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HCl doped PVA/ PAni Blends: DC conductivity studies

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ABSTRACT

PVA/PAni blends of various compositions starting with 90/10 was prepared and was doped with HCl. The UV-Vis spectroscopy showed the two characteristic peaks at 330nm and 560nm in addition to a higher wavelength shoulder showing strong protonation. The DC conductivity measurements from room temperature to 110° C using two-probe technique showed decrease in resistivity by an order of magnitude in the case of doped sample as compared to their undoped samples.

Key words: PVA/PAni blends, doping, Uv-Vis spectrometry, DC conductivity, percolation threshold.

INTRODUCTION

Since the days of Hideki Shirakawa and co-workers at the University of Tsukuba, Japan utilized the Zeiger-Natta polymerization technique to prepare high quality films of polyacetylene, a lot of investigations have been carried out on the new generation of materials due to their unique combination of electronic and optical properties[1-2]. Electrical conductivity is achieved in the conjugated polymers by means of delocalisation of the π-electrons that allow charge mobility along the backbone of the polymer chain.

Various applications of conducting polymers in diverse fields have been proposed as transducers for biosensor [3], electrodes of rechargeable batteries [4], artificial nerves and muscles [5], gas sensors [6], solid electrolytic capacitor, diodes and transistors [7], anti-static electromagnetic shielding [8], and biomedical applications [9].

Through the combination of conventional polymers with conductive polymers the mechanical properties of conducting polymers can be improved. The insulating polymer removes the brittleness and lack of processability that are the main drawbacks hindering conducting polymers. In blend applications it requires that conductivity is achieved at a small weight fraction of conducting polymer. There is also an increased requirement for polymeric materials whose electrical conductivity can be tailored. The combination of conventional polymers with conductive polymers or fillers is an important alternative to obtain new polymeric materials with designed properties.

Polyaniline (PANI) continues to attract considerable attention because its electrical and optical properties that can be changed by oxidation and protonation of the amine nitrogen atoms. PANI is known for its excellent thermal and environmental stability but poor processibility due to insolubility and brittleness that limits its commercial applications. The strong affinity of Polyaniline for water has motivated many groups to investigate the compatibility of PAni with water soluble polymers like PVA and Carboxy methyl cellulose.

MATERIALS AND METHODS

Materials

Ammonium Persulphate and aniline were purchased from Qualigens Fine chemicals, Mumbai. Hydrochloric acid was purchased from SD fine chemicals, Mumbai. Poly vinyl alchol (PVA) was purchased from Aldrich chemicals. All materials were used without further treatment.

Preperation of Polyaniline- PVA composite

The poly aniline composites were prepared using methods similar to the ones in previous reports. [10,11,12]. Chemical polymerization of aniline is carried out in aqueous 1M acidic media containing 10% PVA. The acidic solution of PVA is maintained at -3 to 0°C. Aniline of various concentrations were added to this and stirred vigorously. While the sample is being stirred, ammonium per sulphate of same molar ratio as aniline is added drop by drop over a period of 1 hr. The solution turned green indicating the formation of polyaniline and the reaction mixture was stirred continuously for a period of 6 hrs maintaining at the same temperature. In order to remove the unreacted chemicals such as monomers and oxidants, the polymer solution was dialyzed against distilled water for 48 hrs . Various wt/ wt compositions of PVA/ Polyaniline such as 90/10, 85/15, 80/20, 75/25, 70/30 were prepared using the above method. Stand alone films were prepared by casting the green suspension into petridish and is left for drying at room temperature. PVA/PAni composite films were doped by immersing in 1:1.2 HCl –Acetone solution for 1hr. The film was then placed between two sheets of filter paper and was left for drying at room temperature. [13].

UV- Vis Spectroscopy

The creation of mid-gap state in the conducting polymers due to charge transfer complex formation due to doping can be studied by UV-Visible spectroscopy. It can also be used to detect the homogeneity of the polyaniline blend. The homogenous blends will show the increasing intensity for the characteristic absorption bands for polyaniline with the increase in PAni content.

UV-Visible spectroscopy was done using the "Systronics spectrometer" sweeping the incident wavelengths from 999.9nm to 300nm.

Conductivity measurements

The dc conductivity measurements were carried out by using a two-probe technique. Conductivity measurements were done for the films of different compositions of PVA/PAni blend with and without dopant ions by varying temperature from room temperature to 110°C.

RESULTS AND DISCUSSION

Synthesis of PVA/PAni blend:

A single route *in-situ* polymerization method was employed to synthesis PVA/PAni composite in the presence of hydrochloric acid (HCl).

UV-Visible spectra:

The conducting emeraldine salt form in water has 2 characteristic absorption bands at 420nm and 800nm owing to the radical cation (polaron) state formed on the PAni backbone chain (Figure 1).The peaks 330nm corresponds to the polaron transition bands after doping and corresponds to the localization of electrons. The peak 560nm of electrons corresponds to the strong peak which gives the evidence of strong protonation. There is also a broad shoulder seen to this peak with increase in PAni content in all the samples. PVA does not have any bands of interest in this region.

Conductivity Measurements

The PVA and PAni are both hygroscopic in nature and the presence of adsorbed water and its removal may cause structural changes in the polymer chains. Therefore, while studying the temperature dependence of the conductivity initially the sample has been heated to above 110°C and maintained there for a small time and then it is cooled and readings are taken while cooling so as to remove the adsorbed water. The sample was not further heated as it was observed by many researchers that slight decomposition of PVA takes place over 130° C [14]. The mild annealing that the samples might receive, will help the PAni to experience more ordering. The change of chain structure by thermal treatment and interchain interaction between the two components will have an effect on the morphological changes. During the annealing process, the intermolecular spacing between adjacent chains of the blends decreases [15]. All these will aid the conductivity increase in the sample. The annealing process cannot be taken up above this temperature, as it may also lead to the condensation reaction of –OH groups with the protons of –Cl groups and acid catalysed dehydration of PVA occur after thermal treatment at 150° C. Therefore, a permanent thermal undoping occurs, accompanying a loss of polarons and hence reduction in conductivity [16].

In polyaniline matrix, nitrogen has one pair of electron and when the acid is doped in matrix, a bond formation between the H^+ and nitrogen takes place. This bond formation is responsible for the increased value of electrical conductivity of the doped polyanilines [17,18].

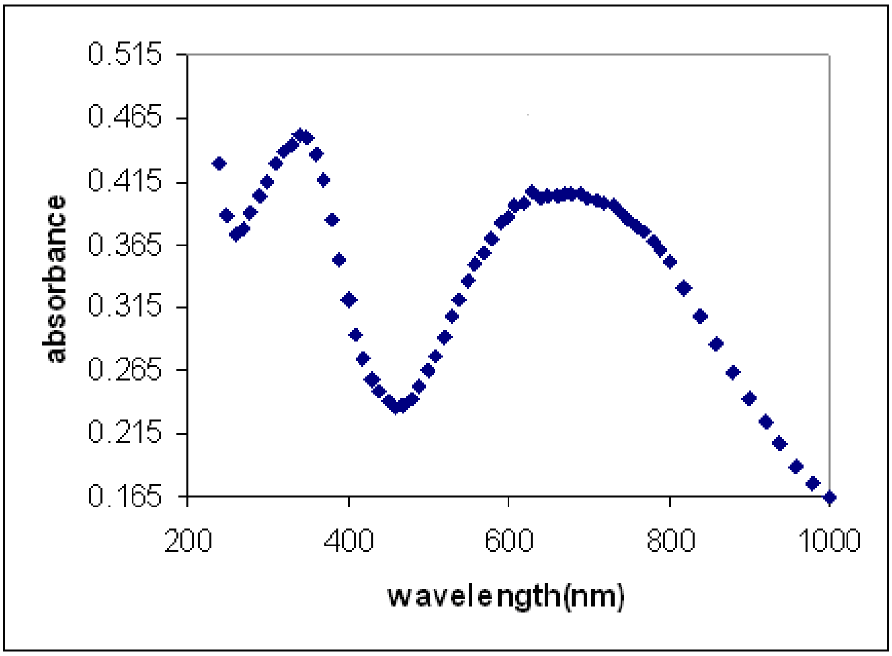

Figure 1: Absorption band of 70/30 PVA/PAni blend

In Figure 2, the variation of resistivity with temperature of one of the compositions (70/30) is shown. It shows that, at all temperatures the resistivity (ohm-cm) of the undoped samples is higher than the corresponding doped samples. In a similar fashion the resistivity has decreased in the doped samples for all blends considered for the study.

In figure 3, it is clearly indicated that the resistivity of the various compositions of undoped PVA/PAni blend is in the order of $10^5 – 10^6$ (ohm-cm) at room temperature. Such an order of magnitude was bserved by some observers . All the samples reaches a saturation stage at around 70° C to 100° C. Above 110°C there is a drastic decrease seen in the resistivity which could be due to the onset of flow or degradation.

From the figure 4 it can be seen that the order of the resistivity of all the samples have decreased by 1 as compared to the undoped PVA/PAni blend. It is observed that the maximum value of σ_{dc} reaches a saturation at roughly 15% PAni with HCl which implies Percolation threshold is attained at below 15% doping. The good conductivity changes in the polymer blends indicate that there are connected pathways existing in the polymer blends. These pathway formation can be further established by looking at the morphology of the samples through an SEM or TEM. At low % of PAni doping the network formation may not be continuous. As the doped PAni weight fraction increases, the interconnected network density increases and hence the conductivity increases or resistivity decreases. According to Pallab Banerji [19], the PAni Particles are directly involved in the formation of the globules of network in the poly blend. The network is found to be considerably empty with nanoparticles pervading through it. It is clear that the particles are involved in making the bridge in the network. Yang et al.,(1993), has suggested that the morphology observed for the solution processed blends is drastically different from usual filled polymers in which conducting particles are dispersed into non-conducting matrix polymers [16]. The electrical conductivity of such systems is supposed to turn on sharply at a volume fraction (f) of conducting particles corresponding to the percolation threshold f ~ 0.16 for conducting globular particles in an insulating matrix. This is very well evidenced by the decrease in resistivity (or increase in conductivity) as can be seen from the 90/10 PVA/doped PAni composites [20]. As concentration increases the conductivity increases sharply. This is called percolation threshold. The conductivity becomes finite as (f) increases. Further above the percolation threshold as the number of connecting paths increases conductivity becomes finite. This is also well seen with the increase in the conductivity of 85/15 PVA/doped PAni blends and then a saturation effect.

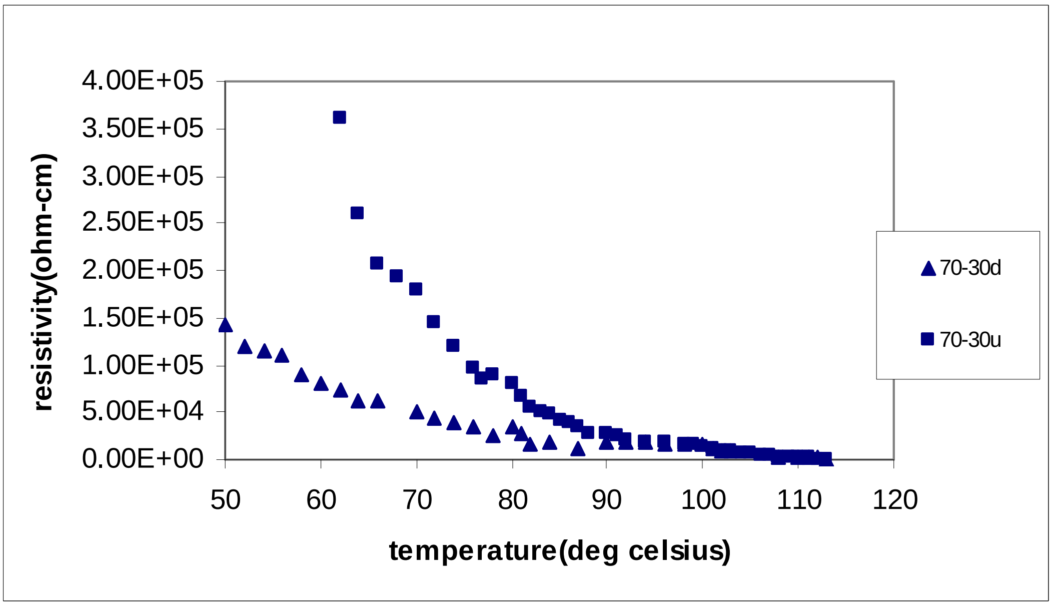

Figure 2: Resistivity Vs temperature of 70/30 doped (70-30d) and undoped (70-30u) films

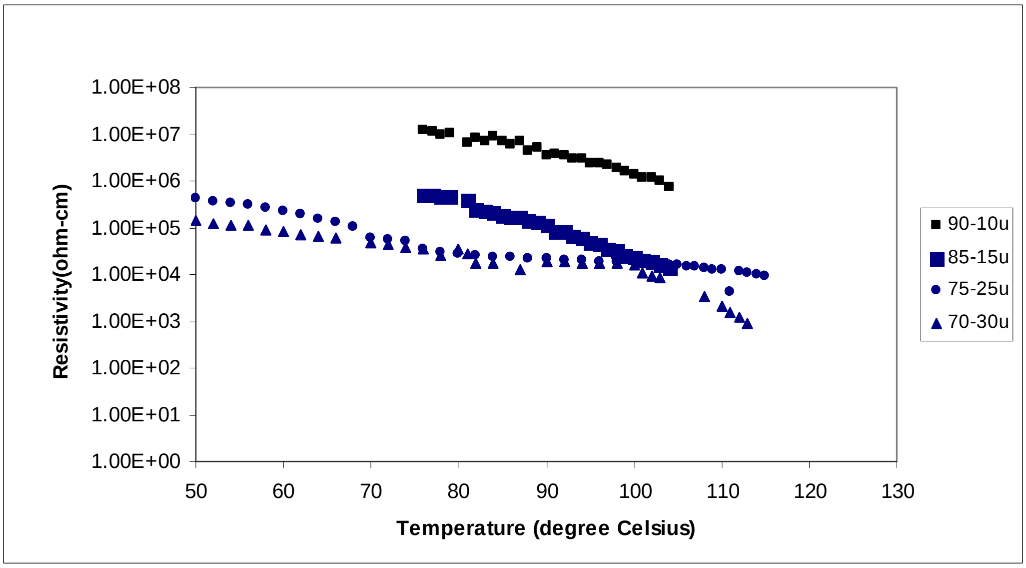

Figure 3: Variation of resistivity vs temperature of all undoped films of PVA/PAni blend

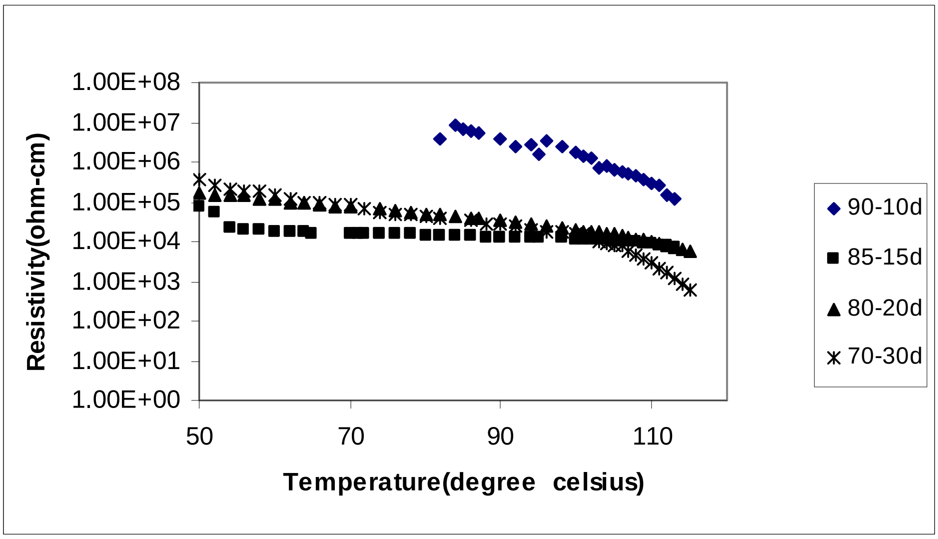

Figure 4: Variation of resistivity vs temperature of all doped films of PVA/PAni blend.

The conductivity is also determined by various factors such as MW(molecular weight) of both the polymer in blends, the viscosity of the polymer blend solution, the drying temperatures, the mode of drying etc [21]. As PAni content increases there is an increase in the conductivity which could be due to large particle size of doped PAni embedded in the matrix. The higher percentages of PAni and doped PAni was not attempted as the samples were brittle and hence leading to a lower processability of the sample.

CONCLUSION

Samples are successfully prepared and UV –Vis spectrophotometry confirms the polymerization and doping. The samples show increase in conductivity at higher doping concentration. The increase in conductivity can be explained on the basis of percolation theory and it is observed that the percolation threshold is reached at a lower value of doped PAni as compared to the available literature which suggests a value of percolation threshold (f = 0.16).

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