some interaction between PAni and metal oxide. There was no white coloured particle of ZnO present in the precipitate containing polyaniline and ZnO, indicating good coating of these ZnO nanoparticles by polyaniline. The poloran band shifted from 825 (PAni)>PAni-ZnO (807)>PAni-PEG-ZnO (796) indicating formation of nano particles **(Table 1)**.

Table 1: UV visible spectra of polyaniline and its composites with PEG and metal oxide.

S.N.	Sample	Wt(g) ratio PAni.: PEG/ PVA : Metal oxide	Π → Π* λ_{max}(nm)	Exciton Band λ_{max}(nm)	Polaron Band λ_{max}(nm)
1.	PAni	5.00 : 0.00 : 0.00	355	427	825
2.	PAni-ZnO (5%)	5.00 : 0.00 : 0.25	383	430	807
3.	PAni-PEG	5.00 : 2.00 : 0.00	367	415	820
4.	PAni-PEG-ZnO	5.00 : 2.00 : 0.35	344	441	796

Table 2: Characteristic I.R. absorptions in polyaniline and its composite with PEG and metal oxide.

Sample	Wt(g) ratio PAni : PEG/ PVA: Metal Oxide	Ring Stretching		υ (C-N) str.	υ (C-C)	υ (C-H) (op)
		Quinoid	Benzenoid			
PAni	5.00 : 0.00: 0.00	1570	1474	1295	1126	799
PAni-ZnO(5%)	5.00 : 0.00: 0.25	1566	1464	1290	1120	796
PAni-PEG	5.00 : 2.00 0.00	1582	1403	1290	1141	818
PAni-PEG-ZnO	5.00:2.00: 0.35	1564	1477	1301	1132	808

FTIR Spectroscopy

The I.R. spectra of polyaniline and its composites with ZnO oxides and PEG have been taken in KBr medium. There spectral

data of peaks values have been given in **Table 2**. For polyaniline, the peaks at 1570 cm^{-1} and 1474 cm^{-1} have been assigned due to ring stretching mode of the quinoid and benzenoid rings [14]. The peak near 3200-3400 cm^{-1} was due to υ (N-H) stretching mode of vibration. The band at 2924 cm^{-1} and 799 cm^{-1} were due to υ (C-H) (Ph-H) stretching mode and υ (Ph-H) C-H out of plane bending vibration respectively. The peak at 1126 cm^{-1} was due to υ (C-C) stretching mode and at 1295 cm^{-1} was due to υ (C-N) stretching mode of vibration. These results are consistent with the results reported earlier [15]. In case of composites of PAni with ZnO, all these peaks shifted slightly indicating that there was some interaction between PAni and ZnO particles. e.g., for PAni/ZnO (0.1 g), peaks at 1569 cm^{-1} and 1478 cm^{-1} were observed due to ring stretching mode of quinoid and benzenoid rings. The bands at 1123 cm^{-1} and 1295 cm^{-1} were due to C-C stretching and C-N stretching mode of vibration respectively. Peaks at 797 cm^{-1} and 2925 cm^{-1} were due to υ (Ph-H) C-H out of plane bending vibration and υ (C-H) (Ph-H) stretching mode of vibration respectively. For PAni/PEG composite, peaks at 1582 cm^{-1} and 1476 cm^{-1} were due to quinoid and benzoid stretching mode. The band at 2927 cm^{-1} and 818 cm^{-1} were attributed to υ (C-H) (Ph-H) in plane stretching and υ (Ph-H) C-H out of plane bending vibration. Peak at 1296 cm^{-1} was due to υ (C-N) stretching mode of vibration. A peak at 1103 cm^{-1} was due to υ (C-O-C) stretching mode.

X-ray Diffraction

X-ray diffraction (XRD) of different samples have been given in **Figure 1**. The sharp peaks of pure PEG indicates its crystalline nature and its composite with PAni-PEG-ZnO also had sharp peaks at d-values of 3.53 × 10^{-10} m and 1.90 × 10^{-10} m with respective diffraction angles of 2θ at 25° and 48° respectively. The d-spacing is calculated with Bragg formula [16].

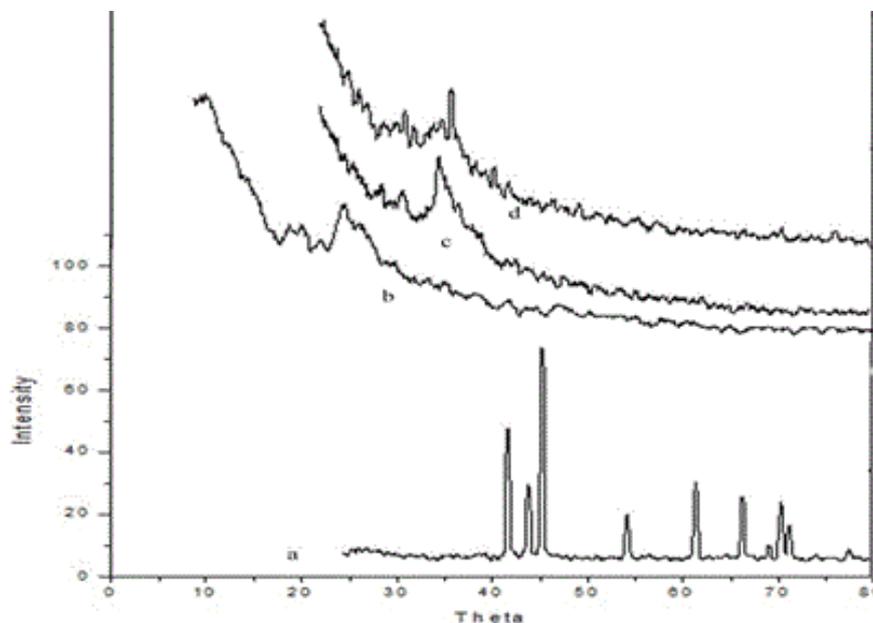**Figure 1.** XRD Spectra(a)PAni/ PEG (b) Polyaniline (c) PAni/ ZnO (d) PAni/PEG/ZnO.

λ=2d sin θ

X-ray diffraction of PAni-PEG composite showed sharp peaks at 2.49 × 10^{-10} m, 1.89 × 10^{-10} m and 1.61x10^{-10} m interplaner spacing with corresponding 2θ values of 36°, 48° and 57° of the crystal. But the polyaniline was amorphous in nature as indicated by broad peak. The sharp peaks of ZnO showed it crystalline nature. PAni-ZnO hybrid exhibit the characteristic peaks for crystalline ZnO (hexagonal. This indicates that the crystal structure of ZnO was not modified due to the presence of PAni [17]. The crystalline domain size L, can be estimated using the Scherrer formula L=0.9 λ/Δ (2θ) cosθ, Where, L=Size of particle, λ=X-ray wave length, Δ(2θ)=full width at half-maximum (fwhm). The average particle size (L) of polyaniline, polyaniline-polyethylene glycol, polyaniline-polyethylene glycol-ZnO, and polyaniline-ZnO were 60.3 nm, 42.7 nm, 16.1 nm and 34.5 nm respectively.

Scanning Electron Microscopy

Scanning Electron Microscopy of three component system of a representative system, Pani/PEG/ZnO has been given in **Figure 2**. The SEM image of ZnO particles were reported earlier [18]. It was demonstrated that a bulk quantity of flower like bunches existed. Each bunches was composed of closely packed nanometer scale rods and formed radiating structures. It was proposed that the ZnO particles had a nucleation effect on the polymerization of aniline leading to homogenous coating of ZnO with polyaniline. The SEM image not only supports these propositions but also the particle size estimated from XRD. These nanostructures also support our equivalent circuit analysis discussed below in terms of (RC) (RC) circuit from grain and electrode contribution.
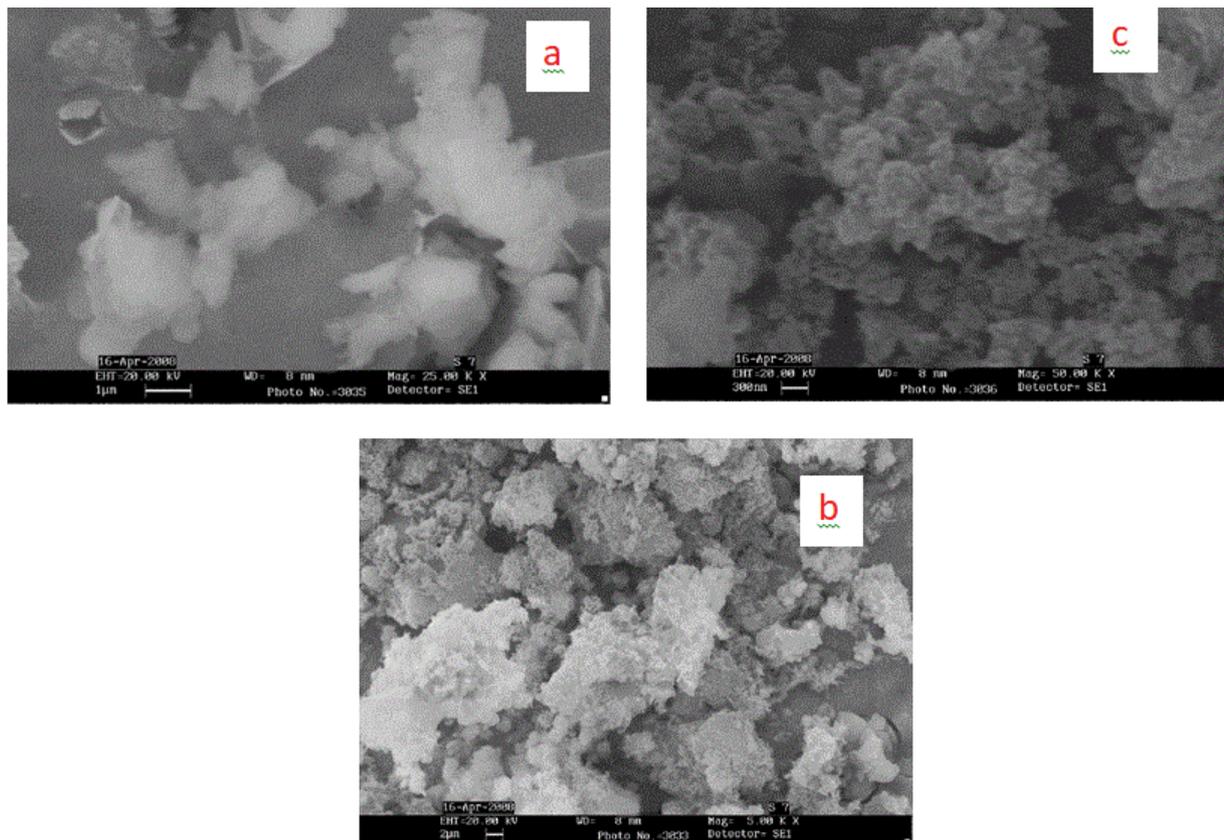
Figure 2: (A-C) SEM micrograph of Polyaniline-Polyethylene glycol at different Resolutions.

Thermogravimetric Analysis

The technique of TGA has been found one of the most useful techniques for evaluating the onset of thermal decomposition temperature and determining the thermal stability of conducting polymers. Thermo gravimetric analysis (TGA) of a representative system, PAni/PEG/ZnO has been given in **Figure 3**. Thermal analysis shows continuous weight loss up to about 280°C due to evaporation of water molecules and acid. The major weight loss occurred above 280°C due to decomposition of PAni and 100% weight loss occurs at 570°C.
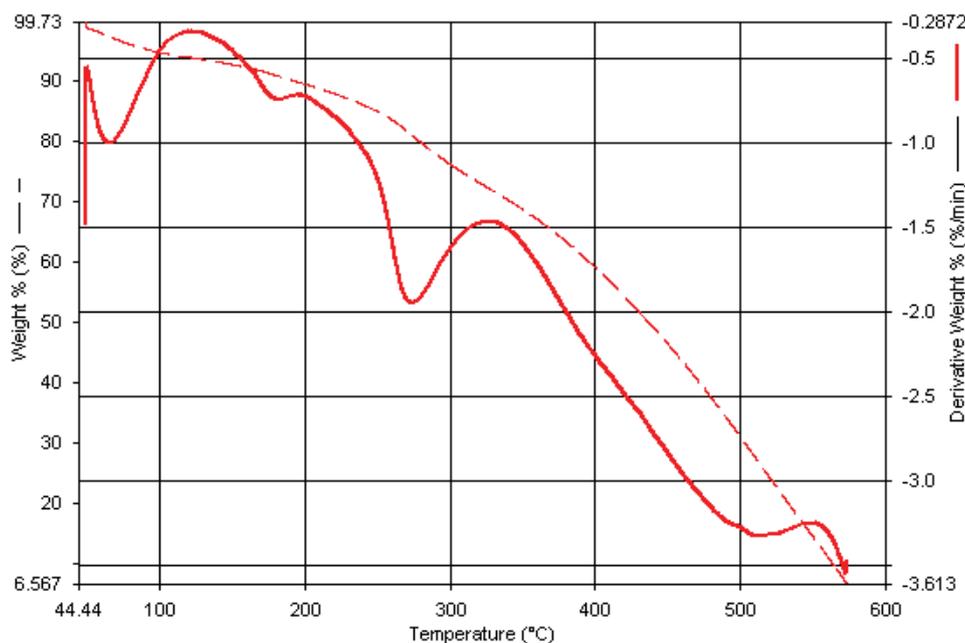
Figure 3: TGA of PAni/PEG/ZnO.

AC Impedance Spectra

The AC Impedance analysis of polyaniline and its composite with ZnO and polyethylene glycol have been done in the

frequency range of 40 Hz to 100 kHz. These measured data were simulated using CNLS fitting software, in the frequency range of 10^{-3} Hz to 10^{11} Hz for best resolution using the parameters of the equivalent circuit [19]. Three semicircles were expected for three components of system, grain, grain boundary, and electrode contributions. Two semicircles indicated contribution from grain and electrode only. Some of the representative plots have been given in **Figure 4**.
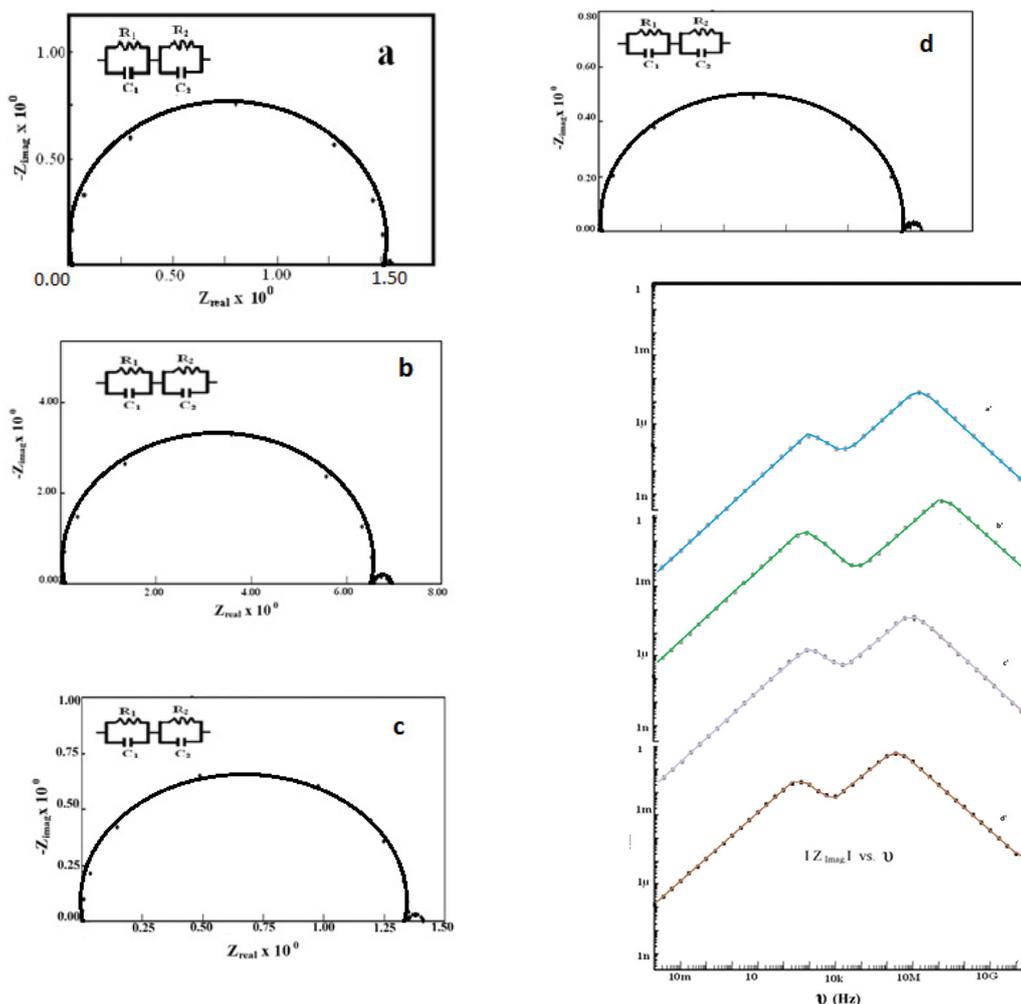
Figure 4: Impedance plot of (a) Polyaniline (b)PAni/ ZnO (c)PAni/ PEG (d) PAni/PEG/ZnO.

The measured AC Impedance data and some of the simulated data and their AC components have been given in **Tables 3-8**.

**Table 3:** Conductivity data summary of polyaniline and its composites with metal oxide (ZnO) and PEG.

Samples	σ_{ac}(S/cm) 100Hz	σ_{ac}(S/cm) 1 KHz	σ_{ac}(S/cm) 10 KHz	σ_{ac}(S/cm) 100 KHz
PAni	1.44×10^{-1}	1.47×10^{-1}	1.48×10^{-1}	1.48×10^{-1}
PAni-ZnO(5%)	1.40×10^{-2}	1.47×10^{-2}	1.49×10^{-2}	1.51×10^{-2}
Pani-PEG	1.64×10^{-1}	1.74×10^{-1}	1.75×10^{-1}	1.78×10^{-1}
PAni-PEG-ZnO	1.54×10^{-1}	1.66×10^{-1}	1.69×10^{-1}	1.70×10^{-1}

Table 4: Measured AC impedance data of polyaniline using ammonium peroxodisulphate as an oxidizing agent.

υ (Frequeny) (Hz)	$Cp \times 10^{-9}$ (Capacitance) (Farad)	|Z| (Impedance) (Ohm)	$G \times 10^{-3}$ (Conductance) (Siemen)	$\sigma \times 10^{-1}$ (Conductivity) (S/cm)
4×10^1	0.00	7.24	137.1	1.33
6×10^1	0.00	7.14	139.4	1.35
8×10^1	0.00	7.10	141.2	1.37
1×10^2	0.00	6.96	143.4	1.39
2×10^2	0.00	6.83	146.3	1.42
3×10^2	0.00	6.78	147.4	1.43
4×10^2	0.00	6.76	147.8	1.43
6×10^2	0.00	6.69	149.3	1.45
7×10^2	0.00	6.67	149.9	1.45

9×10^2	0.00	6.63	150.7	1.46
1×10^3	0.00	6.62	151.0	1.47
2×10^3	3.00	6.61	151.3	1.47
3×10^3	3.00	6.59	151.6	1.47
5×10^3	2.00	6.55	152.6	1.48
7×10^3	2.00	6.54	152.7	1.48
9×10^3	2.00	6.52	153.2	1.49
1×10^4	2.00	6.51	153.5	1.49
2×10^4	1.70	6.50	153.8	1.49
4×10^4	1.30	6.48	154.2	1.50
6×10^4	1.20	6.47	154.4	1.50
8×10^4	1.00	6.44	154.7	1.50
1×10^5	0.90	6.44	154.9	1.50

Table 5: Measured AC impedance data of composite of polyaniline with ZnO (5%) using ammonium peroxodisulphate as an oxidizing agent.

u (Frequeny) (Hz)	$C_p \times 10^{-9}$ (Capacitance) (Farad)	$|Z|$ (Impedance) (Ohm)	$G \times 10^{-3}$ (Conductance) (Siemen)	$\sigma \times 10^{-1}$ (Conductivity) (S/cm)
4×10^1	0.00	7.24	137.1	1.33
6×10^1	0.00	7.14	139.4	1.35
8×10^1	0.00	7.10	141.2	1.37
1×10^2	0.00	6.96	143.4	1.39
2×10^2	0.00	6.83	146.3	1.42
3×10^2	0.00	6.78	147.4	1.43
4×10^2	0.00	6.76	147.8	1.43
6×10^2	0.00	6.69	149.3	1.45
7×10^2	0.00	6.67	149.9	1.45
9×10^2	0.00	6.63	150.7	1.46
1×10^3	0.00	6.62	151.0	1.47
2×10^3	3.00	6.61	151.3	1.47
3×10^3	3.00	6.59	151.6	1.47
5×10^3	2.00	6.55	152.6	1.48
7×10^3	2.00	6.54	152.7	1.48
9×10^3	2.00	6.52	153.2	1.49
1×10^4	2.00	6.51	153.5	1.49
2×10^4	1.70	6.50	153.8	1.49
4×10^4	1.30	6.48	154.2	1.50
6×10^4	1.20	6.47	154.4	1.50
8×10^4	1.00	6.44	154.7	1.50
1×10^5	0.90	6.44	154.9	1.50

Table 6: Simulated AC impedance data of composite of polyaniline with ZnO (5%) using ammonium peroxodisulphate as an oxidizing agent.

u (Frequency) (Hz)	C (Capacitance) (Farad)	$|Z|$ (Impedance) (Ohm)	G (Conductance) (siemen)	$\sigma \times 10^{-2}$ (Conductivity) (S/cm)
1.00×10^{-3}	2.60×10^{-6}	6.91×10^0	0.14	1.40
4.64×10^{-3}	2.60×10^{-6}	6.91×10^0	0.14	1.40
2.15×10^{-2}	2.60×10^{-6}	6.91×10^0	0.14	1.40
1.00×10^{-1}	2.60×10^{-6}	6.91×10^0	0.14	1.40
2.15×10^{-1}	2.60×10^{-6}	6.91×10^0	0.14	1.40
4.64×10^{-1}	2.60×10^{-6}	6.91×10^0	0.14	1.40
1.00×10^0	2.60×10^{-6}	6.91×10^0	0.14	1.40
2.15×10^0	2.60×10^{-6}	6.91×10^0	0.14	1.40
1.00×10^1	2.60×10^{-6}	6.91×10^0	0.14	1.40
4.64×10^1	2.57×10^{-6}	6.90×10^0	0.14	1.41
1.00×10^2	2.48×10^{-6}	6.89×10^0	0.14	1.41
4.64×10^2	1.25×10^{-6}	6.73×10^0	0.15	1.44
2.15×10^3	1.07×10^{-7}	6.59×10^0	0.15	1.47
1.00×10^4	5.63×10^{-9}	6.58×10^0	0.15	1.47
4.64×10^4	7.38×10^{-10}	6.58×10^0	0.15	1.47
2.15×10^5	4.89×10^{-10}	6.58×10^0	0.15	1.48
1.00×10^6	4.78×10^{-10}	6.58×10^0	0.15	1.48
1.00×10^7	4.77×10^{-10}	6.45×10^0	0.15	1.48

2.15×10^{8}	4.77×10^{-10}	1.51×10^{0}	0.15	1.48
1.00×10^{9}	4.78×10^{-10}	3.33×10^{-1}	0.15	1.48
1.00×10^{10}	4.78×10^{-10}	3.34×10^{-1}	.15	1.48
4.64×10^{10}	4.77×10^{-10}	7.20×10^{-3}	0.15	1.48
1.00×10^{11}	4.78×10^{-10}	3.34×10^{-3}	0.15	1.48

Table 7: Measured AC impedance data of composite of polyaniline with PEG using ammonium peroxodisulphate as an oxidizing agent.

u (Frequeny) (Hz)	$C_p \times 10^{-8}$ (Capacitance) (Farad)	|Z| (Impedance) (Ohm)	$G \times 10^{-3}$ (Conductance) (Siemen)	$\sigma \times 10^{-1}$ (Conductivity) (S/cm)
4×10^{1}	0.00	1.50	658.7	1.56
6×10^{1}	10.00	1.47	674.5	1.60
8×10^{1}	10.00	1.45	685.0	1.62
1×10^{2}	10.00	1.44	692.1	1.64
2×10^{2}	10.00	1.41	707.0	1.69
3×10^{2}	10.00	1.40	715.1	1.69
4×10^{2}	10.00	1.39	717.8	1.70
6×10^{2}	10.00	1.38	723.0	1.71
7×10^{2}	10.00	1.38	725.3	1.72
9×10^{2}	9.00	1.37	730.9	1.73
1×10^{3}	9.00	1.36	732.4	1.73
2×10^{3}	8.00	1.36	734.3	1.74
3×10^{3}	8.00	1.36	736.1	1.74
5×10^{3}	7.00	1.35	741.9	1.76
7×10^{3}	6.7	1.34	742.8	1.76
9×10^{3}	6.4	1.34	744.4	1.76
1×10^{4}	6.3	1.34	746.0	1.77
2×10^{4}	5.3	1.34	746.9	1.77
4×10^{4}	4.4	1.34	747.8	1.77
6×10^{4}	3.9	1.33	747.8	1.77
8×10^{4}	3.5	1.33	748.7	1.77
1×10^{5}	3.2	1.33	749.4	1.78

Table 8: Measured AC impedance data of composite of polyaniline with ZnO(5%) and PEG using ammonium peroxodisulphate as an oxidizing agent

u (Frequeny) (Hz)	$C_p \times 10^{-8}$ (Capacitance) (Farad)	|Z| (Impedance) (Ohm)	G (Conductance) (Siemen)	$\sigma \times 10^{-1}$ (Conductivity) (S/cm)
4×10^{1}	0.00	1.14	864.5×10^{-3}	1.42
6×10^{1}	0.00	1.01	901.3×10^{-3}	1.48
8×10^{1}	20.00	1.08	923.8×10^{-3}	1.52
1×10^{2}	20.00	1.06	940.8×10^{-3}	1.54
2×10^{2}	20.00	1.02	969.6×10^{-3}	1.61
3×10^{2}	20.00	1.01	989.5×10^{-3}	1.62
4×10^{2}	20.00	1.00	993.9×10^{-3}	1.63
5×10^{2}	20.00	1.00	997.9×10^{-3}	1.64
7×10^{2}	20.00	0.99	1.01	1.66
9×10^{2}	18.00	0.99	1.0	1.66
1×10^{3}	18.00	0.99	1.01	1.66
2×10^{3}	16.00	0.99	1.01	1.66
3×10^{3}	15.00	0.99	1.01	1.66
5×10^{3}	14.00	0.98	1.02	1.67
7×10^{3}	13.00	0.97	1.02	1.67
9×10^{3}	12.20	0.97	1.03	1.69
1×10^{4}	12.00	0.97	1.03	1.69
2×10^{4}	10.30	0.97	1.03	1.69
4×10^{4}	8.70	0.97	1.03	1.69
6×10^{4}	8.00	0.97	1.03	1.69
8×10^{4}	7.60	0.97	1.03	1.69
1×10^{5}	7.28	0.96	1.04	1.70

As frequency increases, the conductivity also increases for all systems. It might be due to dependence of frequency on polarization process on the frequency such as space-charge polarization at low frequencies, orientation polarization at moderate frequencies and atomic/electronic polarization at high frequencies. For polyaniline, $(R_1 C_1)$ $(R_2 C_2)$ equivalent circuit was obtained having values $R_1 = 2.96 \times 10^{-2} \, \Omega$, $C_1 = 8.85 \times 10^{-3}$ F, $R_2 = 1.52 \times 10^{0} \, \Omega$ and $C_2 = 2.14 \times 10^{-8}$ F. The relaxation times of polyaniline for grain and electrode part were 2.62×10^{-4} s and 3.25×10^{-8} s showed large difference and therefore two fully resolved semicircles

were obtained. In the two component system of PAni/ZnO the weight of ZnO, i.e. 0.25g of ZnO, $(R_1C_1)(R_2C_2)$ equivalent circuit were obtained having values $R_1=3.31 \times 10^{-1}$ Ω, $C_1=1.13 \times 10^{-3}$ F, $R_2=6.58 \times 10^{0}$ Ω, $C_2=4.77 \times 10^{-10}$ F respectively. The relaxation time for grain and electrode part for PAni/ZnO(0.25 g) of grain electrode part were 3.75×10^{-4} s and 3.14×10^{-9} s. In the impedance plot two semicircle were obtained in both cases indicating contribution from both grain and electrode part. For PAni/PEG composite, $(R_1C_1)(R_2C_2)$ equivalent circuit was obtained having values $R_1=1.35 \times 10^{0}$ Ω, $C_1=3.39 \times 10^{-8}$ F and $R_2=5.79 \times 10^{-2}$ Ω, $C_2=4.49 \times 10^{-3}$ F. The relaxation times for grain electrode part were 2.60×10^{-4} s and 4.58×10^{-8} s. In impedance plot two semicircle were found. In the three component system of PAni/PEG/ZnO composites, (RC)(RC) equivalent circuit was obtained having values $R_1=5.47 \times 10^{-2}$ Ω, $C_1=7.03 \times 10^{-3}$ F, $R_2=9.81 \times 10^{-1}$ Ω, $C_2=7.44 \times 10^{-8}$ F respectively. The relaxation time for PAni-PEG-ZnO for grain electrode part is 3.84×10^{-4} s and 7.30×10^{-8} s. In the imaginary impedance vs. frequency plot two peaks showing two different types of relaxation processes for grain and electrode contributions have been obtained. Real and imaginary parts of impedance vs. frequency touch each other at the same point.

CONCLUSION

Synthesis of PAni and its composites with PEG and ZnO have been done. Biomimetic synthesis methods have been used to prepare PAni-PEG, PAni-PEG-ZnO nano hybrid materials. The water soluble organic polymer (Polyethylene glycol) have been act as biomimetic synthetic aid. The particle size decreases from PAni (60.3 nm)>PAni-PEG (42.7 nm)>PAni-ZnO (34.5 nm)>PAni-PEG-ZnO (16.1 nm). It is clear from this sequence that we get smaller nano hybrid materials via biomimetic synthesis method.

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