

Synthesis, Characterization and AC-Impedance Spectroscopic Studies on Interfacial Synthesis of Pani / PEG Nanocomposite

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Abstract Polyaniline/PEG nanocomposite was prepared via a interfacial polymerization method by using ammonium peroxedisulphate as an oxidizing agent. A mechanism of formation of polyaniline-polyethylene glycol has been suggested in which polyethylene glycol works as a medium for diffusion-limited growth of the components during their precipitation. On studied AC impedance spectroscopy Studied, it was found that the electrical conductivity of interfacially synthesized PANi-PEG composite $3.96 \times 10^{-2} \text{ Scm}^{-1}$ was slightly low than bulk PANi ($1.87 \times 10^{-1} \text{ Scm}^{-1}$) due to formation of nanostructures. These materials were characterized by FTIR, UV- Visible, XRD, SEM and AC-impedance spectroscopy.

Keywords Interfacial Synthesis, PEG nanocomposite, AC-Impedance

1. 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 [1]. A variety of synthetic techniques have been used recently to design and develop polyaniline nanostructures [2]. Interfacial polymerization of aniline at the aqueous-organic interface has been one of the most common methods for making a variety of polyaniline based nanostructures in the form of nanorods, nanotubes, nanosheets and nanofibers. The control of structure is offered by the distribution behavior of aniline from organic phase to aqueous phase where the distribution ratio/constant as well as the rate of transfer of aniline depends on nature and composition of both the phases. Nanostructures of polyaniline doped with a novel dopant were synthesized by a template-free method [3]. It was found that the size and room-temperature conductivity of resulting nanorods and nanotubes with 50-300 nm diameter strongly depend on the synthetic conditions. It was proposed that the dopant played a template-like role in forming PANi nanostructures to a surfactant function. Nanofibers of polyaniline in toluene as organic layer and acidic ammonium peroxydisulfate in aqueous layer which could be controlled by using surfactant such as camphor-sulfonic acid (CSA) were prepared [4]. The

influence of dopants and surfactants on morphology of nanofibers and their electrical properties were studied and were attributed to the kinetics of monomer migration and the presence of large soluble oligomeric aggregates at the interface.

The uniform composite films of nano structured polyaniline with polyvinyl alcohol (PVA) were successfully prepared by blending aniline with PVA as a matrix in presence of β -naphthalene sulfonic acid (β -NSA) as a dopant [5]. It was found that the thermal, mechanical and electrical properties of composites were strongly dependent on the content and polymerization conditions of nanostructured, PANi- β -NSA in PVA matrix. A facile synthesis of polyaniline nanofibers under ambient conditions using aqueous-organic interfacial polymerization was reported [6]. The interfacial synthesis of electrically conducting polyaniline nanofiber composites of polyaniline/poly sulfonated polystyrene (PSS) was done by in-situ polymerization which allowed the growth of PANi-2-D nanostructures embedded in PSS host matrix by self-assembly [7]. The mechanism of the growth of such nanostructures was believed to involve the alignment of protonated aniline monomer onto anionic dopant through electrostatic interactions. Synthesis and characterization of polyaniline/Au composites were reported [8]. Conductive polymers are a new class of materials which exhibit highly redox behavior. The conductivity of nano composites increase by doping Au was reported. Interfacial polymerized Polyaniline/graphite oxide nanocomposites toward electrochemical storage. This polymerization method efficiency exfoliated the expanded layer structure of GO into sheets and these significantly enhanced the specific surface

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area [9]. Preparation and characterization of polyaniline- Co_3O_4 nanocomposites were synthesized via a interfacial polymerization method [10]. Pani and Polyaniline- Co_3O_4 were prepared by employing interfacial polymerization by using APS as oxidizing agent. The nanocomposites show weakly ferro magnetic properties at room temperature. The design, synthesis and characterization of a series of polyaniline nanostructures from fiber to star like, net like and coral ball, prepared by controlling the synthetic conditions such as monomer/stabilizer (polyethylene glycol, PEG) ratio, pH, and rate of adding reagents were reported [11].

AC impedance spectroscopic studies on polyaniline nanostructure prepared via interfacial polymerization were reported by us [12]. It was shown that the nature of impedance plots and corresponding equivalent circuits differed significantly depending on experimental conditions. These results indicate that the AC-Impedance spectroscopy can be used as a characterization technique similar to other spectroscopic technique. The morphology, structure and water dispersity of the samples prepared under different conditions were investigated by SEM, XRD, FT-IR, UV-visible and AC- impedance spectroscopy.

The purpose of the present work was to prepare the polyaniline nano composite under a variety of interfacial conditions using PEG and studied their effect on the AC impedance spectra of the materials. This would, not only, help in preparing materials with desired properties; but also, in testing the applicability of this technique in studying organic nanocomposite.

2. Experimental

2.1. Materials and Methods

Aniline (Merck, A.R. grade), was distilled twice before use. Ammonium peroxodisulphate (Merck) was used as received. Polyethylene glycol 6000 (LOBA chemicals, A.R. grade). Triply distilled water was used as aqueous phase.

2.2. Synthesis of Pani/PEG Composite

5.0 mL aniline was taken in 100 mL HCl and 2.0g polyethylene glycol dissolved in 50 mL water was added into this. In this resulting mixture, 14.0 g ammonium peroxodisulphate dissolved in 100 mL distilled water was added slowly for about half an hour with continuous stirring. The reaction temperature was maintained in between 0-5°C. A bluish green solution was obtained. It was kept in refrigerator overnight. The solution was filtered and precipitate was dried in oven at 60°C for 12 hours and then over CaCl_2 . Yield in (g) = 2.2g.

2.3. Interfacial Synthesis of Pani/ PEG Nanocomposite

5.0 mL aniline was added in 100 mL benzene. In this 2.0 g polyethylene glycol dissolved in 50 mL water was added. And in the resulting solution, 14.0g ammonium peroxodisulphate dissolved in 100 mL hydrochloric acid was

added slowly without stirring. The reaction was done in between 0-5°C. Bluish green solution was obtained. The reaction mixture was placed in refrigerator overnight. The solution was filtered and dried in oven. Yield in (g) = 1.8g.

3. Results and Discussion

3.1. FTIR Spectroscopy

Infrared spectroscopy is a versatile analytical tool for characterization of molecular structure via characteristic vibrational absorptions. These spectra have been shown in Fig.1. The I.R. spectra for PANi/PEG nanocomposite (interfacial synthesis), characteristic peak at 1119 cm^{-1} was observed due to ν (C-O-C) stretching mode. Peaks at 1302 and 1145 cm^{-1} were observed due to ν (C-N) stretching mode and ν (C-C) stretching mode of vibration respectively. Peak at 1570 cm^{-1} and 1473 cm^{-1} were assigned due to quinoid and benzenoid stretching mode. All the characteristic peaks of PANi (interfacial synthesis) shifted slightly in PANi/PEG (interfacial synthesis) composite indicating that there was some interaction between these components. On comparing the I.R. spectra of PANi/PEG (bulk polymerization) composite (1582 cm^{-1} , 1403 cm^{-1} , 1296 cm^{-1} , 1117 cm^{-1} , 870 cm^{-1} , 2927 cm^{-1}) with I.R. spectra of PANi/PEG (interfacial synthesis), it was found that all the peaks were shifted slightly indicating that the polymerization of PANi/PEG nanocomposite occur at the interface of aqueous/organic solvent may have some structural differences.

3.2. UV/Visible Spectroscopy

Electronic spectra of polyaniline nanocomposite have been taken in nujol medium in the range of 300 to 1000 nm. They have been shown in Fig.2. For PANi/PEG composite, all the characteristic peaks of PANi were shifted slightly indicating that there was some interaction between PANi and PEG. On comparing the UV/visible spectra of PANi/PEG (bulk Polymerization) composite (peaks at 367 nm, 415 nm and 820 nm) with PANi/PEG (interfacial polymerization) composite (peaks at 352 nm, 425 nm and 811 nm), it was found that all the bands were shifted slightly indicating that there may have structural differences because of interfacial polymerization.

3.3. X-ray Diffraction

The XRD pattern for pure polyethylene glycol has been shown in Fig. 3-curve (a). Sharp peaks are observed at $2\theta = 7.5^\circ$ and 26.4° , which confirm the crystalline nature of the pure polyethylene glycol. The X-ray diffraction patterns of PANi powders polymerized at different aniline/HCl compositions have been shown in Fig. 3-curve (b) which also confirms the amorphous structure. However, it has been reported that PANi prepared at the water/benzene solvent interface may possess a more planar chain conformation and improved π - π inter chain stacking, resulting in elongation of

the effective conjugation length and improved charge carrier transport [13]. As the PANi content increased, the broadening of the peaks indicated an increase in the amorphous nature. The relative intensity of certain diffraction patterns peaks changes significantly with the weight of polyaniline. XRD

spectra of PANi synthesized at the interface of two immiscible solvent Fig. 3 (c) shows semi crystalline nature. However PANi/PEG composite (interfacial polymerization) Fig. 3 (d) showed peaks corresponding to both the peaks of PEG having semi crystalline character.

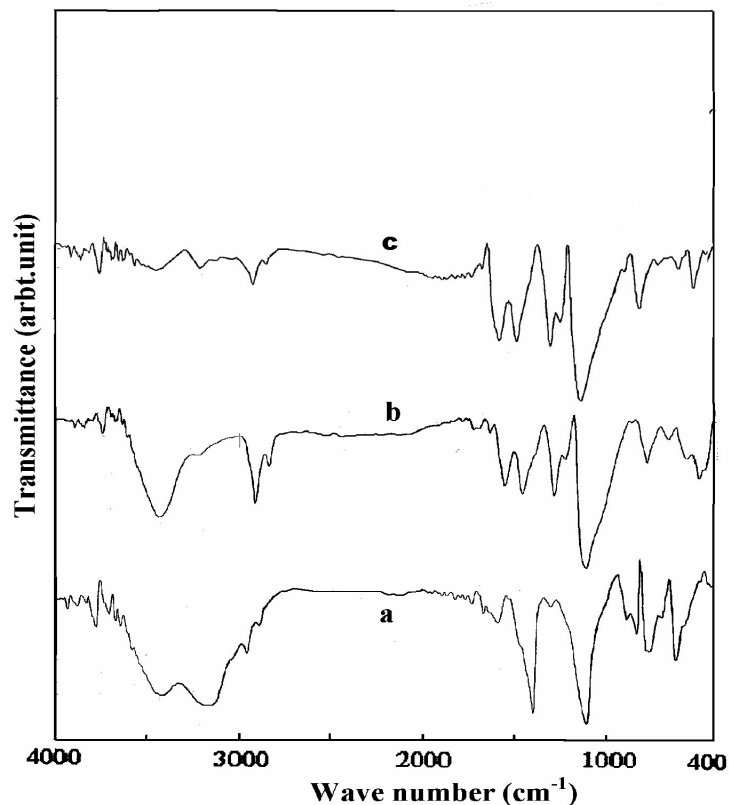


Figure 1. Infra-red spectra of (a) PANi-PEG (bulk polymerization) (b) PANi-PEG (interfacial polymerization) (c) PANi (bulk polymerization)

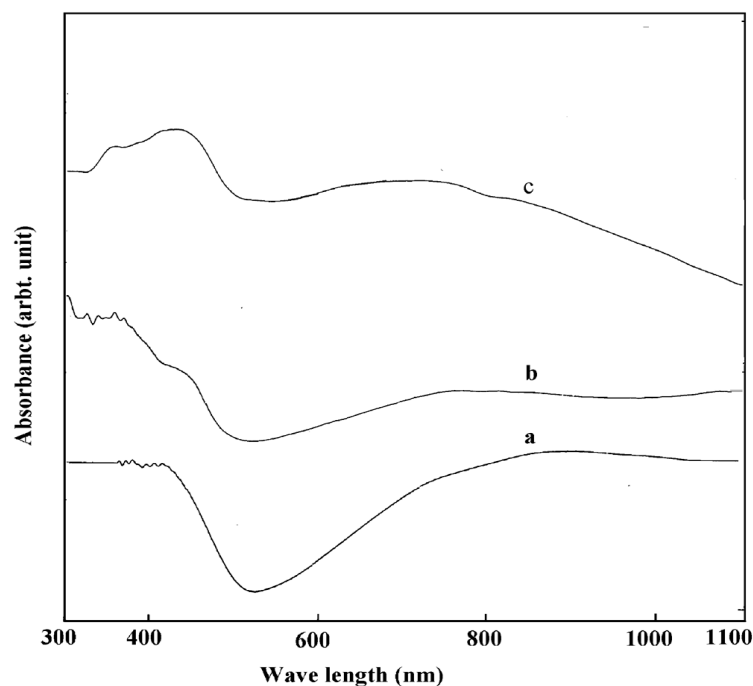


Figure 2. UV visible spectra of (a) PANi-PEG (bulk polymerization) (b) PANi-PEG (interfacial polymerization) (c) PANi (bulk polymerization)

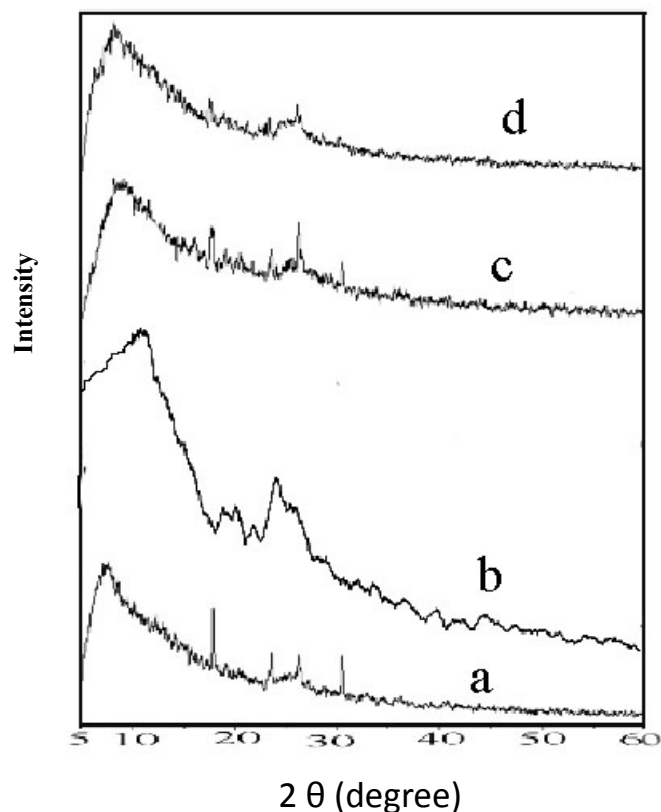


Figure 3. X-ray diffraction spectra of (a) polyethylene glycol, (b) polyaniline (bulk polymerization of 5.0g aniline), (c) polyaniline (interfacial polymerization of 5.0g aniline), (d) polyaniline-polyethylene glycol (interfacial polymerization of aniline 3.0g, polyethylene glycol 2.0g)

3.4. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) studies of polyaniline nano composite images shown in Fig. 4. The SEM images of polyaniline-polyethylene glycol made at the interface between water and benzene respectively. Polyaniline composite with poly ethylene glycol exhibited a fibrillar like structure. Polymerization in the constrained space of these polymer resulted in nearly spherical polyaniline particles with a low mean diameter and nano size distribution [14].

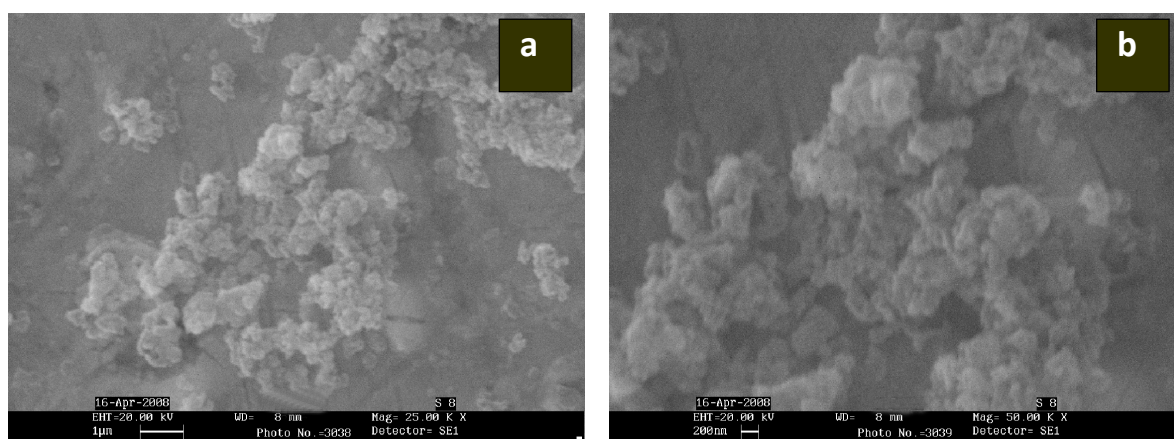


Figure 4. SEM micrographs of (a) polyaniline- polyethylene glycol (interfacial polymerization), low resolution. (b) polyaniline- polyethylene glycol (interfacial polymerization) High resolution

3.5. A.C. Impedance Spectroscopic Studies

Electrical properties of polyaniline and its composite have been found to be highly dependent on synthetic conditions.

AC measurements not only avoid the polarization effects in DC measurements, but also lead to separation of various contributions to total impedance or conductance. The AC impedance measurements for some representative sample of

interfacial synthesized polyaniline composite of PANi/PEG having benzene as organic phase at various frequencies has been given in Table 1(a). The simulated values for the determination of equivalent circuits have been given in Table 1(b) and its representative plots have been given in Fig. 5. Impedance plots for a few representative systems have been given in Fig.6. For PANi/PEG composite (interfacial synthesis), $(R_1C_1)(R_2C_2)$ circuit were obtained having values $R_1= 2.31 \times 10^{-1}\Omega$, $C_1= 1.58 \times 10^{-3} F$, $R_2= 3.58 \times 10^0 \Omega$, $C_2= 6.17 \times 10^{-9} F$ respectively. In the impedance plots, two semicircles were obtained one big and other small indicating that there was grain and electrode contribution which was comparatively greater than grain boundary contribution. Pure polyaniline and its composite with polyethylene glycol have two similar arcs and circuit elements. However, interfacially synthesized polyaniline using benzene as an organic phase had three arcs indicating significant contributions from grain, grain-boundary and electrode. Two peaks in the Bode plots (imaginary impedance vs. frequency); indicated two different types of relaxation processes for grain and electrode contributions. The conductivities calculated from the grain resistances match very well with the values for different samples. The relaxation times determined from respective R & C values lie in the range of $3.67 \times 10^{-9}s$ to $4.58 \times 10^{-8}s$ for grain, and $8.80 \times 10^{-5}s$ to $2.62 \times 10^{-3}s$ for electrode and $3.51 \times 10^{-5}s$ for grain boundary processes. In all the systems, conductivity increased with

temperature indicating the semiconductor behavior of materials.

Arrhenius plots have been shown in Fig. 7. The thermal energy of activation determined from the temperature dependence of electrical conductivity has been given in Table 4. The value lie in the range of 0.03 – 0.08 eV which are typical values for organic semiconductors. A representative regression analysis of the temperature dependence of AC conductivities for the interfacial polymerized PANi–PEG has been shown in Fig. 8. The regression analysis of conductance data as a function of temperature for this system indicated three-dimensional variable range hopping charge transport in these materials. It was found that polyaniline synthesized by interfacial polymerization had their room temperature conductivities lower (around 10^{-2} Scm^{-1}) than the bulk synthesized polyaniline using the standard IUPAC conjugation method (around 10^{-1} Scm^{-1}). The room temperature conductivities of interfacially synthesized polyaniline using benzene as organic phase has almost same value than interfacially synthesized polyaniline using xylene as organic phase. Addition of polyethylene glycol in the interfacial synthesis of polyaniline using benzene as organic phase leads to slightly lower conductivity from $1.87 \times 10^{-1} \text{ Scm}^{-1}$ to $3.96 \times 10^{-2} \text{ Scm}^{-1}$. These results indicate that conducting polyaniline nanostructures and their composites can be prepared by this route.

Table 1(a). Measured AC impedance data of interfacial synthesized polyaniline PEG composite using benzene as an organic solvent and ammonium peroxy disulphate as an oxidizing agent

Y (Frequency) (Hz)	$C_p \times 10^{-8}$ (Capacitance) (Farad)	Z (Impedance) (Ohm)	$G \times 10^{-3}$ (Conductan) (Siemen)	$\sigma \times 10^{-2}$ (Conductivity) (S/cm)
4×10^1	0.00	4.01	247.4	3.54
6×10^1	0.00	3.95	251.6	3.60
8×10^1	0.00	3.91	255.2	3.65
1×10^2	0.00	3.87	257.7	3.69
2×10^2	0.00	3.76	264.7	3.79
3×10^2	2.00	3.71	268.8	3.84
4×10^2	2.00	3.69	270.2	3.86
5×10^2	2.00	3.67	271.7	3.89
7×10^2	2.00	3.64	274.4	3.92
8×10^2	2.00	3.61	275.9	3.95
1×10^3	2.00	3.61	276.9	3.96
2×10^3	2.00	3.59	278.0	3.98
3×10^3	1.90	3.58	279.2	3.99
5×10^3	1.90	3.56	280.3	4.01
7×10^3	1.80	3.52	281.2	4.02
9×10^3	1.70	3.54	282.2	4.04
1×10^4	1.70	3.53	283.1	4.05
2×10^4	1.50	3.53	283.5	4.05
4×10^4	1.30	3.52	283.7	4.06
6×10^4	0.87	3.53	282.9	4.05
8×10^4	0.72	3.52	283.6	4.06
1×10^5	0.57	3.51	284.7	4.07

Table 1(b). Simulated AC impedance data of interfacial synthesized polyaniline PEG composite using benzene as an organic solvent and ammonium peroxy disulphate as an oxidizing agent

Y (Frequency) (Hz)	C (Capacitance) (Farad)	Z (Impedance) (Ohm)	Conductance (siemen)	$\sigma \times 10^{-2}$ (Conductivity) (S/cm)
1.00×10^{-3}	5.43×10^{-6}	3.81×10^0	2.62×10^{-1}	3.76
2.15×10^{-3}	5.43×10^{-6}	3.81×10^0	2.62×10^{-1}	3.76
4.64×10^{-2}	5.43×10^{-6}	3.81×10^0	2.62×10^{-1}	3.76
2.15×10^{-1}	5.43×10^{-6}	3.81×10^0	2.62×10^{-1}	3.76
1.00×10^0	5.43×10^{-6}	3.81×10^0	2.62×10^{-1}	3.76
2.15×10^0	5.43×10^{-6}	3.81×10^0	2.62×10^{-1}	3.76
1.00×10^1	5.43×10^{-6}	3.81×10^0	2.62×10^{-1}	3.76
2.15×10^1	5.42×10^{-6}	3.80×10^0	2.63×10^{-1}	3.76
1.00×10^2	5.20×10^{-6}	3.80×10^0	2.63×10^{-1}	3.77
4.64×10^2	2.81×10^{-6}	3.69×10^0	2.63×10^{-1}	3.87
1.00×10^3	1.02×10^{-6}	3.62×10^0	2.76×10^{-1}	3.95
4.64×10^3	6.37×10^{-9}	3.58×10^0	2.77×10^{-1}	3.99
2.15×10^4	8.88×10^{-9}	3.58×10^0	2.79×10^{-1}	3.99
1.00×10^5	6.30×10^{-9}	3.58×10^0	2.79×10^{-1}	3.99
2.15×10^5	6.20×10^{-9}	3.58×10^0	2.79×10^{-1}	3.99
4.64×10^5	6.18×10^{-9}	3.57×10^0	2.79×10^{-1}	3.99
1.00×10^6	6.19×10^{-9}	3.55×10^0	2.79×10^{-1}	3.99
4.64×10^6	6.18×10^{-9}	3.01×10^0	2.79×10^{-1}	3.99
1.00×10^7	6.18×10^{-9}	2.09×10^0	2.79×10^{-1}	3.99
4.64×10^7	6.18×10^{-9}	5.49×10^{-1}	2.79×10^{-1}	3.99
4.64×10^8	6.18×10^{-9}	5.54×10^{-2}	2.79×10^{-1}	3.99
4.64×10^{10}	6.18×10^{-9}	5.55×10^{-4}	2.79×10^{-1}	3.99
1.00×10^{11}	6.18×10^{-9}	2.58×10^{-4}	2.79×10^{-1}	3.99

Table 2. AC components along with its values of interfacial synthesis of polyaniline and its composite PEG

Solvent	Electrical Properties					
	Grain		Electrode		Grain Boundary	
	R(Ohms)	C(Farad)	R(Ohms)	Q/C(Farad)	R(Ohms)	C(Farad)
PAni(C ₆ H ₆)	1.57×10^{-1}	5.37×10^{-3}	7.22×10^{-2}	4.86×10^{-4}	1.10×10^0	6.82×10^{-8}
PAni-PEG	1.35×10^0	3.38×10^{-8}	5.79×10^{-2}	4.49×10^{-3}	-----	-----
PAni-PEG-C ₆ H ₆	2.31×10^{-1}	1.58×10^{-3}	3.58×10^0	6.17×10^{-9}	-----	-----

Table 3. Relaxation time data of composite of PAni/PEG and interfacial synthesized PAni/PEG using benzene as an organic solvent

Polymer	T ₁	T ₂
PAni-PEG	4.58×10^{-8}	2.60×10^{-4}
PAni-PEG-C ₆ H ₆	2.21×10^{-8}	3.52×10^{-4}

Table 4. Energy of activation and Conductivity value of polyaniline and its composite using ammonium per sulphate as oxidant

Sample	Energy of activation (eV)	Conductivity (S/cm) at room temp.
Polyaniline (bulk polymerization)	0.08	0.35
Polyaniline (interfacial polymerization)	0.18	0.19
Polyaniline- polyethylene glycol (bulk polymerization)	0.10	0.17
Polyaniline – polyethylene glycol (interfacial polymerization)	0.07	0.04

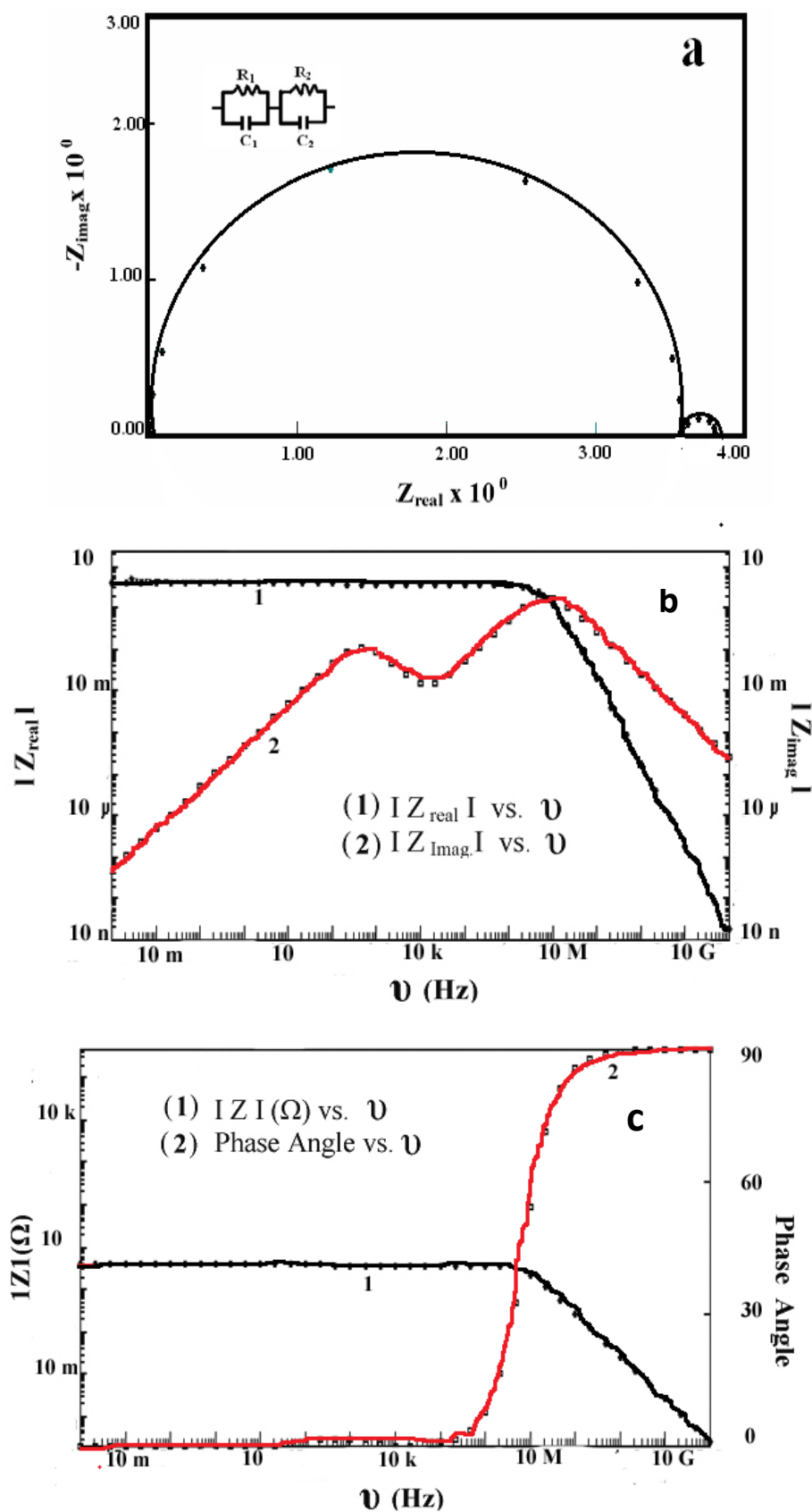


Figure 5. Complex Immittance plots for PANi/PEG (interfacial polymerization), (a) complex Impedance plot, (b) Bode-plot, (c) Bode IZI alpha plot

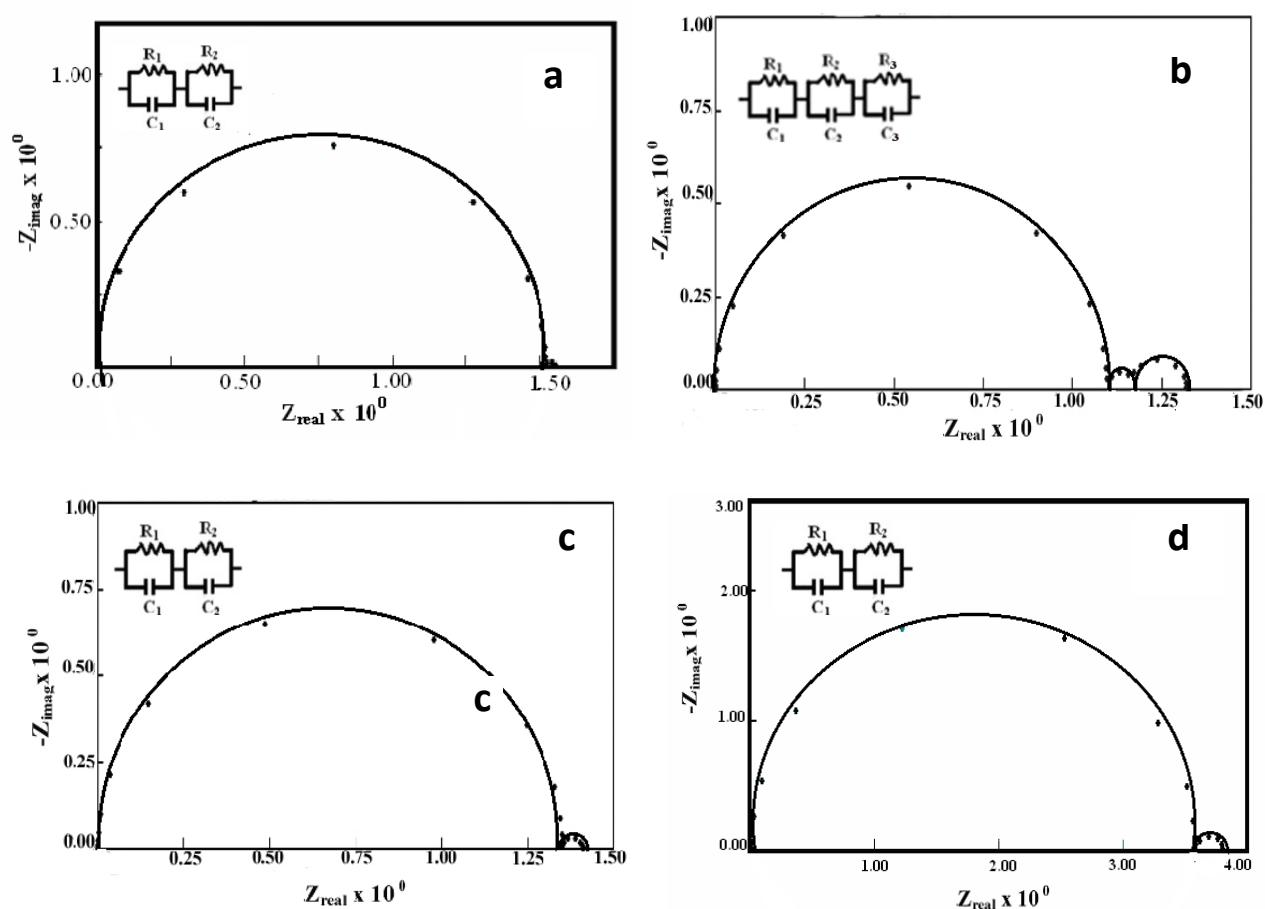


Figure 6. Complex Impedance plots for (a) PANi (bulk polymerization), (b) PANi (interfacial polymerization), (c) PANi /PEG (bulk polymerization), (d) PANi/PEG (interfacial polymerization)

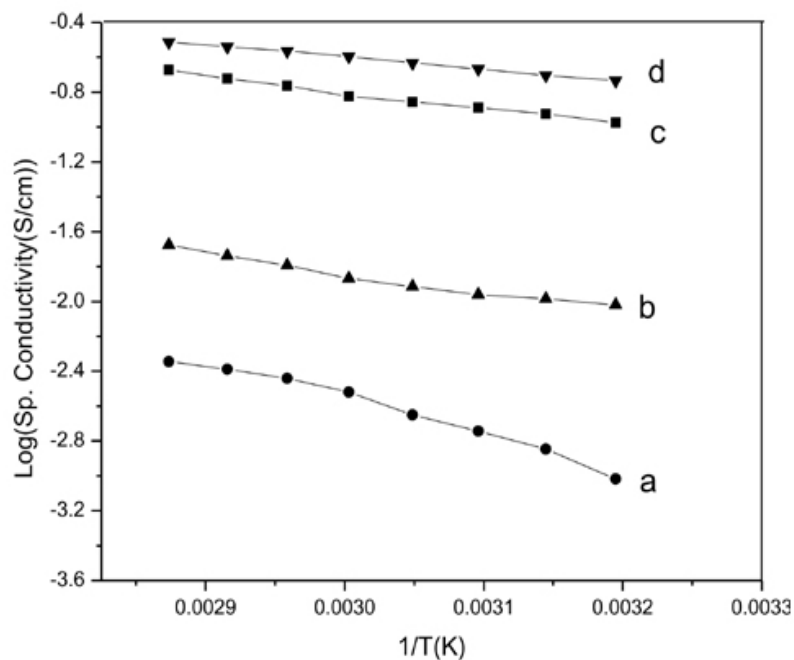


Figure 7. Arrhenius plots for- (a) polyaniline (interfacial polymerization using benzene as solvent). (b) polyaniline polyethylene glycol (bulk polymerization). (c) polyaniline (bulk polymerization). (d) polyaniline-polyethylene glycol (interfacial polymerization using benzene as solvent)

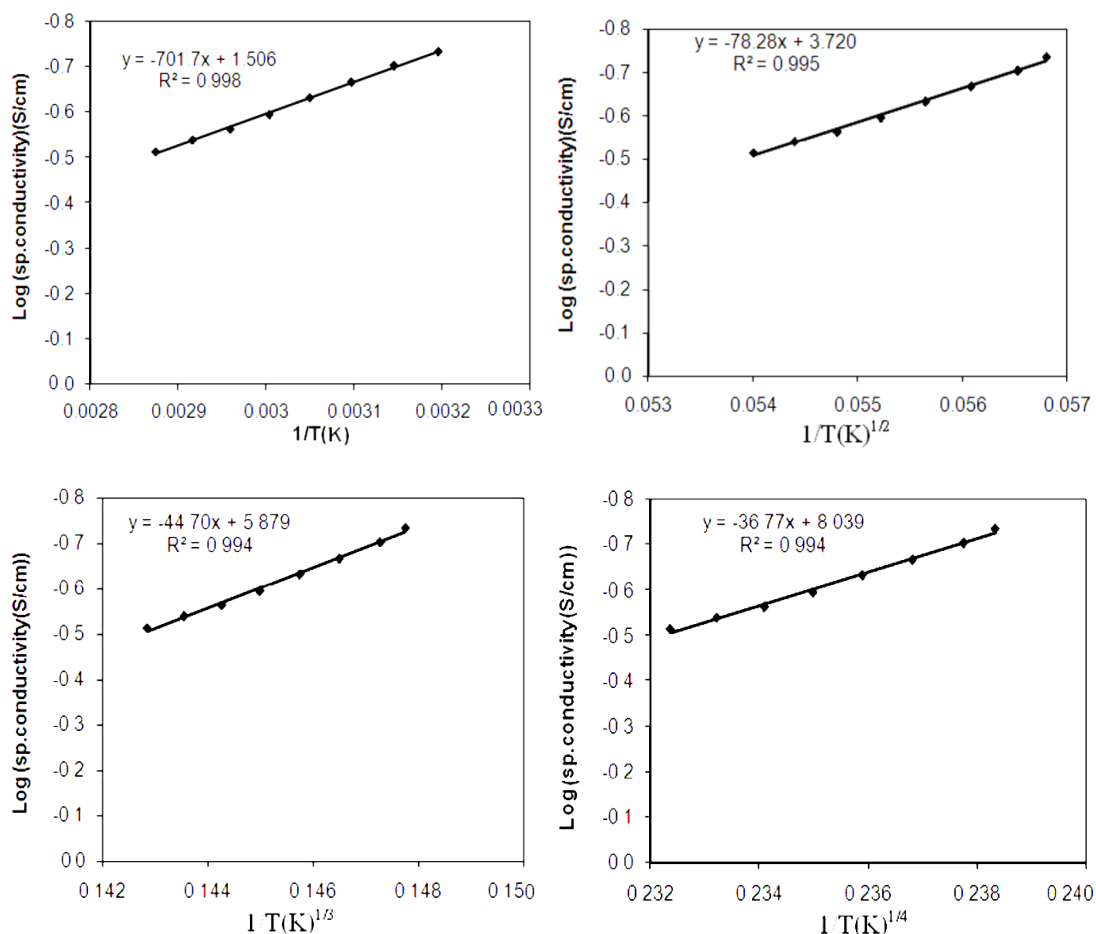


Figure 8. The regression analysis graph of polyaniline– polyethylene glycol (interfacial polymerization using benzene as solvent)

4. Conclusions

PANi/PEG nanocomposite was successfully synthesized by interfacial polymerization method. A mechanism of formation of polyaniline-polyethylene glycol has been suggested in which polyethylene glycol works as a medium for diffusion-limited growth of the components during their precipitation. AC impedance spectroscopy studied have been done to find the electrical conductivity and it was found that the electrical conductivity of PANi/PEG composite $3.96 \times 10^{-2} \text{ Scm}^{-1}$ was slightly lower than bulk PANi ($1.87 \times 10^{-1} \text{ Scm}^{-1}$) due to formation of nanostructure.

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