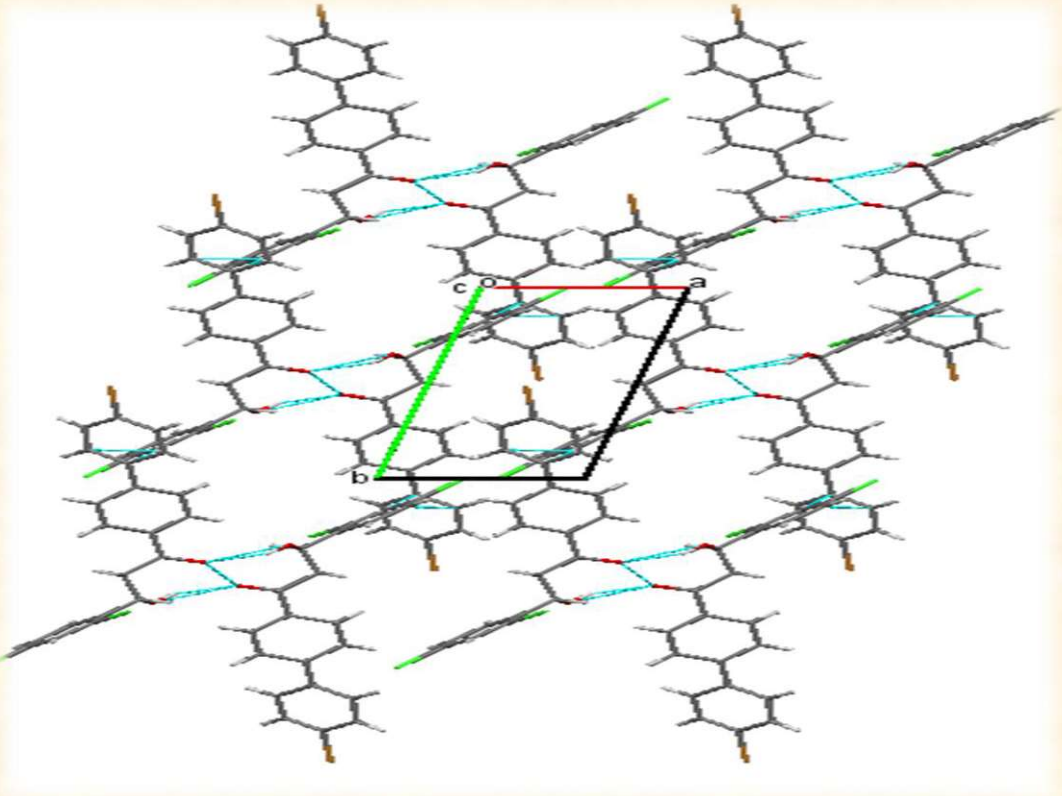
Recent Advances in Materials Science and Biophysics

Proceedings of International conference RAMSB

Editor
Yerol Narayana



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THERMAL AND ELECTRICAL TRANSPORT PROPERTIES IN FILMS OF $CdCl_2$ DOPED PVA-PVP BLEND

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Introduction

Solid polymer composites have attracted many researchers due to their interesting structural properties. The study of polymer composites is a matter of contemporary research interest, due to the range of choices available to tailor material properties, in order to suit particular needs. Inorganic salt doped polymer nano composites show interesting optical properties, suitable for various applications. Modification of their properties can be effected by adding inorganic salt to polymer blends/composites [1, 2].

Polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) have gained attention in recent times, due to their important features like solubility in water, good film formation capacity and charge storage ability [3]. Due to hydrogen bonding among PVA and PVP, compatibility of PVA/PVP composites is an established fact. In the present study, cadmium chloride monohydrate ($CdCl_2.H_2O$) has been chosen as a dopant. $CdCl_2.H_2O$ is a crystalline, divalent inorganic salt, which has many applications, and the potential applications in energy storage devices and optoelectronics, on its incorporation in PVA-PVP blend needs to be further explored [4].

The microstructural changes and behaviour of prepared $CdCl_2$ doped PVA/PVP composite films with increase in their temperature have been studied using Differential Scanning Calorimetry (DSC). Compatibility (complete mixing) of polymer blends can also be determined using DSC curves. Miscible blend films exhibit one phase and a single T_g. Thermal stability of PVA/PVP composites has been studied using thermogravimetry (TG). To understand the band structure and transport phenomenon, DC electrical measurement has been performed using two probe method. On the basis of involvement of type of charge carrier in conduction processes, electrical conductivity is either electronic or ionic. In the case of electronic conductivity, electrons carry the current whereas in ionic conductivity, ions are responsible for charge transport. Electrical conductivity is not same in all variety of materials; it depends on their band-structure.

Materials and Methods

Semicrystalline PVA (140,000 molecular weight), amorphous PVP (50,000 molecular weight) and white crystalline $CdCl_2$. H_2O (201.33 molecular weight) were purchased from HiMedia Laboratories Pvt. Ltd, Mumbai, and used for the preparation of doped polymeric samples. The solution casting method of preparing samples is an easy, low cost, chemical technique. Hence solution casting method is used to prepare $CdCl_2$ doped PVA-PVP films.

Aqueous solutions of PVA-PVP blends are prepared by taking PVA and PVP in different proportion (100:0, 70:30, 50:50, 30:70 and 0:100) by weight and dissolved in double distilled water taken in different glass beakers. Transparent, homogeneous solutions of PVA-PVP blend are obtained by stirring the mixture (of PVA and PVP in distilled water) continuously, using a magnetic stirrer. The standard solution of $CdCl_2$ is obtained by dissolving cadmium chloride monohydrate ($CdCl_2.H_2O$) in double distilled water, using a magnetic stirrer. Different volumes of this standard solution are added to PVA/PVP aqueous solutions in order to prepare the $CdCl_2$ doped PVA/PVP aqueous composite solutions.

$$Doping\ Level,\ DL\ (wt\%) = \frac{M_d}{M_d+M_p} \times 100 \qquad (1)$$

In equation (1), M_d is weight of dopant ($CdCl_2$) and M_p is weight of polymer host (PVA/PVP blend). After doping, the mixture is stirred to get homogeneous solution, and poured into glass petri-dishes. These are then kept inside a temperature controlled, air cooled oven maintained just above room temperature (fixed at 40°C), in order to obtain the dried $CdCl_2$ doped PVA/PVP composite films. After drying, the films were peeled off and stored in a desiccator, in order to avoid absorbance of ambient moisture.

DSC curves are recorded in the temperature range 50 ˚C to 450 ˚C, by using TA instruments DSC Q20 V24.10 Build 122, at 0.03 ºC resolution. Thermograms are recorded using SDT Q 600 TA Instruments, USA Q 20 TA Instruments, USA, with temperature varying from room temperature up to 800°C, at a constant heating rate 10°C/min, in nitrogen atmosphere. Samples having weight ranging from 1 mg up to 3 mg were sealed in aluminium pans and covered with lid. An electrical set-up comprising two probe set up with a digital pico-ammeter (model: DPM-111), high voltage supply (model: EHT-11) and temperature variation apparatus with PID controlled oven (model: PID-200) from SES instruments Private Limited, Roorkee, Uttarakhand (UK), India have been used to study the temperature dependent conductivity measurements. In order to study the capacitive action of $CdCl_2$ doped PVA/PVP composite films, dielectric measurements have been done using a precision LCR meter, GWINSTEK LCR-821, research grade equipment from Good Will instruments Co. Ltd., Taiwan. The dielectric studies were performed at room temperature in the frequency range from 12 Hz up to 200 kHz.

Results and Discussion

The microstructural changes and behaviour of $CdCl_2$ doped PVA/PVP blend films with increase in their temperature have been studied using DSC curves. In DSC spectra of pure and $CdCl_2$ doped PVA/PVP blend films, there are four different main regions as seen in fig.1 (a & b). First, a broad endotherm around 100°C, which is due to evaporation of water content; secondly, a sharp endotherm around 150°C due to melting of $CdCl_2.H_2O$; third, a broad endotherm around 320˚C, which is due to melting of polymer (PVA) - dopant complexes; also, there is melting of Cd atoms (aggregations) after the reduction process (from Cd^{2+}) and partial decomposition of polymer component. Fourth stage of decomposition, around 433 ˚C, is due to second stage degradation of PVA and onset of degradation of PVP. An interesting result that is observed is a sharp melting endotherm at 150 °C, observed at 6.3 wt% doping level for polymer blend composition of PVA/PVP: 50/50. The TG thermograms of pure and $CdCl_2$ doped PVA/PVP blend films reveal multiple regions of decomposition. Compared to pure blend, $CdCl_2$ doped blends show an additional mass loss between temperatures varying from 510°C up to 670°C. Hence, $CdCl_2$ doped PVA/PVP blend films undergo thermal changes (volatilization and decomposition) in five different stages, over a temperature region varying from 40°C up to 800°C.

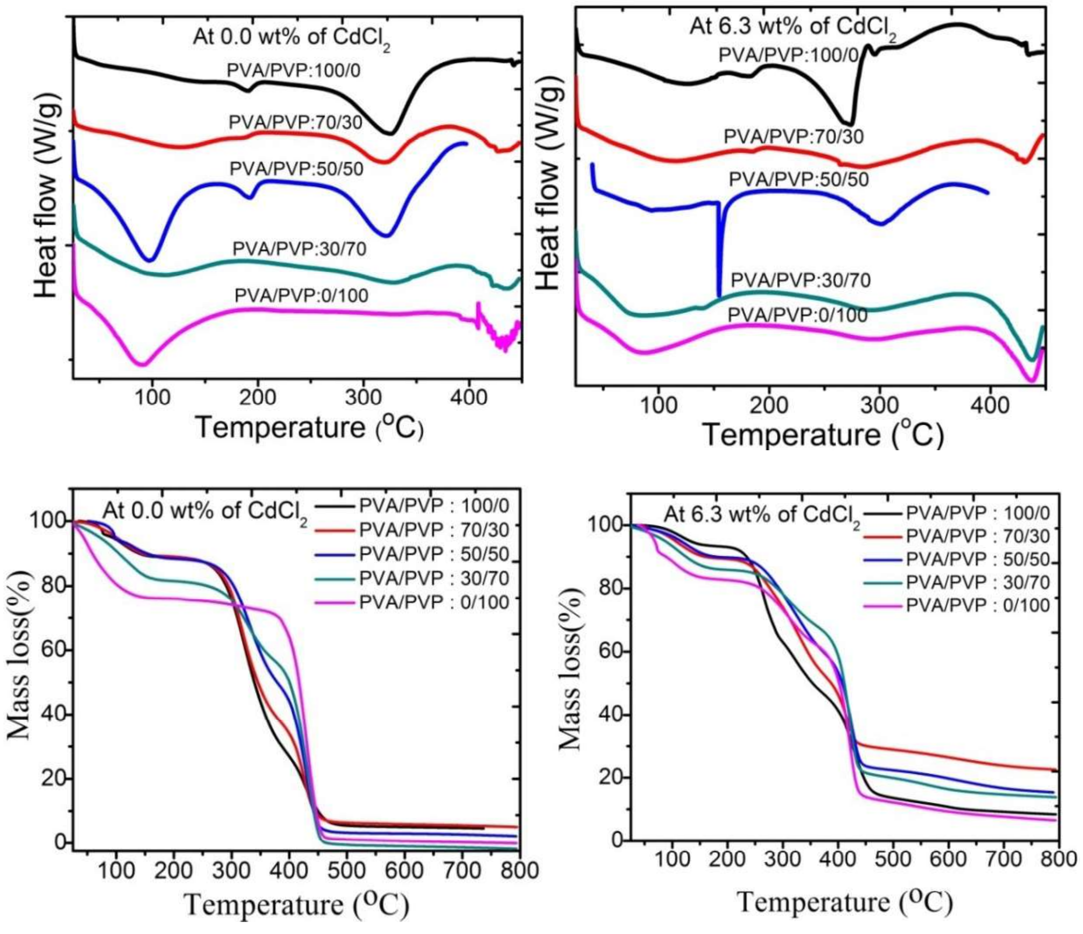

Fig.1. a & b) Differential Scanning Calorimetric (DSC) scans; c & d) Thermogravimetry (TG) scans for films of pure and $CdCl_2$ in PVA/PVP composites.

DC electrical measurements were carried out at varying (different) temperatures for doped polymeric materials gives an idea about nature of charge transport in them. The temperature dependent electrical measurements at 6.3 wt% of $CdCl_2$ doped PVA/PVP composite filmsave been studied. Fig. 2a shows linear regions with two different slopes, at higher and lower temperatures. From the slope of linear regression to the plot of ln σ versus 1000/T shown in fig.2a, activation energy (E_a) is determined using the Arrhenius relation; see equation (2) and the values listed in table 1. Activation energy for 6.3 wt% $CdCl_2$ doped to PVA/PVP : 100/0 proportion is low (1.201±0.076 and 1.078±0.090), whereas the film with 6.3 wt% $CdCl_2$ doped in PVA/PVP : 0/100 shows high activation energy. Increase of PVP concentration relative to PVA enhances activation energy for thermally assisted charge transport, due to which, a decrease in electrical conductivity is observed.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_b T}\right) \tag{2}$$

Hence, time dependent electrical polarization studies have been done for 6.3 wt% $CdCl_2$ doped PVA/PVP : 100/0 composite and 6.3 wt% $CdCl_2$ doped PVA/PVP : 70/30 composite and the transference number was determined using equation (3) and equation (4). To study the polarization effect using Wagner's method, the set voltage is 1 volt, and experiment (time dependent electrical study) was performed for 9 to 10 hours, continuously.

$$t_e = \frac{I_e}{I_t} \tag{3}$$

$$t_i = 1 - t_e \tag{4}$$

where I_e is final current (I_f) due to electrons and total current, I_t is initial current (I_i), i. e. current immediately after step voltage is applied, due to migration of both ions and electrons.

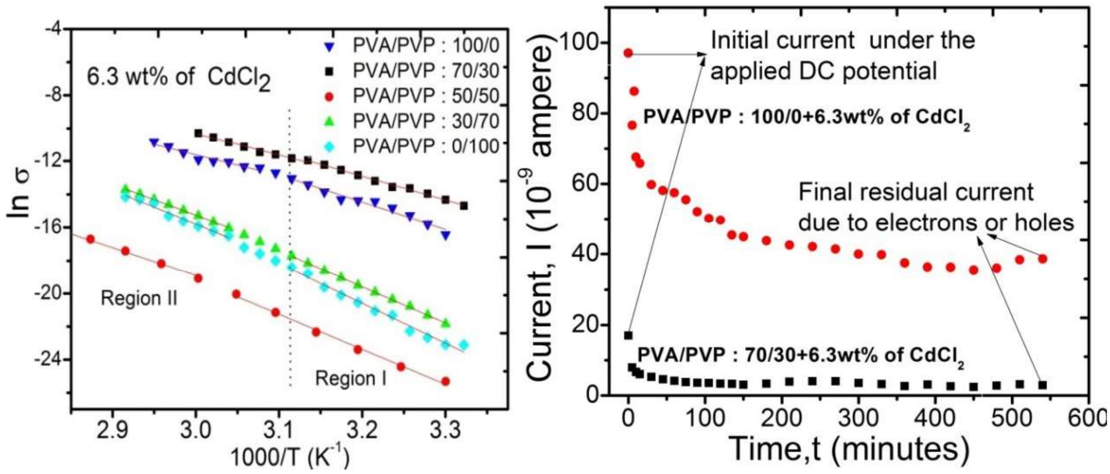

Fig. 2. a) Plot of lnσ versus 1000/T ; b) DC polarization plot; for films of pure and $CdCl_2$ in PVA/PVP : composites.

Table 1: Estimated activation energy from electrical measurements.

6.3 wt% $CdCl_2$ doped PVA/PVP Composites	Activation energy, E_a (eV)	
	Region I Low T region	Region II High T region
100/0	1.201±0.076	1.078±0.090
70/30	1.237±0.025	1.131±0.056
50/50	1.832±0.060	1.452±0.015
30/70	1.903±0.008	1.618±0.014
0/100	2.088±0.042	1.759±0.064

From the experimental results, it is seen that there is both electronic and ionic contribution to electrical conduction behavior of the samples investigated, because t_e=0.398 and t_i= 0.602 for 6.3 wt% $CdCl_2$ doped PVA/PVP: 100/0 composite and t_e=0.173 and t_i= 0.827 for 6.3 wt% $CdCl_2$ doped PVA/PVP: 70/30 composite film. Hence, results of all these studies indicate structural modifications and modified properties at different proportion of PVA and PVP components, as well as on addition of the inorganic salt, $CdCl_2$.

References

1. Baraker, B. M., Lobo, B., (2016) Experimental study of PVA-PVP blend films doped with cadmium chloride monohydrate, *Ind. J. Pure and Appl. Phys*., **54**, 634-640.
2. Baraker, B. M., Lobo, B., (2017) Spectroscopic analysis of $CdCl_2$ doped PVA-PVP blend films, *Can. J. Phys*., **95**, 738-747.
3. Ramaswamy, M., Malayandi, T., Subramanian, S., Srinivasalu, J., Rangaswamy, M. (2017) Magnesium ion conducting polyvinyl alcohol–polyvinyl pyrrolidone-based blend polymer electrolyte, *Ionics*, **23**, 1771-1781.
4. Baraker, B. M., Lobo, B., (2017) UV irradiation induced microstructural changes in $CdCl_2$ doped PVA – PVP blend, *J. Mater. Sci: Mater. Electron.* (in Press);16 pages; https://dx.doi.org/10.1007/s10854-017-8355-7

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