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Electrical Properties of Pure and Doped (KNO_3 & MgCl_2) Polyvinyl Alcohol Polymer Thin Films

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Abstract: Polymer thin film technology has made tremendous growth due to the range of technological applications such as coatings, light emitting diodes, photodiodes, sensors and batteries. These applications of thin films are possible as they are easy to fabricate and the effects due to confinement and interfacial interactions are responsible for different physical phenomenon that depend on thickness of thin films which cannot be observed in bulk materials. In the present work pure and doped (KNO_3 & MgCl_2) Polyvinyl Alcohol thin films are synthesized using solution casting technique. Electrical conduction in polymers has been studied aiming to understand the nature of the charge transport prevalent in these materials. The variation of conductivity with temperature shows Arrhenius behaviour. Activation energies are calculated from these studies and noted that these depend on the type of dopant material.

Keywords: Polymer thin films (PVA), DC conductivity, Arrhenius behaviour, Activation energy.

1. INTRODUCTION

Polymer thin film technology has made tremendous advancement in the last decade because of the range of technological applications that include coatings, lithography, and organic light emitting diodes, sensors and electrochemical cells. In polymer thin films effects due to confinement and interfacial interactions are responsible for different physical phenomena that change with film thickness. They have high conductivity, light in weight, inexpensive, flexible etc. Polyvinyl Alcohol (PVA) is a good protective colloid for aqueous emulsions. The electrical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix Potassium and Magnesium are soft alkali metals with low melting point. Jain et al [1] studied the effect of dopants on the electrical conductivity of solution grown polyvinyl alcohol films of $10\mu\text{m}$ thickness. The films were doped with CuSO_4 , CuCl_2 , FeCl_3 , ZnCl_2 and NaCl and it was reported that these dopants affect the electron traps in the forbidden band of the dielectric and modulate the current flow. Electrical conductivity studies in pure and iodine doped poly vinyl acetate films were made by Mehendru et al [2]. The electrical conductivity was found to increase significantly with iodine doping. The charge transport mechanism was found to be Poole-Frenkel type. D.C. electrical conductivity of iodine doped poly (2-vinylpyridine) films of thickness $80\text{-}100\mu\text{m}$ was studied

by Audenaert et al [3] as a function of iodine concentration and temperature. The electrical conduction mechanism was found to be governed by electronic hopping between random localized states. Sinha et al [4] studied the electrical transport properties in undoped and acrylic acid doped polystyrene films in a

cylindrical configuration in the temperature range $35\text{-}115^\circ\text{C}$. The conductivity initially decreased as function of dopant concentration but at higher concentrations it began to increase with increasing dopant concentration. The conduction behavior for undoped and doped films was found to be different and lowering of the activation energy due to doping with acrylic acid was also observed. Sharma AK et al[5] studied the increase in conductivity with increasing concentration of KBrO_3 is attributed to the decrease in the degree of crystallinity and increase in the degree of amorphosity. Sharma et al [6] studied the d.c. electrical conductivity of pure and doped with Fe^{3+} polystyrene films and it was reported that the conductivity increased for lower doping concentrations. Venugopal Reddy and NarasimhaRao [7] investigated the conduction mechanism in iodine-doped cellulose acetate-butyrate films as a function of the dopant concentration, field and temperature, and explained it on the basis of the formation of charge-transfer complexes. The decrease in the activation energy above T_g upon doping was attributed to an increase in the crystallinity of the polymer and to the formation of molecular aggregates of iodine. ShuklaPK et al[8] studied that due the phase change, the conductivity

shows a sudden increase in polyvinyl alcohol based electrolyte films. Ch.V. Subba Reddy et al [9] prepared and characterized the films of (PVP+NaClO₄) electrolytes for battery applications. The nature of mechanism response for transport phenomena in these materials is elucidated by the study of electrical conduction on pure and doped polymer films. In this paper pure and doped (KNO₃& MgCl₂) polyvinyl alcohol thin films are synthesized using Solution-Casting technique. The electrical properties are measured using Keithley Electrometer and conductivity at different temperatures show Arrhenius behaviour.

2. MATERIALS AND METHODS

Polyvinyl Alcohol (PVA), potassium Nitrate (KNO₃) and Magnesium Chloride (MgCl₂) are used with weight percentage of 90:10. Triple distilled water is used for preparation of various solutions.

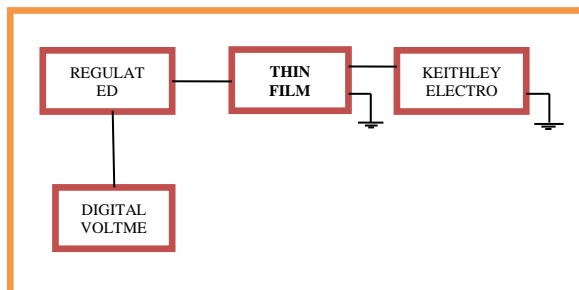
2.1 Apparatus and instruments

Experimental Jig, Power Supply, Keithley Electrometer (Model 614), Digital voltmeter, thermocouple.

2.2 Synthesis of Polymer thin films

Films of pure polyvinyl alcohol (PVA) and pure PVA doped with potassium (KNO₃) and pure PVA doped with Magnesium Chloride (MgCl₂) with weight percentage of 90:10 were prepared using solution casting technique. PVA and dopants were dissolved in triple distilled water and the mixtures were stirred at room temperature for 10-12 hours. The stirred solution was cast on to polypropylene dishes and allowed to evaporate slowly at room temperature. After some time solid polymer layers are formed as thin films with a thickness of 150µm at the bottom of dishes. These films were dried rigorously in a high vacuum (10⁻³torr) to eliminate the residual traces of water. Finally films were carefully separated from the dishes.

2.3 Electrical conductivity measurements



Figure(1). Block diagram of experimental setup used for conductivity measurements

The block diagram of the experimental arrangement used for measuring the electrical conductivity is as shown in Figure (1).The thin film specimen is mounted in an experimental Jig. A heating coil is wound on the muffle of the experimental Jig. The two ends of winding are

connected to the temperature controller, which regulates the temperature of the jig. The temperature of the sample is measured by thermocouple whose output is fed to the digital panel meter. By varying the temperature, the corresponding current passing through the film is measured by Keithley electrometer (Model 614). The currents were measured at different temperature at 5°C interval while temperature is increasing. The measurements of conductivity were carried out in the temperature range of 298K to 358K. The surface of the films is coated with silver for good electrical contact. Before taking the reading the films are annealed in two ways. The process of heating and cooling was repeated until the reproducibility in the resistance was obtained. The increase in resistance may be due to film getting crystallized on annealing.

3. RESULTS AND DISCUSSION

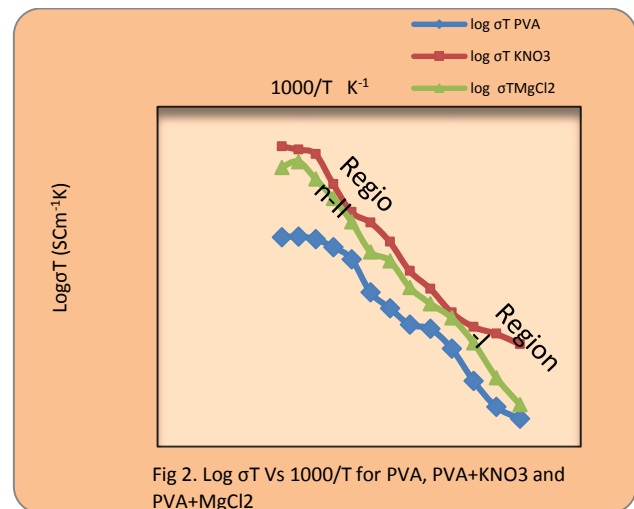


Fig 2. Log σT Vs $1000/T$ for PVA, PVA+KNO₃ and PVA+MgCl₂

Figure (2): Log σT Vs $1000/T$ for PVA, PVA+KNO₃ and PVA+MgCl₂

The temperature dependence of d. c. conductivity of PVA and PVA doped with KNO₃ and MgCl₂ studied in the temperature range of 298-358K is as shown in Figure (2). The increase in conductivity with dopant type is based on the ionic character of the dopant. In the amorphous regions, the chains are irregular and entangled where as in crystalline regions the chains are regularly arranged. Hence, it is very easy to move the molecular chains in the amorphous state rather than the crystalline state. The molecular packing in the amorphous state is weak and so the density is smaller than that of crystalline regions. Thus chains in amorphous phase are more flexible and are capable of orienting themselves relatively more easily and rapidly. From the figure (2) it is clear that the conductivity increases with increase in temperature in pure PVA, PVA+MgCl₂ and PVA+KNO₃. The increase in conductivity with temperature follows Arrhenius Behaviour with two regions above and below a certain temperature. In the region below certain temperature i.e. in Region I the conductivity of all electrolyte systems

increases slowly with temperature. At that temperature there is a sudden increase in conductivity. However in the region above this temperature i.e. in Region II the conductivity again increase slowly with increase of temperature. The existence of two regions in the conductivity Vs temperature plots and the sudden increase in the conductivity may be attributed to the transition from semi-crystalline phase to amorphous phase.

Conductivity in these regions is given by Arrhenius relation $\sigma = \sigma_0 e^{-E_a/KT}$ Where ' σ_0 ' is proportionality constant ' E_a ' is Activation Energy, T is Absolute temperature, K is Boltzmann Constant

The existence of two regions in the conductivity Vs temperature plots and sudden increase in the conductivity may be attributed to the transition of electrolyte from semi crystalline phase to amorphous phase. Due to this change of phase, conductivity shows a sudden increase as shown in Table (1).

Table (1): Conductivity data For Pure PVA, PVA+MgCl₂ and PVA+KNO₃

Polymer Electrolyte (Wt%)	Conductivity " σ " (Scm ⁻¹)			
	303K	323K	343K	358K
Pure PVA	0.18 × 10 ⁻⁷	1.55 × 10 ⁻⁷	1.13 × 10 ⁻⁶	0.14 × 10 ⁻⁵
PVA +MgCl ₂ Weight % (90:10)	0.4 × 10 ⁻⁷	0.59 × 10 ⁻⁶	0.40 × 10 ⁻⁵	1.4 × 10 ⁻⁵
PVA +KNO ₃ Weight % (90:10)	1.3 × 10 ⁻⁷	0.64 × 10 ⁻⁶	0.59 × 10 ⁻⁵	1.55 × 10 ⁻⁵

The increase in conductivity in region I is due to the hopping mechanism between coordination sites, local structural relaxation and segmental motion of polymer chain. But in region II where the amorphous region predominant, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion, this in turn favours the hopping inter chain and intra chain movements and the conductivity of the polymer electrolyte become high. Activation energies evaluated from the slopes of plots Log σT Vs 1/T for the two regions are given in the Table (2). In both regions I and II the activation energies show decrease with the type of dopant. In the region I the activation energy is due to hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer blends in semi crystalline phase. In the region II the activation energy is due to as amorphous regions progressively increase, however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion.

Table (2): Activation energies for Regions I and II of Pure PVA, PVA+MgCl₂ and PVA+KNO₃

Sample	Activation Energy (eV)	
	Region I	Region II
Pure PVA	0.39	0.55
PVA +MgCl ₂ Weight % (90:10)	0.6	0.72
PVA +KNO ₃ Weight % (90:10)	0.77	0.8

3.1 Dopantdependenceofconductivity

The dopants used for the present study are KNO₃ and MgCl₂ are ionic in nature. With remarkable ionic character the dissociation of ions takes place with which the mobility of ions increases thereby increasing conductivity. Potassium Nitrate is more electropositive and good ionic salts. Due this ionic nature the dissociation takes at lower temperature and the mobility of ions increases which results in increased conductivity for PVA doped with KNO₃ compared to pure PVA. Magnesium Chloride is less electropositive and less ionic salt. Due to this the dissociation is less and mobility of ions is slow process leading to less conductivity. The conductivity values are as shown in table (1). The values in the table indicate that the conductivity increase with doping. The magnitude of change is of the order of 10² times more in complexed films compared to the pure film.

4. CONCLUSIONS

In this study the polymer thin films of PVA and doped (KNO₃ and MgCl₂) PVA are synthesized using Solution Casting Technique. However KNO₃ has been found to be more ionic than MgCl₂. From the studies it has been found that,

- The polymer thin films were synthesized economically, conveniently and quickly.
- The conductivity of pure PVA at room temperature is of the order of 0.18×10⁻⁷ Scm⁻¹.
- The conductivity Vs temperature plots show an increase in conductivity with temperature in pure PVA film and further increase is observed in KNO₃ and MgCl₂ doped films.
- The conductivity Vs temperature plots follow Arrhenius behaviour throughout, but with two regions and with low activation energies above and below transition temperature of the film.
- At the transition temperature, there is a sudden increase in conductivity and this has been explained as due to the change of phase from semi crystalline to amorphous.
- A linear variation in σ Vs 1/T plots below and above transition temperature suggests an Arrhenius

thermally activated process. The conductivity in these regions is expressed as $\sigma = \sigma_0 e^{-E_a/KT}$.

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