

STRUCTURE AND PROPERTIES OF PROCESSIBLE CONDUCTIVE POLYANILINE AND POLYETHELENE OXIDE COMPOSITE

Dr.Sarika A. Khapre¹, S.P. Yawale², S.S. Yawale³

¹*Department of Physics, Genba Sopanrao Moze College of Engineering, Balewadi, Pune*

²*Vidarbha Institute of Science and Humanities, Amravati, Maharashtra (India)*

ABSTRACT

In the Present work blend was studied with the help of characterization, electrical conductivity and comparative study of PANi-PEO, The Scanning Electron Microscopy (SEM) has been carried out to characterize the samples. From the IR spectroscopy, it was noticed that, conductive blends were formed. And the corresponding peak observed in all shows the presence of PANi, PEO TGA/DTA data shows that, interaction between the polymers. Thermal analysis is the analysis of a change in a property of a sample, which is related to an imposed change in the temperature. TG measures mass changes in a material as a function of temperature (or time) under a controlled atmosphere and In DTA, the temperature of a sample is compared with that of an inert reference material during a programmed change of temperature.. DC conductivity measurement shows that, blends follow Arrhenius law. It was noticed that at 9wt% of PANi-PEO blend showed maximum conductivity. It was found to be $6.78439 \times 10^{-07} \text{ S cm}^{-1}$. From observations it is clear that all blends show the ionic conduction. The ionic transference number was measured for all wt% of PANi –PEO.

Keywords: *Polaniline, Polyethylene oxide*

I. INTRODUCTION

Polymers are a large class of materials consisting of many small molecules called monomers, that can be linked together to form long chains thus, they are known as macromolecules. A typical polymer may include tens of thousands of monomers. Because of their large size, polymers are classified as macrom.

The field of conducting polymers becomes one of the most promising fields of research and development. These polymers have tremendous applications in different fields, especially in the electronics industry. However, the major concern in this area is the lack of processibility of these polymers. Nowadays, the rapidly expanding field of nano conducting a polymer composite is generating many exciting new materials with novel properties.

Most commercially produced organic polymers are electrical insulators. Conductive polymers, which are almost always organic, have extended delocalized bonds (often comprised of aromatic units) that creates a band structure similar to silicon, but with localized states. When charge carriers (from the addition or removal of electrons) are introduced into the conduction or valence bands the electrical conductivity increases dramatically. Technically almost all known conductive polymers are semiconductors due to the band structure, however so-

called zero band gap conductive polymers may behave like metal. The most notable difference between conductive polymers and inorganic semiconductors is the mobility which, until very recently, was dramatically lower in conductive polymers than their inorganic counterparts, though recent advancements in self assembly are closing that gap.

II. MATERIAL AND METHOD

The aniline monomer was A.R. grade reagent obtained from M/S S.D. Fine Chem. (India), the chemical ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ was received from M/S Loba Chemie India and was used as such. The concentrated hydrochloric acid was obtained from M/S S.D. Fine Chem. (India). PEO (polyethylene oxide) was received from Merck company. Solvents NMP (1-methyl 2-pyrrolidone), distilled water and methanol were used after purification, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and LiCl were received from M/S Loba Chemie India and were used as such.

III EXPERIMENTAL

3.1 PREPARATION OF SAMPLE

Polyaniline was synthesized in conventional route in aqueous medium using mineral acid such as HCl as dopant ion and oxidizing agent ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as initiator. Aniline monomer, acid dopant and oxidizing agent were taken in the molecular ratio of 1:1:1.1. Hydrochloric acid was taken in distilled water in which aniline monomer was added and stirred to get aniline-acid complex and kept in the freezing mixture to attain the reaction temperature of 0 - 5 °C. In another beaker, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was dissolved in distilled water and kept in the freezing mixture. After both of these solutions attained the reaction temperature, they were mixed together and stirred well and kept for six hours for the completion of reaction. Polyaniline powder formed was filtered, washed thoroughly with water to remove excess salts and dried under the vacuum (10^{-3} torr) for 24 hrs to make it moisture free. [1]

PAni and PEO were added to NMP (1-methyl 2-pyrrolidone) which was stirred for 30 min [2]. Films containing PAni, PEO were obtained by drying the mixtures at 75 °C for 24 h. Film was deposited on Teflon sheet, so that it is easy for removing the film. Different percentage of composite film have been prepared such as 3, 5, 7, 9, 11 wt %

IV. RESULT AND DISCUSSION

4.1 Scanning Electron Microscopy images (SEM/EDAX):

The surface morphology of 9wt% PAni-PEO film was examined by Scanning Electron Microscope (SEM). (Fig 4.1) shows the scanning electron microscopy (SEM) image of the blend PAni-PEO film. A homogeneous surface, with uniformly distributed particles is seen. Some cracks are also seen. Due to the interaction between electron and sample, considerable amount of heat is generated which causes the development of small cracks during SEM recording. [3]

The quantitative analysis for energy dispersive X-ray analysis (EDAX) was performed for PAni-PEO film.

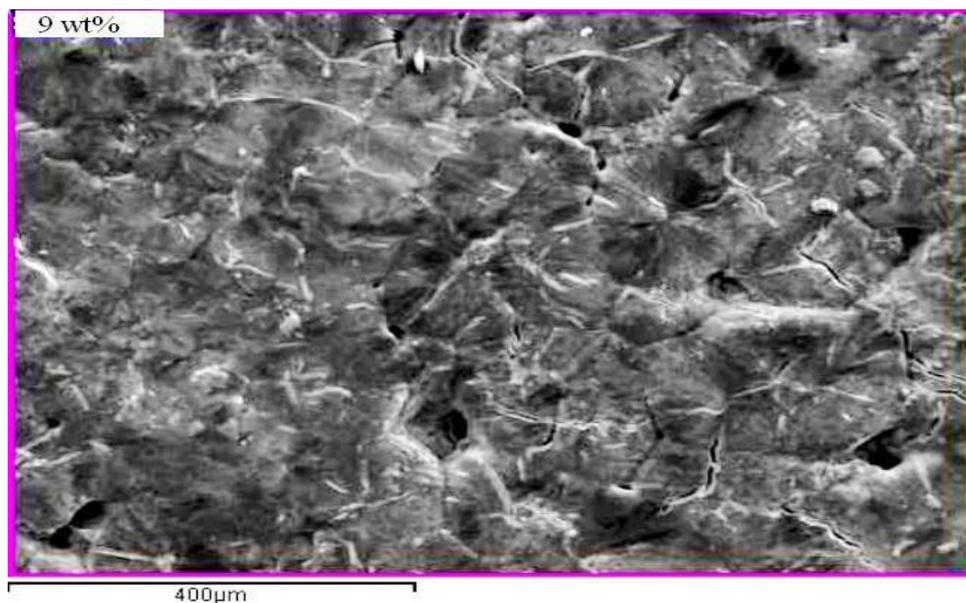


Fig.4.1: Scanning electron micrographs of 9wt% PANi-PEO blend.

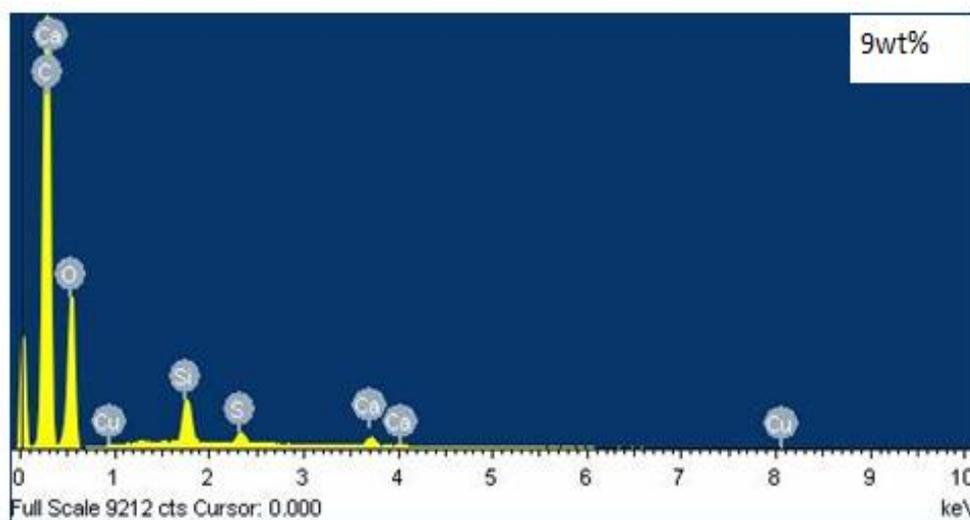


Fig4.2: EDAX spectra of of 9wt% PANi-PEO blend.

Table 4.1: EDAX data for 9wt%PANi-PEO blend samples.

Element	Weight%	Atomic%
C	58.30	65.80
O	39.01	33.06
Si	1.54	0.74
S	0.44	0.19
Ca	0.49	0.16
Cu	0.22	0.05

A typical EDAX spectrum is presented (Fig4.2). Peaks of C and O are clearly shown which are demonstrating PANi-PEO composites .were successfully prepared by this one step process. In addition image obviously indicates the position of each element as display in table 4.1.Due impurity some unwanted element is observed.

4.2 Fourier transform infrared spectroscopy (FTIR) analysis:

In order to know the structure of the material have we studied FTIR spectra of PANi-PEO blend. The Fig (4.3) shows the FTIR spectra for PANi -PEO having peaks 1583.61, 1358.41cm⁻¹ nearly match with wave numbers 1579, 1490, and1367, cm⁻¹respectively. Most of the characteristic peaks of PANi as described in literature [4, 5, 6]. The peaks at wave numbers 1583.61 and 1466.9 cm⁻¹ are attributed to C- N and C- C stretching mode for the quinoid and benzenoid rings; while the peak at wave number 1446 cm⁻¹ is attributed to C–C aromatic ring stretching of the benzenoid diamine unit. The peaks at wave numbers 1285.6, and 1358 cm⁻¹ are attributed to C–N stretching; the band near 1560 cm⁻¹ involves both C–N stretch and C–N–H in-plane bend in the stretch–bend mode [7], however it may be noted that these peaks are slightly shifted with respect to their normal positions as seen for pure PANi films. These peak sifting might be due to the presence of PEO in the PANi matrix.

The band has two features at 3607.01cm⁻¹ showing in the presence of two types of O-H groups isolated OH groups and those involved in hydrogen bonding [8] 1466 cm⁻¹ CH₂ de-formation of PEO [9] vibration appears at 855 cm⁻¹, which is near to a band at 827 cm⁻¹ due to C–C stretching of PEO [10]. Two clear CH₂ vibration modes appear in PEO at 1466.91 cm⁻¹ [11] 968.3cm⁻¹ (strong peak corresponds to C–O deformation in PEO branches) of [12].Table 4.2 shows the Peak position for 9wt% PANi (PANi-PEO) blend samples.

Table 4.2: Peak position for 9wt%PANi-PEO blend samples

Sr. No.	1	2	3	4	5	6
Peak position (cm ⁻¹) of 9wt% PANi-PEO	855	968.3	1358.41	1466.9	1583.61	3607

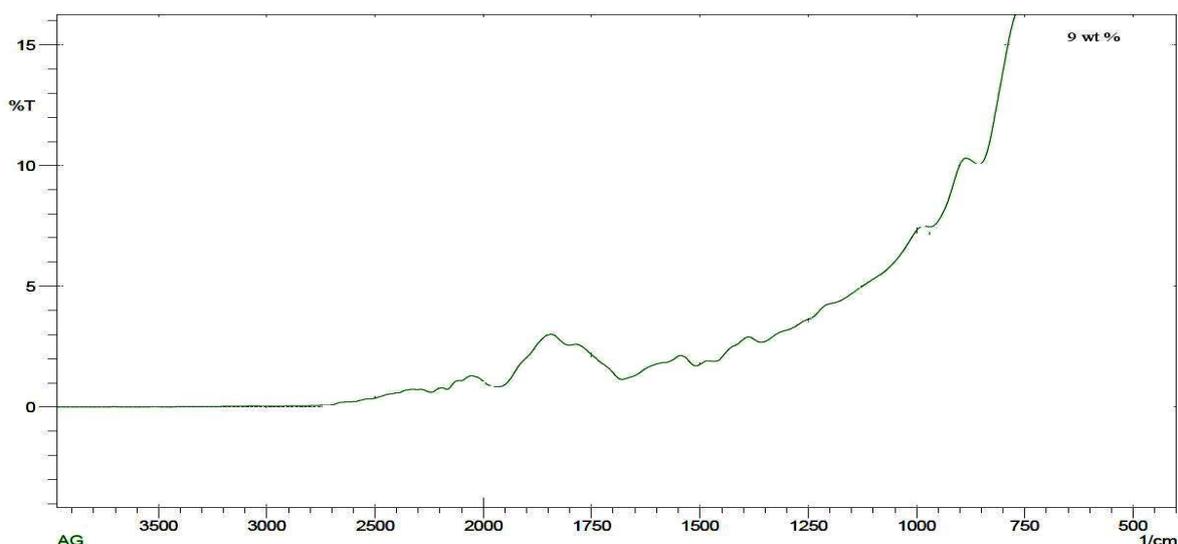


Fig.4.3: FTIR spectrum of 9wt%PANi-PEO blend.

4.3 Thermogravimetry (TG) / Differential thermal analysis (DTA):

Thermo gravimetric analysis was carried out for various samples to determine the weight loss at different temperatures. Thermal stability of the PANi-PEO- blend was assessed from analysis of the TG and DTA curves (Fig4.4) the main data is summarized in Table 4.3.

In (Fig. 4.4) the film demonstrated two step degradation. The first one was in the temperature range of 265 to 370 °C, the second one from 385 to 495°C. One endothermic event and three exothermic events are observed in the PANi-PEO thermograms (Fig.4 4). The first event occurs at 71.46°C temperature, it is called as glass transition temperature because at this temperature there is transition from a disordered solid to a liquid. The first event is accompanied by a 3.380% weight loss and is related to the removal of the physically adsorbed water. Three exothermic events occur at 328.84°C, 402.66°C and 461.56°C. These two events is accompanied 87.105% and 7.237% weight loss. The TG /DTA data for 9wt% PANi-PEO blend samples are summarized in Table 4.3.

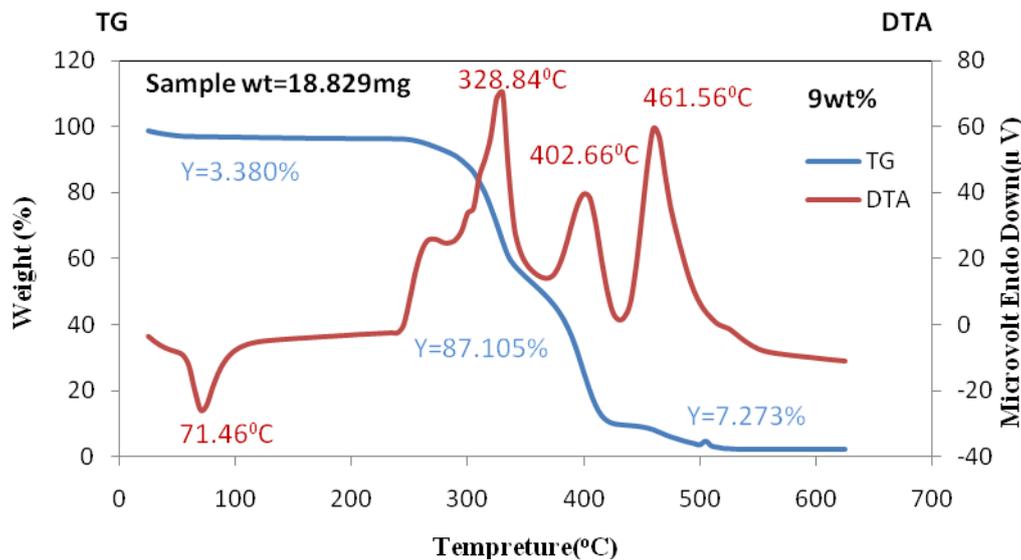


Fig 4.4: TG/DTA curves 9 wt% of PANi-PEO- blends.

Table 4.3: TG /DTA data for 9 wt% Pani-PEO blend samples.

Sample	Peak I (Glass transition) Endothermic events		Peak II Exothermic events		Peak III Exothermic events		Peak VI Exothermic events	
	Tmax (°C)	Peak Height (µV)	Tmax (°C)	Peak Height (µV)	Tmax (°C)	Peak Height (µV)	Tmax (°C)	Peak Height (µV)
9%	71.46	-18.167	328.8	62.709	402.7	31.549	461.56	59.304

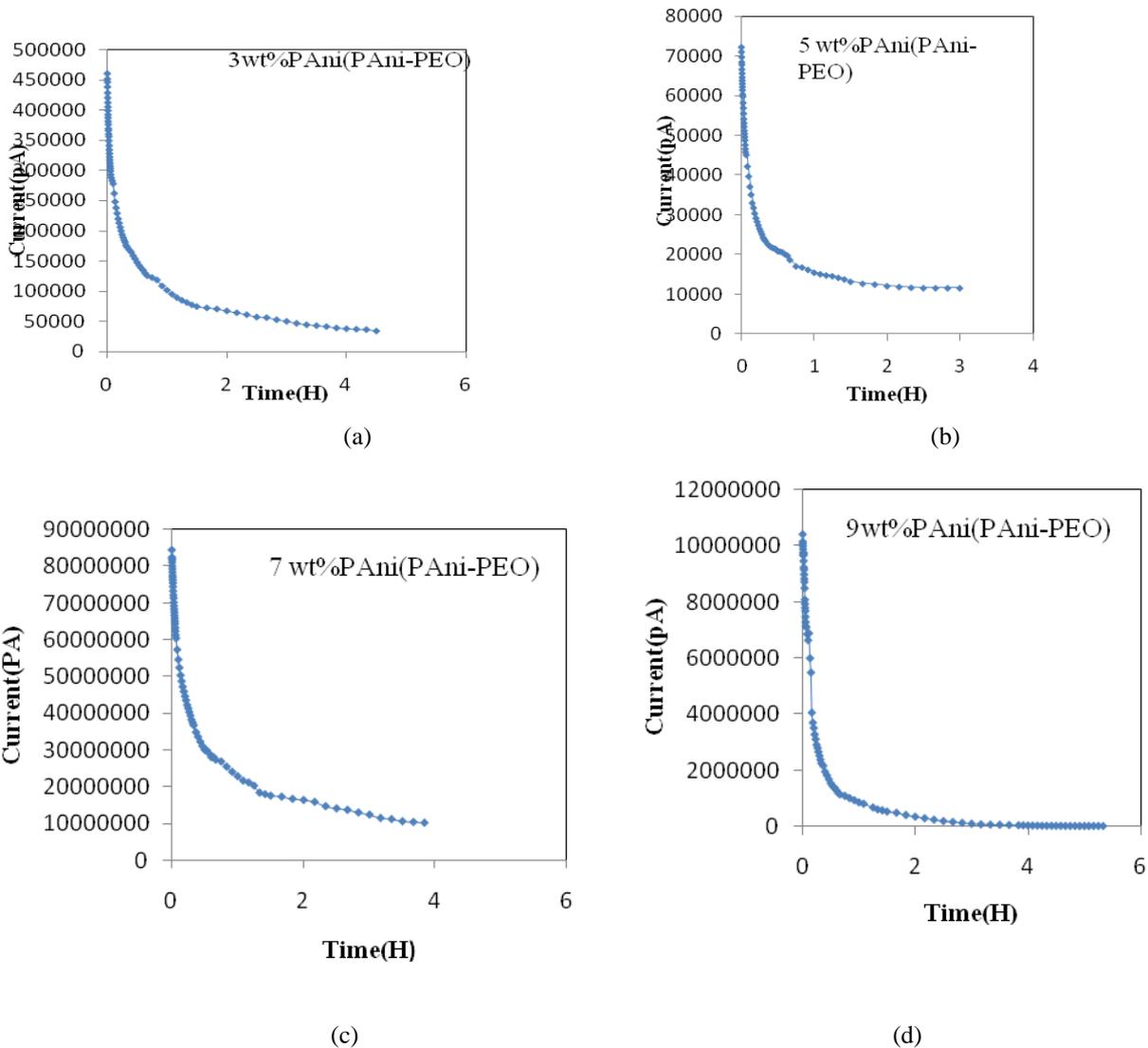
4.4 Transference number measurements:

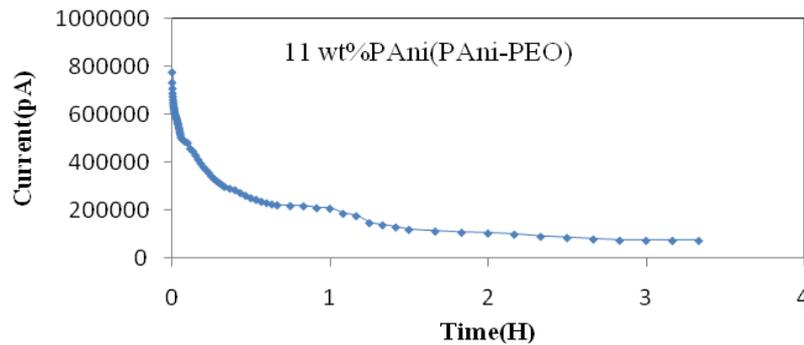
The ionic transference number was measured for all wt % of PANi-PEO blend by Wagner's polarization technique using blocking electrodes .Figure 4.5. (a-e) shows variation of current as a function of time. The total

current consists of both ionic current (i_{ion}) and electronic current (i_e). The ionic transference number was obtained by using standard formula [13]

$$t_{ion} = (i_t - i_e) / i_t \tag{1.1}$$

From figure 4.5 it has been observed that at initial time period all samples shows maximum current (i_{total}) and it start decreasing with increase in time and then it gets saturated. This maximum current (i_{total}) at the initial stage is due to the flow of both electrons and ions. The exponential decrease in current with time may be due to pile up of the ions at the silver electrode because film is sandwiched between blocking (graphite) and non blocking (silver) electrodes and constant dc voltage (1V) is established across the sample. Hence the saturated current is only due to the flow of electrons. Ionic transference numbers for all samples were found to be in the range of 0.880 to 0.998. Thus it is clear that PANi-PEO blend shows the ionic conduction. The calculated values of t_{ion} for different composite films are listed in table 1.4. From the table it appears that 9wt% sample has higher ionic transference number.





(e)

Fig4.5: (a-e) variation of current as a function of time a) 3wt% b) 5wt% c) 7wt% d) 9wt% and e) 11wt% of PANi-PEO blend.

Table 4.4: Ionic transference number for the PANi-PEO blend.

PAni-PEO blend. (Wt %)	Ionic transference number. (t_{ion})	Electronic transference number (t_{elec})
3	0.923	0.076
5	0.839	0.160
7	0.880	0.119
9	0.998	0.001
11	0.903	0.096

4.5 DC conductivity:

The variation of log of dc electrical conductivity with temperature ($\log \sigma$ Vs $1/T$) for all PANi-PEO composite films in the temperature range 308 to 328 K is shown in figure(4.6) The conductivity measurements were carried out by a two-probe method for the films of different wt% of PANi-PEO blend. From the fig 1.6 it is observed that. The dc electrical conductivity (σ) of these films increases with increase in temperature, indicating negative temperature coefficient (NTC) of resistance.

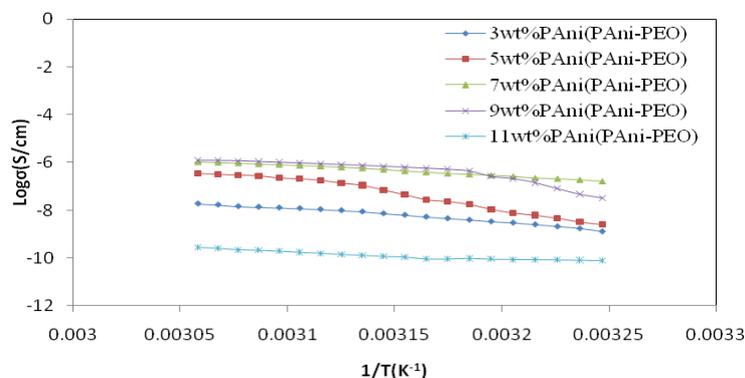


Fig4.6: Temperature dependence of dc electrical conductivity of Pani-PEO composite film of different wt %

The dc conductivity follows Arrhenius equation

$$\sigma = \sigma_0 \exp \left(\frac{-E_a}{kT} \right) \quad (1.2)$$

Where σ_0 is the pre-exponential factor, E_a is activation energy and k is the Boltzmann's constant. For the present composite films, these plots ($\log \sigma$ Vs $1/T$) show straight lines with negative slope indicating the temperature dependence of conductivity. The fig 4. 7 shows that conductivity increases with increase in wt% of PANi and is maximum for 9 wt% .Hence optimized wt% is 9wt% of PANi having conductivity value 6.78439×10^{-07} (ohm-cm⁻¹).

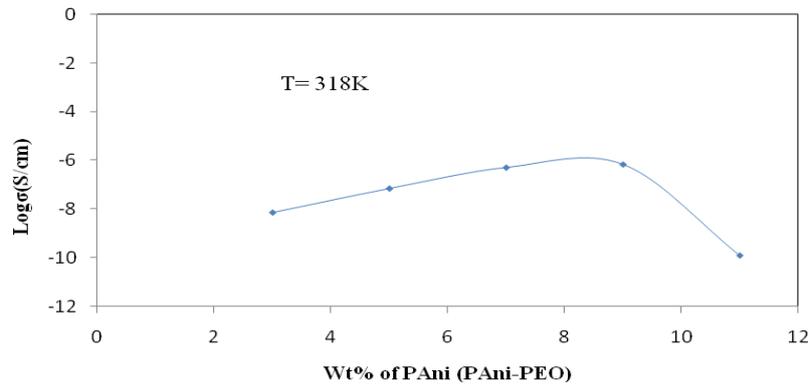


Fig 4.7: Variation of Logσ(S/cm) with wt% of PANi (PANI-PEO)blend at 318K.

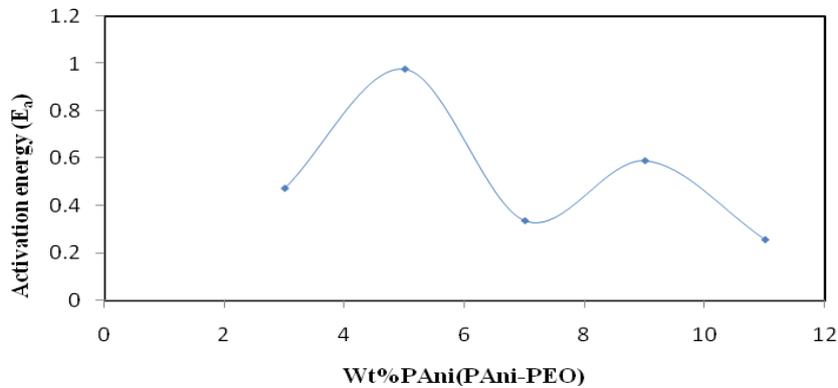


Fig 4.8: Variation of activation energy for D.C. electrical conductivity with wt% of PANi(PANI-PEO) blend.

At high temperature the activation energy of dipole segmental processes decreases due to disturbance of the cooperative movement of segments. This explains the decrease of activation energy with increase in temperature [14-15]. The activation energy is calculated from the slope of $\log \sigma$ Vs $1/T$ curve. Activation energy value are found to be in the range of 0.25 to 0.97 eV. The variation of activation energy (E_a) with different wt% of PANi of (PANI-PEO) is shown in fig 4.8. The activation energy is found to be maximum for 5 wt% of PANi. Further increase wt% of PANi decreases the activation energy and again increase and then decrease for 11 wt% of PANi.

4.5 Impedance spectroscopy:

The behavior of the film under alternating field is studied via Impedance spectroscopy. The impedance of the composite film (PANI-PEO) is measured at different temperature range (308 to 328K) in frequency range 100Hz

to 200KHz. The real (Z') and imaginary (Z'') plots of impedance are evaluated using Z and θ values. The impedance spectra are usually drawn using Z' vs Z'' to yield the Cole–Cole plot. Figure 4.9 shows the complex impedance plots (Z'' vs Z') of PANi-PEO blend with 9wt % at different temperatures. It is observed that with increase of temperature the slope of the lines decreases and their curve shift towards real (Z') axis. The inset of fig. (4.9) represents the enlarged view of Cole–Cole plot corresponding to the temperature of 45-55°C. It can be seen that the single semi-circle has been observed at all the measuring temperatures. The capacitances (C) can be calculated using the relation $2\pi f_m RC = 1$, given in Table 4.5 where f_m is the frequency corresponds to the maximum of semicircle. The radius of the semi-circle decreases with increase in temperature, which is due to the decrease in bulk resistance, i.e., increase in conductivity. The negative temperature coefficient of resistance (NTCR) is a typical behavior of semiconducting materials [16]. The value of bulk resistance is calculated by intercepting high frequency semi-circles on the X-axis at low frequency side.

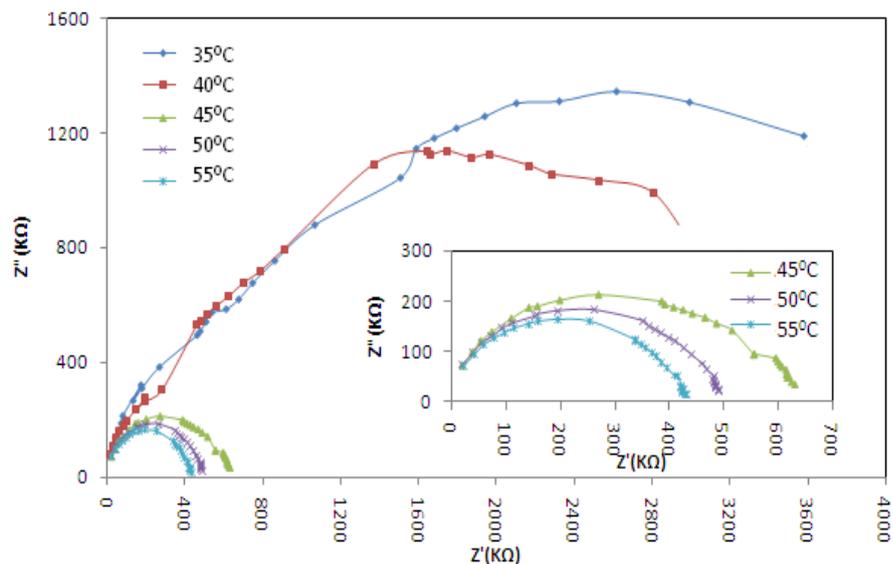


Fig 4.9: Complex impedance spectra of PANi-PEO blend 9wt% at different temperatures

Table 4.5: Capacitance values of 9wt% PANi-PEO blend for all temperature.

Sr. No.	Temperature (°C)	Capacitance(pF) 9wt% PANi (PANi-PEO) composite	Bulk Resistance (R_b) (KΩ)
1	35	133	4000
2	40	56.9	3500
3	45	76.4	695
4	50	96.5	550
5	55	108.3	490

Fig 4.10 shows the variation of the imaginary part of impedance (Z'') with frequency at different temperatures. The value of Z'' decreases with increase in temperature and shifts towards the high frequency side.

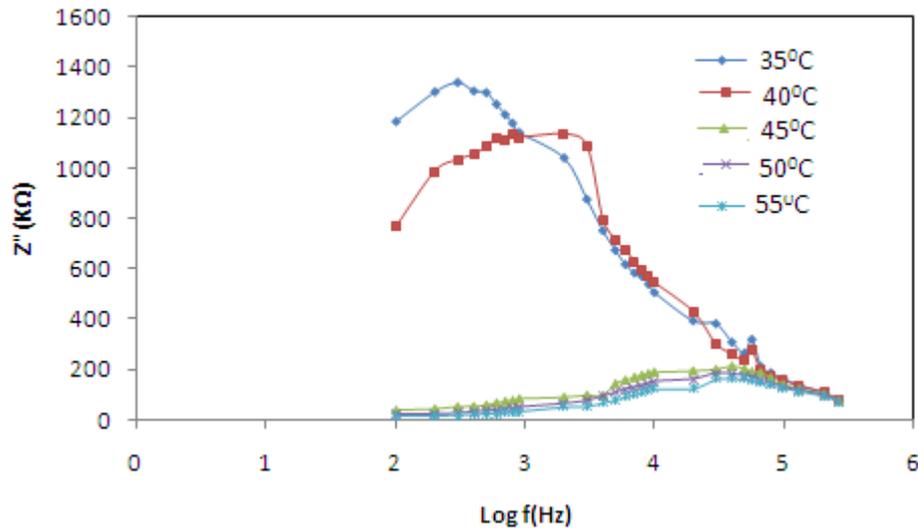


Fig.4.10: Variation of Z'' with frequency at different temperatures for 9wt% of PAni-PEO blend.

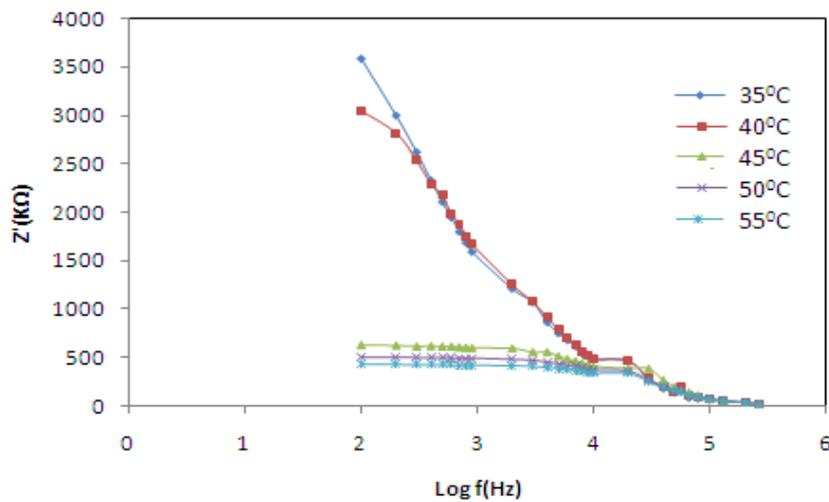


Fig 4.11: Variation of Z' with frequency at different temperatures for 9wt% of PAni-PEO blend.

Figure 4.11 shows the variation of real part of impedance (Z') with frequency at different temperatures. The curve indicates that the real part of impedance (resistance) decreases with rise in frequency, which infers that the conduction process increases with temperature and frequency. At higher frequencies all the curves merge together for the entire temperature, which attributes the release of space charge as a result of lowering of barrier properties of materials [17].

Dielectric relaxation energy and relaxation time :

When $\log f_r$ versus reciprocal of temperature is plotted a straight line is observed shown in fig 4.12.

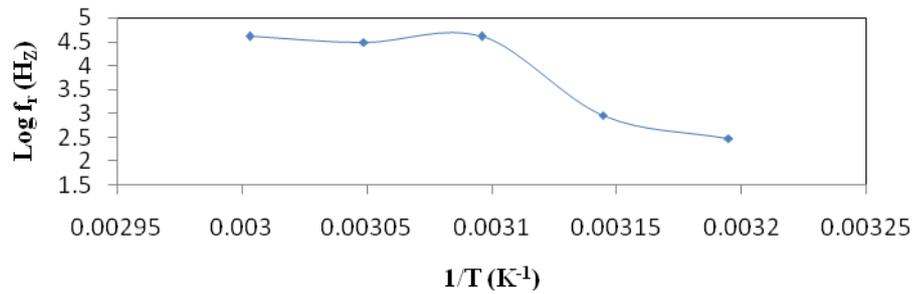


Fig 4.12: Variation of frequency with 1/T for 9 wt% of PANi(PANi-PEO) blend.

The plot is fitted with the relationship

$$f_r = f_{r_0} \exp\left(-\frac{\varepsilon}{kT}\right) \quad (1.3)$$

where ε is a Dielectric relaxation energy and K is Boltzmann's, the relaxation time (τ) of the individual PANi-PEO blend is calculated using the Cole–Cole plots by the relation

$$\tau = \frac{1}{2\pi f} \quad (1.4)$$

where f is the value of frequency for maximum peak position of Cole–Cole plot. Relaxation energy and Relaxation time is tabulated in the table 4.6

Table 4.6: Relaxation energy and relaxation time for the PANi-PEO blend.

PANi-PEO blend (wt%)	Relaxation energy (eV)	Relaxation time(S)
9	0.988	1.12×10^{-18}

V CONCLUSION

Conducting polymers have become important materials in various fields of electronics, sensors, safety devices, biomedical applications etc. The Polyaniline has already been given considerable importance among conducting polymers, because of its ease of synthesis, low cost, better environmental stability as well as other properties. For majority of applications, the achievement of processibility is importance from the industrial viewpoint. From the SEM of PANi-PEO blend, a homogeneous surface was observed with uniformly distributed particles which conclude the amorphous nature of blend. The SEM-EDX study indicates the presence of PEO and PANi. Verification of amorphous nature can also be confirmed by FTIR spectra. From the IR spectroscopy, it was noticed that, conductive blends was formed and the corresponding peak observed PANi, PEO. TGA/DTA is a type of testing performed on samples that determines changes in weight in relation to change in temperature. Thermal analysis of polymeric materials provides some basic information regarding thermal stability of material. The PANi-PEO gives two step degradation. In which, the total loss is nearly 97 %. The PANi-PEO blend indicating a thermal stability of the materials up to approximately 450 °C. The end of the decomposition is at about 500°C. from ionic transference observations it is clear that all blends shows the ionic conduction. Ionic transference numbers for PANi-PEO blend was found to be in the range of 0.880 to 0.998 Temperature dependant conductivity of PANi-PEO blend doped follows Arrhenius nature. On the basis of dc conductivity,

activation energy and pre-exponential factors are calculated. The impedance spectra of PANi-PEO films was found to consist of only one arc which may be taken to mean that the conduction processes have identical time constants. The variation of real axis Z' with $\log f$ shows negative temperature coefficient of resistance (NTCR) behavior. The variation of imaginary axis Z'' versus $\log f$ shows asymmetric peaks at different temperatures that lead to Debye type of relaxation. On the basis of impedance spectra various parameters such as relaxation time, bulk resistance, bulk capacitance, dielectric activation energy etc. are calculated.

REFERENCES

- [1.] Sreejith V. J. Polymer Science and Engg Chemical Engg Division NCL, Pune, 5(2004).
- [2.] Xiang-Wu Zhang et al. Center for Electrochemical Systems and Hydrogen Research, Texas Engineering Experiment Station, Texas A & M University, College Station, TX, USA, 31 May(2002)77843-3402.
- [3.] S.C.Raghavendra,Syed. Khasim, M. Revanasiddappam,V.N Prasad , Bull. Mater. Sci. (26)7(2003) 733–739.
- [4.] N.G. Deshpandea,c, Y.G. Gudagea, Ramphal Sharmaa,J.C. Vyasb, J.B. Kimc, Y.P. Leec, Sensors and Actuators B **138** (2009) 76–84.
- [5.] T. Abdiryim, Z.X. Gang, R. Jamal, Comparative studies of solid-state Synthesized polyaniline doped with inorganic acids, Mater. Chem. Phys. **90**(2005) 367–372.
- [6.] S. Quillard, G. Louarn, S. Lefrant, A.G. MacDiarmid, Vibrational analysis of polyaniline: a comparative study of leucoemeraldine, emeraldine, and pernigraniline bases, Phys. Rev. B **50** (1994) 12496–12508.
- [7.] Hechavarría, Hailin Hu*, Marina E. Rinco'n,J. Thin Solid Films **441** (2003) 56–62 .
- [8.] F.M. Gray, Solid Polymer Electrolytes, Fundamentals and Technological Applications. ScotlandVCH Publishers Inc, (1991)
- [9.] Mustafa Türk1, Zakir M. O. Rzayev, Gülcihan Kurucu, HEALTH 2 (2010) 51- 61.
- [10.] K.Balachandaran, Dr.R.Venckatesh, Dr. Rajeshwari Sivaraj, International J .Engineering Science and Technology (IJEST) **3** (2011)4200-4203.
- [11.] M. Türk ,M.O.Zakir, G.Kurucu , HEALTH 2 (2010) 51-61.
- [12.] C. H. Manoratne ,R.M.Rajapakse,M.A.Dissanayake, J. Electrochem. Sci, **1**(2006)32-46.
- [13.] T.K.Vishnuvardhan, V.R.Kulkarni, C. Basavaraja, S. C. Raghavendra, Bull.Mater. Sci. **29** (1) (2006) 77-83.
- [14.] H.C.Shinha and A.P.Shriwastav, Indian J. Pure Appl. Phys. **17** (1979) 726.
- [15.] A.R.Tiwari, K. K. Saraf and A.P.Shriwastav, R.Nath, Electrical and Optical Behavior of Solids, 187.
- [16.] J.Rose MacDonald, Impedance Spectroscopy: Emphasizing Solid Material and System, John Wiley & Sons, NewYork, (1987).
- [17.] A. Shukla, R.N.P. Choudhary, A.K.Thakur, D.K.Pradhan, Physica B **405** (2010) 99.