



Investigation of Dc-Conductivity and Morphology of PMMA/PANI Composite

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Abstract: Various inorganic acid doped PMMA/PANI composite are prepared by *in-situ* polymerization technique. Morphology, room temperature (RT) conductivity and DC-conductivity with temperature variation (77-300 K) are analyzed by scanning electron microscopy (SEM) and linear four probe technique, respectively. Fibril structures with different diameter are observed in doped PMMA/PANI composite, whereas smooth texture is found in PMMA polymer film. Room temperature DC conductivity is found 0.1497×10^{-2} S/cm for H₂SO₄-and 0.309×10^{-3} S/cm for H₃PO₄-, 0.244×10^{-3} S/cm for HCl-doped conductive composite, respectively. Temperature dependent DC Conductivity is measured and it behaves like semiconductor.

Keywords: PMMA, PANI-ES, Dopant, Conductivity, Organic semiconductor.

1. Introduction

It is well known that intrinsic conducting polymers (ICPs) have considered much more scientific community interest over the last few years due to potential commercial applications in different fields such as electrochromic devices, light emitting diodes supercapacitors, rechargeable batteries, sensors, corrosion inhibitors and artificial muscles [1-7]. Polyaniline (PANI) is a member of ICPs family. It has both good thermal and environmental stability coupled with easy processable and doping-dedoping mechanism [8]. In spite of above advantages, PANI has poor processability due to insolubility and brittleness limits for its commercial applications. PANI can be made more processable in the composite form with electroactive polymer which is act as stabilizer [9]. Now a day, a variety of PANI composite have been studied using many types of synthetic electroactive polymers such as poly (methyl methacrylate), polyvinyl chloride, polystyrene, and polyurethane [10-13]. Poly (α -hydroxy acid), polylactide (PLA), polyglycolide and their co-polymers have been widely used in tissue engineering because of their good biocompatibility, mechanical properties, bioresorbable degradation products and adjustable degradation rate [14-16]. The efficient polymerization of aniline was achieved only in acidic medium. A variety of inorganic acids at same concentration have been used in the synthesis of PANI; resulting PANI-salts, protonated with various acids,

differs in solubility, conductivity and stability [17]. Till now, it is difficult to understand the mechanism of its structural, thermal, magnetic and electrical properties of conducting polyaniline. So a lot of research has been devoted. Jing Li and co-workers [18] proposed a variable range of hoping (VRH) model which described the transport mechanism of HCl-doped and DBSA-doped PANI. Atul Kapil et al [19] analyzed transport mechanism by Arrhenius model, variable range hoping (VRH) model and Kivelson model over wide range of temperature 30-300K. Nadra Bohli [20] suggested the conduction mechanism of PANI organic film in the temperature range 100-300K. Y. Long and co-workers used variable range hoping (VRH) and charge energy limited tunneling (CELT) models to explain conductive property of PANI [21].

In this work, PMMA/PANI composite doped with different inorganic acid *i.e.*, HCl, H₂SO₄ and H₃PO₄ are prepared by oxidation-polymerization process using aniline, PMMA film, ammonium persulphate (APS) with appropriate amounts of water as precursors. DC conductivity (σ) is estimated in both low- and room-temperature. Morphological analyses of composites are explored.

2. Experimental Details

2.1. Chemicals and Materials

Laboratory grade aniline, ammonium persulphate (APS) ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) sulphuric acid (H_2SO_4), ortho-phosphoric acid (H_3PO_4), chloroform (CHCl_3) diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$) are purchased from Merck, India. Deionized water is used during the preparation of composite. Poly (methylmethacrylate) (PMMA) is used as base materials.

2.2. PMMA/PANI Composite Preparation

CHCl_3 solvent is poured into a beaker (100 ml), which is contained PMMA Polymer. The mixtures are stirred for 3 h and a soluble mass is formed. The mass is cast into petridish (diameter~10 cm). Films are formed after solvent evaporation. It is removed from petridish and is cut into small pieces (1.5 cm \times 1.5 cm) *i.e.*, square sized. Thickness of film is 0.2 cm.

PMMA /PANI composite are prepared by chemical-oxidation polymerization process from aniline monomer coupled with base materials at room temperature. Two type of solution is prepared during the composite preparation. Former one is monomer solution

and later one is oxidant solution. During the preparation of monomer solution, 105 ml of 1 (M) H_2SO_4 solution with 3 mL of aniline is taken and square sized PMMA films are dipped into the solution. The solution is stirred continuously (10 h) in a magnetic stirrer (800 rpm). Oxidant solution is prepared using 7.47 g ammonium persulphate and 60 mL of 1 (M) H_2SO_4 solution. It is added drop wise to the monomer solution with continuous stirring. The polymerization process is carried out. The color of PMMA film(s) is becomes light green to dark green. The reaction mixture is maintained under stirring for 10 h. The resulting composite is washed with deionized water several times. The wet PMMA/PANI films are dried in heating oven in a 60 $^\circ\text{C}$ for 6 h [22]. For comparison study, doped- H_3PO_4 PMMA/PANI composite are also prepared under similar conditions.

3. Characterization Techniques

Surface morphology of PMMA polymer film, PANI, and PMMA/PANI composite are analyzed by scanning electron microscopy (Carl Zeiss Supra 40). Samples are coated with gold before the measurement.

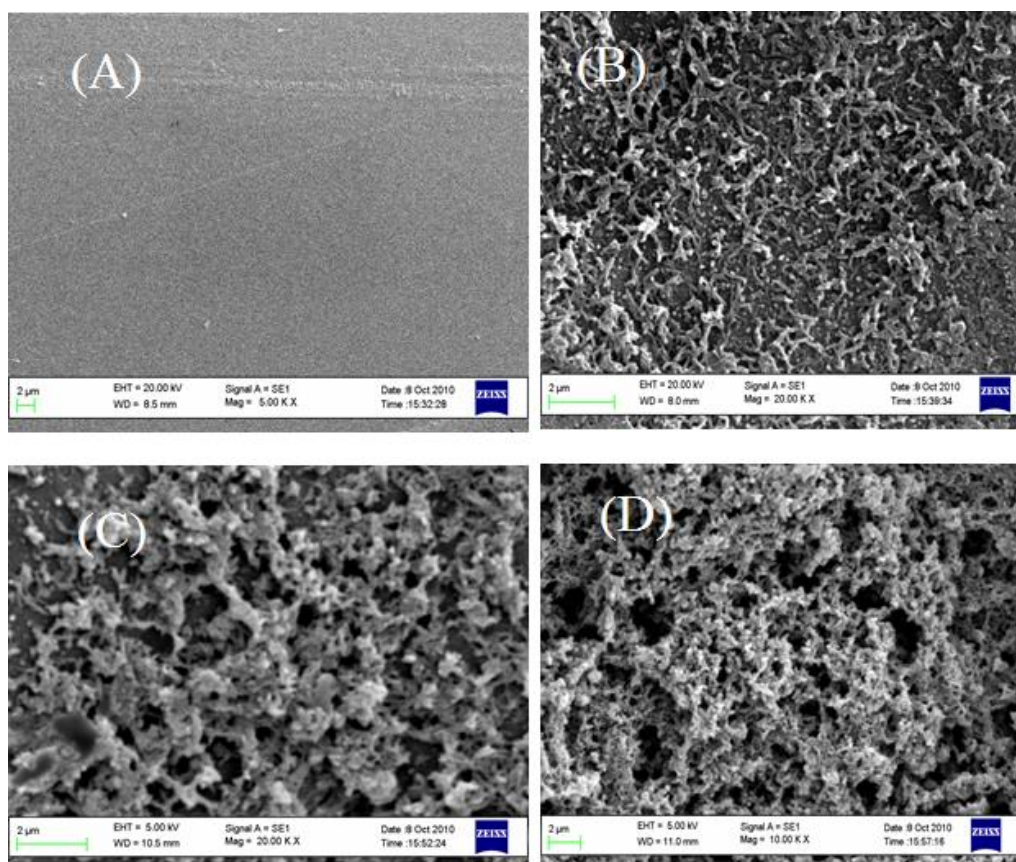


Figure 1 FESEM images of PMMA polymer film (A), 1 M HCl doped PMMA PANI composite (B), 1 M H_3PO_4 doped PMMA PANI composite (C), and 1 M H_2SO_4 doped PMMA PANI composite (D)

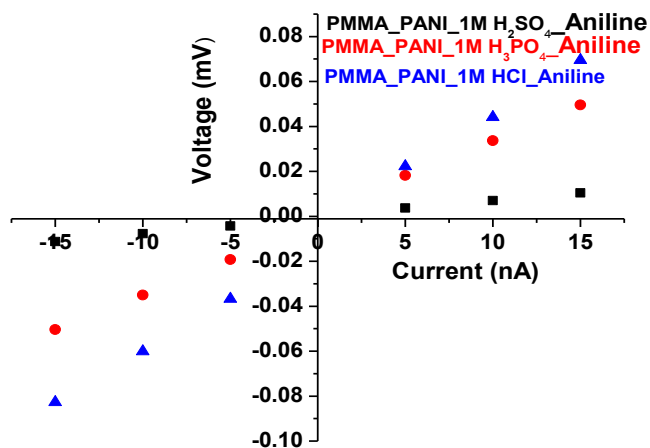


Figure 2 I-V characteristics of PMMA/PANI Composite (1 M H₂SO₄) (A), PMMA/PANI Composite (1 M H₃PO₄) (B), PMMA/PANI Composite (1 M HCl) (C)

Table 1 Room Temperature DC Conductivity of doped PMMA/PANI Composite

Doped PMMA/PANI Composite	Conductivity (S/cm)
1M HCl PMMA/PANI Composite	0.244×10^{-3}
1M H ₂ SO ₄ PMMA/PANI Composite	0.1497×10^{-2}
1M H ₃ PO ₄ PMMA/PANI Composite	0.309×10^{-3}

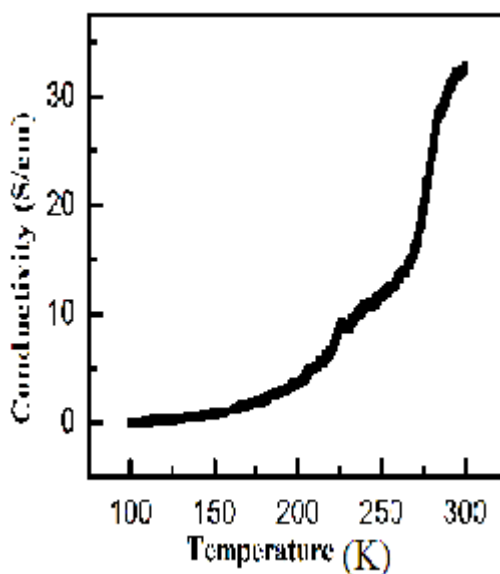


Figure 3 Temperature dependent DC Conductivity

DC-conductivity of the conducting samples (at room temperature and low to high temperature) is measured using a linear four-probe technique. DC-conductivity are calculated using the relation $\rho = 2\pi S (V/I)$ where S is the probe spacing (mm), 'I' is the supplied current (nA) and 'V' is the corresponding voltage (mV). The conductivity (σ) is calculated using the expression $\sigma = 1/\rho$.

4. Results and Discussion

SEM images for pure PMMA polymer film and doped PMMA/PANI Composites are shown in Figure 1. Smooth texture is observed in Figure 1A, whereas fibrous structures are showed in all doped PMMA/PANI Composites. Three dopants viz., HCl, H₂SO₄ and H₃PO₄ are used to prepare doped PMMA/PANI Composites. It is also found that size and formation probability of PANI is strongly dependent on dopant strength, structure and

reaction conditions. Moreover, the diameter size of PANI nano-fibrous is affected by dopant structure. Average (av.) diameters of PMMA/PANI composites are found to be 178 nm, 152 nm, and 165 nm, respectively. The diameter is related to aspect ratio *i.e.*, surface area/volume. The surface area of nanofibers increases as the average diameter of nanofibers decreases. It could be important, particularly for gas sensor application.

I-V Characteristics of HCl-, H₂SO₄- and H₃PO₄-doped PMMA/PANI composites are plotted and is shown in Figure 2. In Figure 2, voltage (mV) is linearly related with current (nA), which is passes through origin. This is the indication of ohmic behaviour [xxx]. DC conductivity of doped composites is presented in Table 1. It is cleared from the Table 1 that the DC conductivity of H₂SO₄-doped PMMA/PANI composite showed 0.1497×10^{-2} S/cm higher than other doped PMMA/PANI composites.

H₂SO₄ dopant has bigger size counter ion and higher strength than other two dopants. Therefore, H₂SO₄ exert less force against ordering and closing of PANI chains leading to higher compactness of PANI chains. The compactness is a favorable factor for intermolecular mobility of charged species along the chain and some extent inter molecular hopping because of better and closer packing and hence, higher conductivity than the latter's [22, 23].

Figure 3 shows the temperature dependence DC Conductivity of H₂SO₄- doped PMMA/PANI composite.

It is evident from the Figure 3 that the conductivity increases with increase in temperature. The composite represent temperature dependent conductivity. This behaviour is similar to a semiconductor. Hence, the composite is called organic semiconductor.

5. Conclusions

PMMA/PANI composite uses HCl, H₂SO₄ and H₃PO₄ as dopants are prepared by *insitu* polymerization technique. The entire prepared composite are shown nonofibriles structure having average diameter 178 nm for HCl doped PMMA /PANI composite, 153 nm for H₂SO₄-doped PMMA /PANI composite, and average diameter 163 nm for H₃PO₄-doped PMMA /PANI composite. As prepared conducting composites show ohmic behaviour at room temperature. Highest room temperature DC conductivity is found to be 0.1497×10^{-2} S/cm for H₂SO₄-doped PMMA/PANI composite. Temperature dependent of conductivity indicate the organic semiconductor.

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Conflict of interest

The Author has no conflicts of interest to declare that they are relevant to the content of this article.

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