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Doping and Irradiation Dependence of Electrical Conductivity of Fe^{3+} and Ni^{2+} Doped Polyvinyl Alcohol Films

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PVA and doped PVA films were prepared by solution casting. The Change in electrical conductivity of pure PVA and transition elements $FeCl_3$ and $NiCl_2{\cdot}6H_2O$ doped PVA films with and without γ-irradiation in the temperature range 50–130 ℃ has been investigated using four point probe technique. The dc electrical conductivity increases with increase in dopant concentration, with temperature and γ-irradiation. The results revealed that γ-irradiation enhances the electrical conductivity. The variation of electrical conductivity σ with temperature, before and after irradiation is due to the intermolecular hydrogen bonding between Fe^{3+} with OH group of PVA and Ni^{2+} with OH group of PVA. We found that Fe^{3+} doped PVA films show higher conductivity than Ni^{2+} doped PVA films.

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1. Introduction

Considerable attention has been focused recently on the synthesis of conducting organometallic polymers. One of the most interesting areas of metal-containing polymers is that of electrically conducting organometallic polymers. The most promising conducting polymer should demonstrate good solution or melt processability, in addition to environmental stability, mechanical integrity and controllable conductivities. Because the ability to tailor the electrical properties of these materials is one of the most attractive features and coupled with improved stability and processability relative to the original conducting polymer systems. Applications of these polymers include Remotely Readable Indicators, Biosensors, Storage Battery and Fuel Cell Electrodes, Capacitors, Electrochromics, Chemical and Biochemical Sensors, Ion Exchange release devices and Neutron detection.

A vinyl polymer, namely polyvinyl alcohol (PVA) is semicrystalline, water soluble, and low electrical conductivity material [1]. PVA exhibits certain physical properties resulting from crystal-amorphous interfacial effects [2, 3]. Electrical conductivity of PVA can be tailored to a specific requirement by the addition of suitable dopant material. Depending on the chemical nature of the doping substances and the way in which they interact with the host matrix, the dopant alters the physical properties to different degrees [4–8]. The method of choice for producing conducting organometallic polymers involves complexing transition metals with conjugated bridging ligands. The ability to alter the oxidation state of the metal ion, and thus the charge density along the polymer backbone, provides an alternative route to charge carrier creation as opposed to redox doping. Its electrical conductivity depends on the thermally generated carriers and the addition of suitable dopants [9, 10]. In addition, γ-irradiation has become one of the most common process to change the electrical conductivity in polymers [11–14]. In this regard we have made an attempt to study the electrical conductivity of pure PVA, Fe^{3+} and Ni^{2+} doped PVA films. Authors are also interested to know the influence of Fe^{3+}/Ni^{2+} on PVA film in answering better electrical conductivity.

2. Experimental

2.1. Preparation technique

The PVA, $FeCl_3$ and $NiCl_2{\cdot}6H_2O$ used in this work have been taken from Sigma–Aldrich company. PVA, PVA: Fe^{3+} and PVA: Ni^{2+} organometallic polymers films were prepared at room temperature by solution casting method. A known quantity of PVA was dissolved in double distilled water and then heated gently, using a water bath to prevent thermal decomposition of polymer. The hot solution was stirred until the polymer is completely dissolved and forming a clear viscous solution. This is called PVA stock solution. Also required quantity of $FeCl_3$ and $NiCl_2{\cdot}6H_2O$ was dissolved in doubly distilled water to get the desired concentrations (10, 15, 20 mol%) and mixed with PVA stock solution, stirred thoroughly with a magnetic stirrer. The PVA: Fe^{3+} and PVA: Ni^{2+} solutions were filtered to remove air bubbles trapped in the solution while stirring and kept aside for required amount of duration to get proper viscosity. Known quantity of obtained solution was poured on to a leveled clean glass plate and left to dry at room temperature. After 48 h, the films were peeled off from the glass plate and kept in vacuum decicator for further study [15]. The peeled film was cut into pieces of suitable size for measurements.

The samples were irradiated for different dosages of γ-rays using $^{60}C_0$ ($T_{1/2} = 5.26$ yrs) at room temperature.

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2.2. Measurement technique

The dc electrical conductivity σ of pure PVA, Fe^{3+} and Ni^{2+} doped PVA films with and without γ-irradiation has been studied in the temperature range 50–130 °C using four point probe technique. The conductivity of the films has been measured by taking current values as a function of temperature using a constant voltage source.

3. Results and discussion

The doping, temperature and irradiation dependence of dc electrical conductivity σ was studied for the pure PVA, Fe^{3+} and Ni^{2+} (10, 15, 20 mol%) doped PVA films, for the irradiation dosages 300 CGY/min, 600 CGY/min and 900 CGY/min. The variations of $\log(\sigma)$ *vs.* $1/T$ for all the films were studied. It has been observed that dc conductivity increases with increase in dopant concentration, temperature and γ-irradiation. Figures 1a and b represent the plots of $\log(\sigma)$ *vs.* $1/T$ for pure PVA and Fe^{3+} and Ni^{2+}(10 mol%) doped PVA films. Figures 2a and b represent the plots of $\log(\sigma)$ *vs.* $1/T$ for pure PVA and Fe^{3+} and Ni^{2+} (15 mol%) doped PVA films. Where as Figs. 3a and b represent the plots of $\log(\sigma)$ *vs.* $1/T$ for pure PVA and Fe^{3+} and Ni^{2+} films containing 20 mol% of the dopant.

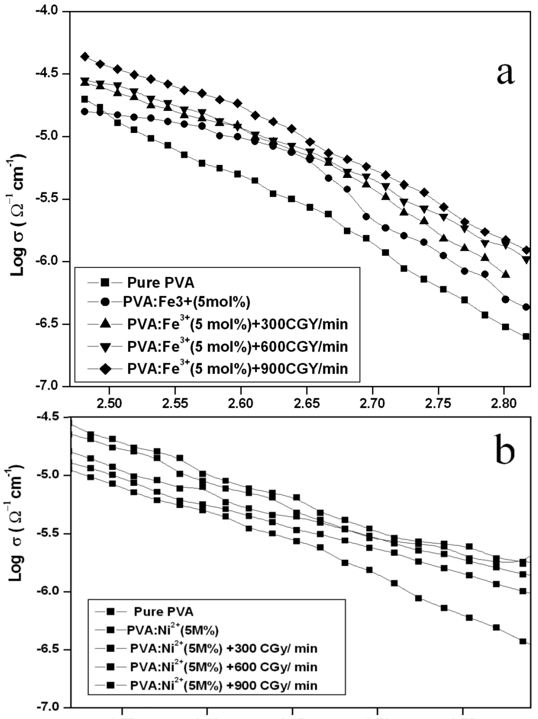

Fig. 1. (a) represents the plots of log σ *vs.* $1/T$ for pure and PVA: Fe^{3+} (5 mol%) films; (b) represents the plots of $\log(\sigma)$ *vs.* $1/T$ for pure and PVA: Ni^{2+} (5 mol%) films.

The electrical conductivity σ of pure PVA film is less than that of the transition metal ions doped PVA films. The electrical conductivity σ increases with dopant concentration. The induced conductivity in Fe^{3+} and Ni^{2+} doped PVA is shown to be dose dependent and can be attributed to the creation of induced charge carriers in the PVA matrix as shown in Figs. 1a–3b. This is because of the dopant ions Fe^{3+} and Ni^{2+} ions coordinated through ionic bonds with hydroxyl group belonging to the different chains in PVA [16]. Addition of dopant results in the reduction of the intermolecular interaction between the PVA molecules or the addition of Fe^{3+} and Ni^{2+} increases the volume required for ionic carriers to drift in the polymer matrix. This enhances the ionic mobility and hence increases the conductivity. The dopant dependence of electrical conductivity σ of PVA: Fe^{3+} and PVA: Ni^{2+} (20 mol%) at 387 K are shown in Table I. Ionic clusters will be formed if the dopants are not distributed homogeneously the dispersed ions will result in less conductive or insulating polymer matrix. Appreciable ionic conductivity is observed only when a critical volume fraction of the ionic conducting clusters is reached and material actually undergoes an insulator to conducting transition. As the volume fraction of the dopant increases, there is initially very little change in the polymer resistance. At this point the highly conductive clusters are well separated and do not form continuous path through the polymer. At this stage the resistance of the doped polymer is controlled by

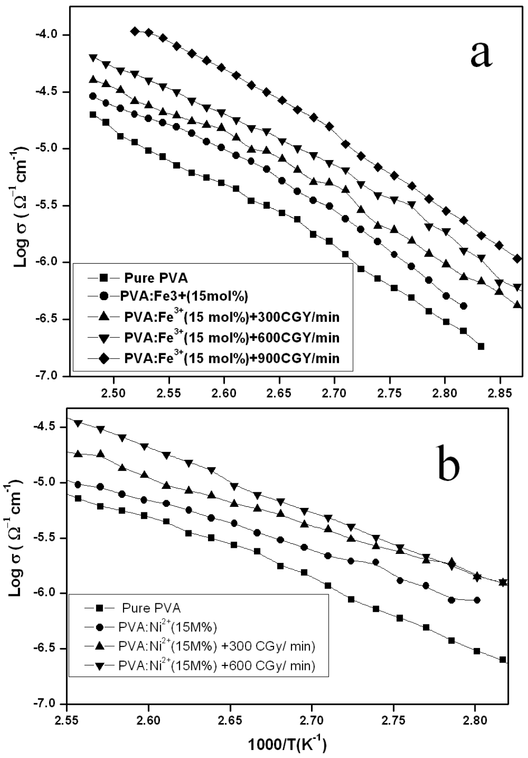

Fig. 2. (a) represents the plots of $\log(\sigma)$ *vs.* $1/T$ for pure and PVA: Fe^{3+} (15 mol%) films; (b) represents the plots of $\log(\sigma)$ *vs.* $1/T$ for pure and PVA: Ni^{2+} (15 mol%) films.

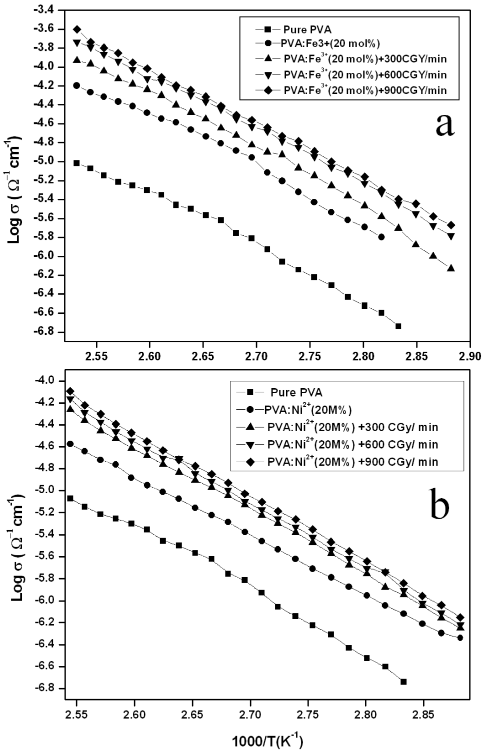

Fig. 3. (a) represents the plots of $\log(\sigma)$ *vs.* $1/T$ for pure and PVA: Fe^{3+} (20 mol%) films; (b) represents the plots of $\log\sigma$ *vs.* $1/T$ for pure and PVA: Ni^{2+} (20 mol%) films.

the poorer conducting phase. At a critical volume fraction of the dopant, the highly conductive phase forms a continuous path across the polymer and gradual decrease in resistance occurs.

TABLE I

Dopant dependence of electrical conductivity σ of PVA; Fe^{3+} and PVA: Ni^{2+} at 387 K. Pure PVA is 5.5795 $\mu\Omega^{-1}$ cm^{-1}.

Fe^{3+} and Ni^{2+} Concentration	σ [$\mu\Omega^{-1}$ cm^{-1}] at 371 K	
	Fe^{3+}	Ni^{2+}
PVA + 5 mol%	10.0936	6.0687
PVA + 15 mol%	16.9121	8.9350
PVA + 20 mol%	38.4604	17.3837

Doped PVA films showed higher conductivity than undoped film and conductivity increases with film temperature. The temperature dependence of electrical conductivity σ of pure and Fe^{3+} and Ni^{2+} doped PVA films are shown in Figs. 1a–3b and the values are given in Table II. The result obtained in the present work is of the same order as it is reported in the literature [17].

The electrical conductivity of pure PVA films and doped PVA films is less than that of the γ-irradiated films. This can be observed in the Figs. 1a–3b. The dependence of dc conductivity on the γ-dose might be explained as follows. At the beginning, the conductivity is due to the presence of dopants, the γ-dose would result in an increase in the number of charge carriers created. This can be explained on the basis, that irradiation of polymer is to rupture the ionic bonds and release of ions, electrons and free radicals which are able to migrate through the network resulting to a change in electrical conductivity [13]. This process will continue to take place as γ-dose increases until we approach a situation at which most of the possible charge carriers are already created. After this threshold dose limit we might expect no more increase in the dc conductivity and a saturation limit might be achieved as shown in Fig. 3a for Fe^{3+} and in Fig. 3b for Ni^{2+} and the corresponding values are shown in Table III. Behavior reveals almost complete saturation for any further increase in irradiation dosages.

TABLE II

Temperature dependence of electrical conductivity σ of PVA: Fe^{3+} (5 mol%).

Temperature [K]	σ [$\mu\Omega^{-1}$ cm^{-1}]
355	0.4341
365	1.4265
375	3.6515
385	6.6130
395	13.9570
405	15.8160

TABLE III

Irradiation dependence of electrical conductivity σ of PVA: Fe^{3+} and PVA: Ni^{2+} (20 mol%) at 387 K. Pure PVA is 5.5795 μ^{-1} cm^{-1}.

Fe^{3+} and Ni^{2+} Concentration in PVA	σ [$\mu\Omega^{-1}$ cm^{-1}] at 371 K	
	Fe^{3+}	Ni^{2+}
20 mol%	38.4604	17.3837
20 mol% + 300 CGY/min	65.8540	29.7988
20 mol% + 600 CGY/min	95.0385	34.4675
20 mol% + 900 CGY/min	111.6606	40.2911

In fact, at high temperature reaching this saturation limit is very difficult because of the existence of more complicated conduction mechanism. At high temperature the conductivity is due to the liberation of electrons or ions through the amorphous region of PVA and also probably the internal stress in the doped PVA [18, 19]. In addition to this, since irradiation was carried out in air and, the obtained gaseous ions around the films might have been produced on the surface of the film [20]. From the graphs it is evident, that the increase in conductivity due to dopant, temperature and γ-irradiation depicts semiconducting nature of PVA.

4. Conclusions

Investigation has been carried out carefully to know both the dopant and irradiation dependence of electrical conductivity.

Dopant generally increases the electrical conductivity. This can be explained on the basis, that the Fe^{3+} and Ni^{2+} ions coordinated through ionic bonds with hydroxyl group belonging to different chains in PVA. This causes to reduce the intermolecular interaction between PVA molecules or the addition of Fe^{3+} and Ni^{2+} increases the volume required for ionic carriers to dirft in the polymer matrix. Compared to Ni^{2+}, Fe^{3+} has coordinated through ionic bonds with hydroxyl group in a better way, also resulting in increase in volume favorable for ionic carriers to drift in the polymer matrix.

Irradiation of polymers also increases their electrical conductivity. During irradiation rupture of ionic bonds take place and release of ions, electrons and free radicals which are able to migrate through the network resulting in an increase in the electrical conductivity.

Therefore it is worth mentioning that addition of a dopant to polymer and subjecting it to irradiation brings about the change in electrical conductivity and helps in tailoring the electrical property of the polyvinyl alcohol films.

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