

Experimental study of PVA-PVP blend films doped with cadmium chloride monohydrate

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The microstructure and properties of poly vinyl alcohol (PVA)-poly vinyl pyrrolidone (PVP) blend films doped with cadmium chloride monohydrate ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$) have been experimentally studied using scanning electron microscope (SEM), atomic force microscope (AFM), X-ray diffraction (XRD), optical, electrical and differential scanning calorimetry (DSC) techniques in the doping range from 0.5 wt% up to 45 wt%. The SEM images reveal the formation of self-grown nanostructures in the form of nano-spheres and nano-rods in the doping range from 0.5 wt% up to 2.2 wt%. The XRD reveals formation of additional sharp peaks superposed on the amorphous pattern of PVA-PVP blend. This is attributed to the crystalline nature of dopant induced nanostructures. AFM scans show spike-like structures due to the dopant and also an increase in surface roughness. At 35 wt% of CdCl_2 , the surface of the film is smooth. The sample is found to be completely amorphous at 21.5 wt% and at higher doping levels, up to 45 wt%.

Keywords: Nano-structured polymeric blend, PVA-PVP, Cadmium chloride monohydrate, SEM, XRD

1 Introduction

Poly vinyl alcohol (PVA) and poly vinyl pyrrolidone (PVP) are good encapsulating materials for metallic nano-particles, forming core-shell nanostructures. On doping (with red-ox agents), the conductivity of polymers can be increased and the electrical, optical and thermal properties can be tailored to suit particular needs¹⁻³. PVA is a semi-crystalline material, having important features like water solubility, adhesive nature, film formation ability and applications in biomedical fields^{4,5}. PVP is an amorphous polymeric material, which is hygroscopic in nature and has complex formation ability^{6,7}. In addition, PVP is a non-toxic material and has biomedical applications⁸. Both PVA and PVP are water soluble and miscible polymers⁹. PVA-PVP blends are amenable to film formation, due to hydroxyl group in PVA and carbonyl group in PVP^{10,11}. PVA-PVP blends have application as skin dressing materials, and are also used as electrochemical membranes¹². In order to improve the properties of PVA-PVP blend, cadmium chloride monohydrate ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$) is used as a dopant. This dopant has water soluble nature and various applications^{13,14}. Some work on $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ doped

PVA-PVP blend has already been done¹⁵⁻¹⁷. The micro-structural properties of PVA-PVP blends doped with $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ have been studied and the results of this work are discussed in this paper.

2 Experimental

2.1 Sample preparation

The CdCl_2 is incorporated as a dopant in PVA-PVP blend, and films with doping level ranging from 0.5 wt% up to 45 wt% were prepared by solution casting technique. PVA (with molecular weight 1,40,000), PVP (with molecular weight 50,000) and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ were purchased from HiMedia Laboratories Pvt Ltd, Mumbai. Aqueous solution of PVA-PVP blends were prepared by taking PVA and PVP in equal proportion by weight and dissolved in double distilled water. The standard solution of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ was prepared by dissolving molecular weight of CdCl_2 in double distilled water, and different volumes of this standard solution were added to aqueous solutions of PVA-PVP blends. The mixtures were stirred for more than 24 h using Teflon magnetic bead and the filtered transparent, homogeneous solutions are poured into glass petri-dishes. To dry the samples, an air cooled, temperature controlled oven maintained at 40 °C was used. The dried samples were peeled off carefully from the glass substrate and stored in desiccators with proper labeling.

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2.2 Instrumentation

Morphological studies have been done using scanning electron microscope (SEM) and atomic force microscope (AFM) images. SEM images were acquired using the instrument JSM-6390 with 15 kV accelerating voltage. AFM images were recorded using Nanosurf Easyscan2 system. Scanned topographic images were recorded in the static force, lithographic operating mode and 4 $\mu\text{m/s}$ tip speed. X-ray diffraction pattern (intensity vs 2θ) was obtained over scattering angle (2θ) varying from 10° up to 80° , using $\text{Cu K}\alpha$ radiation of wavelength 1.5406 \AA . Hitachi U 3310 UV-Visible-NIR spectrometer was used to record the optical spectra in the wavelength range varying from 200 nm up to 1000 nm. The UV-Visible spectra were quantitatively analyzed in order to determine the type of electronic transition and the optical band gap. To study the temperature variation of electrical conductivity of the doped films, dc electrical measurements have been done using a research-grade apparatus, a product of an ISO 9001:2000 SES Instruments Pvt Ltd, Roorkee, India (www.sestechno.com). A two probe set up (Fig. 4(a)) with a digital picoammeter model: DPM-111, high voltage power supply model: EHT-11 and suitable temperature variation apparatus PID controlled oven model: PID-200 has been used, which is accurate to 0.1 $^\circ\text{C}$ (Fig. 4(b)). The variation of electrical conductivity with temperature was studied at constant applied voltage, by sandwiching the sample between two metal electrodes as shown in Fig. 4(b)). In order to understand the thermal behavior of CdCl_2 doped PVA-PVP blend films, differential scanning calorimetry (DSC) curves are recorded by using TA instruments DSC Q20 V24.10 Build 122, at 0.03 $^\circ\text{C}$ resolution.

3 Results and Discussion

SEM is an important tool to study the morphology of the materials. As seen in SEM images (Fig. 1), structural modifications take place in the samples due to interactions of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ with PVA-PVP blend. Miscibility of PVA and PVP components (in the blend) is confirmed by a uniform and homogeneous surface (Fig. 1(a)) at 0.0 wt%. (This is confirmed by single glass transition temperature (T_g) from DSC scan, shown in Fig. 3(b)). In the sample containing 0.5 wt% of CdCl_2 in PVA-PVP blend, there are self-grown nano-particles (nano-spheres) of dimension (diameter) varying from 130.4 nm up to 347.8 nm. The average dimension (diameter) of these nano-

spheres is 260.8 ± 10.7 nm (determined manually from the SEM micro-graphs). When the dopant level is increased to 2.2 wt% (Fig. 1(c)), we observe nano-rods of average length $2.4 \pm 0.11 \mu\text{m}$, having diameter 170 nm. The length of these nano-rods is found to vary from 0.5 μm up to 4.0 μm . At 5.4 wt% of CdCl_2 , more complex distribution of nano particles of average linear dimension 873.3 nm, which is shown in Fig.1(d) and (i). At 10.2 wt% of CdCl_2 ,

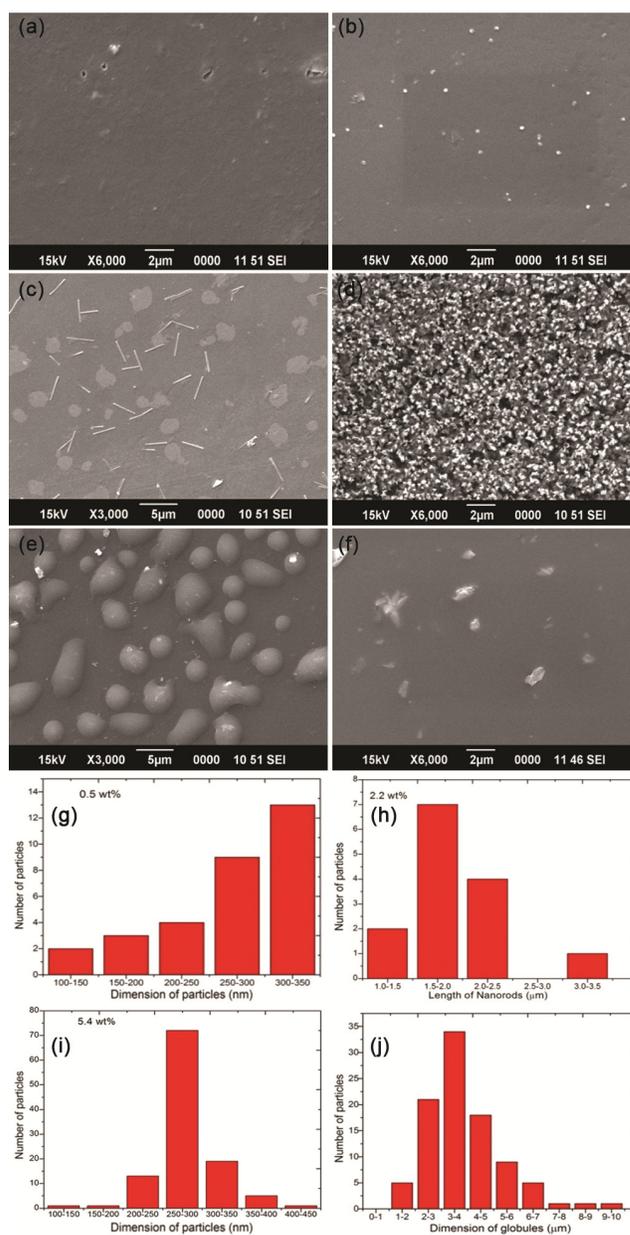


Fig. 1 — SEM images of PVA-PVP blends doped with (a) 0.0 wt%, (b) 0.5 wt%, (c) 2.2 wt%, (d) 5.4 wt%, (e) 10.2 wt% and (f) 21.5 wt% of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$. The particle size distribution analysis done manually is presented in (g) 0.5 wt%, (h) 2.2 wt%, (i) 5.4 wt% and (j) 10.2 wt%.

agglomeration of dopant takes place (in the host polymer matrix) to form new regions having ball (globule) like structures which are $4.0 \pm 0.15 \mu\text{m}$ in size (average dimension). The size distribution of self-formed nanostructures is studied manually from the SEM micrographs (shown in Fig. 1 (g-j)). These nanostructures in CdCl_2 doped PVA-PVP blends reveal the existence of different crystalline domains and that there is an increase in the degree of crystallinity of PVA-PVP samples doped with CdCl_2 from 0.5 wt% up to 5.4 wt%, which are also reflected from the XRD and DSC scans (see Fig. 3(b) and Fig. 3(c)). At higher dopant (21.5 wt%) concentration, a smooth and homogeneous surface is observed, which reveals that there is no phase separation in the PVA-PVP blend at higher CdCl_2 content and also that the sample has become amorphous in nature.

AFM study gives an idea of surface modifications in a material. As seen in AFM images (Fig. 2 (a-f)), bright regions are identified as dopant ions, and spike (needle-like) structures are result of added dopant ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$). A different surface morphology is observed at each dopant level, which confirms the interaction between PVA-PVP and Cd^{2+} ion/ Cd atom and Cl^- ion. Surface roughness of the doped blend increases from 0.5 wt% up to 5.4 wt% doping level.

At 10.2 wt% CdCl_2 doping level, the AFM scans reveal a decrease in surface roughness and it becomes smoother at a higher dopant level (21.5 wt%).

In XRD scans (intensity vs 2θ ; Fig. 3(c)), a crystallite peak is observed at $2\theta=20^\circ$, which indicates the semi-crystalline nature of the PVA-PVP blend film. The decrease in intensity of this peak with increase in the CdCl_2 concentration indicates the enhancement in amorphousness of PVA-PVP blend films. The variation of degree of crystallinity of the doped films with variation in CdCl_2 doping level is listed in Table 1. In the low dopant concentration region, from 0.5 wt% up to 5.4 wt%, there is an increase in degree of crystallinity of CdCl_2 doped PVA-PVP samples, due to self assembled nanostructures (evidenced from SEM images) in PVA-PVP matrix and hence, appearance of additional peaks (at 0.5 wt% and 5.4 wt% dopant level) in the XRD scans. At higher dopant levels, from 10.2 wt% up to 45 wt%, there is a significant decrease in intensity of crystalline peaks which reveals the decrease in degree of crystallinity (enhancement in amorphousness) of samples. The decrease in peak intensity is accompanied by increase in width (full width at half maximum (FWHM)) due to decreased inter-molecular interaction between dopant and

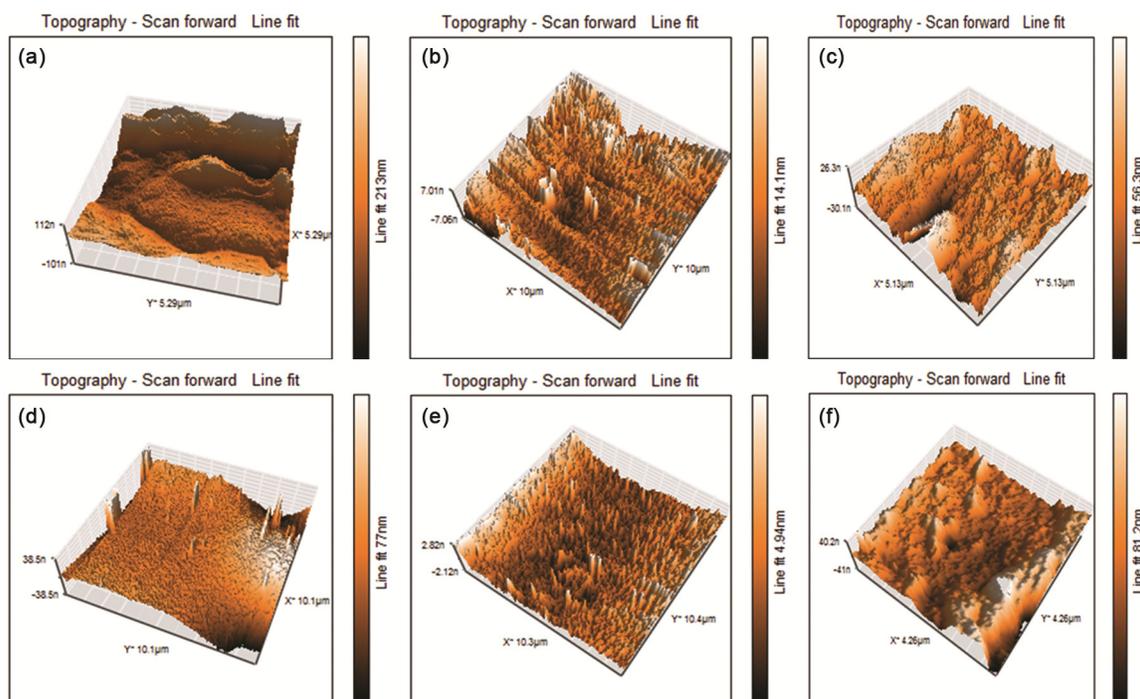


Fig. 2 — AFM images of PVA-PVP blends doped with (a) 0.0 wt%, (b) 0.5wt%, (c) 2.2 wt%, (d) 5.4 wt% (e) 10.2 wt% and (f) 21.5 wt% of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$.

polymer blend. Using the area under the crystalline peaks and full width at half maximum (FWHM denoted by the symbol β) of crystalline peak at scattering angle $2\theta = 20^\circ$, structural parameters such as degree of crystallinity (X_c), average crystallite size (P) and average separation between the crystallites (R) were estimated, using Eqs. (1-3):

$$X_c = \frac{A_c}{A_c + A_A} \quad \dots (1)$$

In Eq. (1), A_c and A_A are the area under the crystalline peaks and amorphous profiles, respectively:

$$P = \frac{0.9\lambda}{\beta \cos\theta} \quad \dots (2)$$

$$R = \frac{5\lambda}{8 \sin\theta} \quad \dots (3)$$

In Eqs. (2) and (3), the symbol λ refers to the wavelength of incident X-rays (Copper K_α X-rays of wavelength $\lambda = 1.5406 \text{ \AA}$). The value of full width at half maximum, β , of the crystalline peak is substituted in Eq. 2 (in radians).

In order to understand the band structure of doped polymeric materials, analysis of optical (UV-VIS) absorption spectra is essential. The optical band gap corresponding to direct allowed transition (E_d) and indirect allowed transitions (E_i) are determined for $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ doped PVA-PVP blends. The optical band gap of non-crystalline materials is determined using Tauc's plot and Mott-Davis relation^{18, 19}:

$$\alpha h\nu = B(h\nu - E_g)^m \quad \dots (4)$$

In Eq. (4), α is absorption coefficient, h is the Planck's constant, ν is frequency of the incident radiation and E_g is the band gap. The parameter m can take values $\frac{1}{2}$ and 2 for direct allowed transition and indirect allowed transition respectively.

Multiple optical transitions have been observed in the absorbance spectra (Fig. 3(a)) due to interaction of ions of dopant with the polymer matrix. From 0.5 wt% up to 2.2 wt%, there is an increase in band gap due to increased intra/ inter molecular interaction of PVA and PVP, in addition to dopant (Cd^{2+} and Cl^-) ion interactions with functional groups (hydroxyl

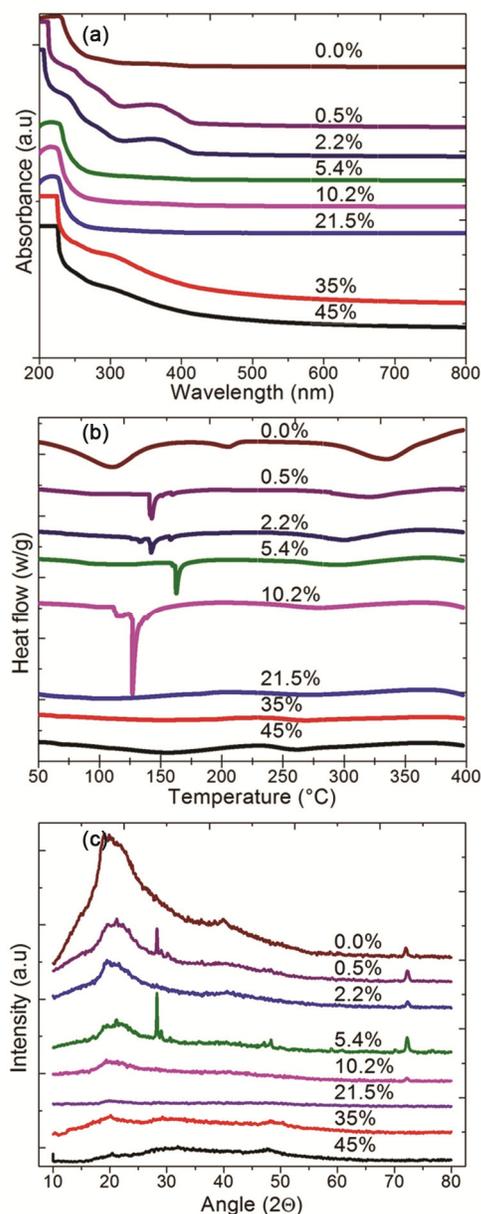


Fig. 3 — (a) Absorbance spectra, (b) DSC spectra and (c) XRD spectra of PVA-PVP blends doped with different concentrations of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$.

Table 1 — List of measured and calculated structural parameters (from XRD scans): scattering angle (2θ), percentage of degree of crystallinity ($\%X_c$), average crystallite size (P) and average crystallite separation (R)

DL (wt%)	2θ (degree)	X_c (%)	P (nm)	R (\AA)
0.0	20.4	7.42	1.69	5.44
0.5	21.1	15.00	1.58	5.25
2.2	20.7	18.02	1.37	5.35
5.4	21.1	17.16	1.66	5.26
10.2	20.5	12.00	1.57	5.41
21.5	20.5	10.27	2.24	5.41
35.0	18.4	2.50	1.28	6.03
45.0	19.8	1.42	2.44	5.58

(OH) and carbonyl (C=O) groups) of the polymer blend. A decrease in band gap is seen in PVA-PVP samples doped from 5.4 wt% up to 21.5 wt% dopant level. There is formation of micro globules at 10.2 wt%, as a result of PVA + Cd²⁺ and PVP + Cl⁻ complex formation (Fig. 1(c)). The dopant induced intermediate energy states in the band gap of PVA-PVP blend are identified as E_{d2} and E_{i2} (Table 2 and Fig. 3(a)). The experimental study of temperature dependence of electrical conductivity has been done in order to study the modified band structure in doped PVA-PVP blends. Activation energy has determined using Arrhenius relation (Eq. 5):

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad \dots (5)$$

In Eq. (5), σ is electrical conductivity, E_a is activation energy for mobility of charge carriers, k_B is Boltzman constant and T is the absolute temperature. The estimated data of dc electrical conductivity ($\ln \sigma$ at 304 K) and activation energy (E_a) with error are listed in Table 3. From the plot of $\ln \sigma$ vs $\frac{1}{T}$ (Fig. 4(d)), it is clearly observed that there is an increase in electrical conductivity with the temperature in un-

doped and CdCl₂ doped PVA-PVP blends. The activation energy, E_a , has been estimated from the slope of the straight line fit of the plot of $\ln(\sigma)$ vs $\frac{1}{T}$. The doping of PVA-PVP blend with CdCl₂ has resulted in increased electrical conductivity, when compared to un-doped PVA-PVP blend. The increase of dopant concentration from 0.5 wt% to 5.4 wt% leads to a decrease in the electrical conductivity which indicates that nano-clusters formed in the sample (Fig. 1(b) and 1(c)) are hindering the movement of mobile charge carriers in polymer matrix and hence, there is an increase in activation energy for mobility of charge carriers. At the dopant level 10.2 wt% (of CdCl₂), there is an increase in electrical conductivity due to more number of conducting paths provided for mobile charge carriers due to aggregated dopant atoms. In the dopant range from 21.5 wt% up to 45 wt%, the electrical conductivity is saturated due to increased amorphousness of the doped samples (Fig. 3(c)). Meanwhile, the increase in activation energy from 1.57 eV up to 1.72 eV in the dopant region varying from 0.5 wt% up to 5.4 wt% (Fig. 4) is due to increase in degree of crystallinity of the samples due to formation of cluster of dopant ions in the host polymer blend (Table. 1), which consequently results in the nano-phase formation due to reduction of cadmium ions (Cd²⁺) by the host polymeric material, forming cadmium (Cd) metal nano-structures. At 10.2 wt%, E_a decreases to 1.34eV due to aggregation of Cd atoms in the PVA-PVP matrix, which helps in the movement of charge carriers under the influence of an applied electric field. Beyond 10.2 wt%, E_a becomes smaller and then saturates, as expected. The increased DC (electrical) conductivity at higher temperature is due to thermally stimulated free movement of mobile charge carriers in the sample.

The improved thermal stability in CdCl₂. H₂O doped PVA-PVP blends have been determined by analyzing the DSC spectra. The broad valley at 100 °C for pure blend shows removal of H₂O from the sample, a sharp endotherm at 195 °C and the broad endotherm at 320 °C are as a result of melting and degradation of pure PVA-PVP blend, respectively. In doped samples, melting temperature is observed to increase from 142 °C up to 150 °C, in the dopant region from 0.5 wt% up to 5.4 wt%. This is due to the formation of nano-crystalline regions of various dimensions. As seen from the DSC curves (Fig 3(b)), a melting peak is observed around 140 °C. The other

Table 2 — Optical band gap corresponding to direct allowed transitions (E_{d1} and E_{d2}), indirect allowed transitions (E_{i1} and E_{i2})

DL (wt%)	E_{d1} (eV)	E_{d2} (eV)	E_{i1} (eV)	E_{i2} (eV)
0.0	5.10	2.98	4.35	2.41
0.5	5.60	2.96	5.43	2.59
2.2	5.85	3.07	5.44	2.68
5.4	5.17	2.91	4.67	1.94
10.2	5.21	2.86	4.79	1.95
21.5	5.25	2.90	4.81	2.26
35.0	5.41	–	5.11	1.81
45.0	5.39	–	5.09	1.48

Table 3 — Activation energy (E_a) from DC electrical measurement at different CdCl₂ dopant levels (DL) in PVA-PVP blends

DL (wt%)	E_a (eV)	$\ln \sigma$
0.0	1.60±0.010	-21.8
0.5	1.57±0.020	-12.6
2.2	1.66±0.012	-10.6
5.4	1.72±0.012	-16.1
10.2	1.34±0.016	-12.3
21.5	1.20±0.006	-13.8
35.0	1.20±0.010	-13.2
45.0	1.30±0.014	-13.9

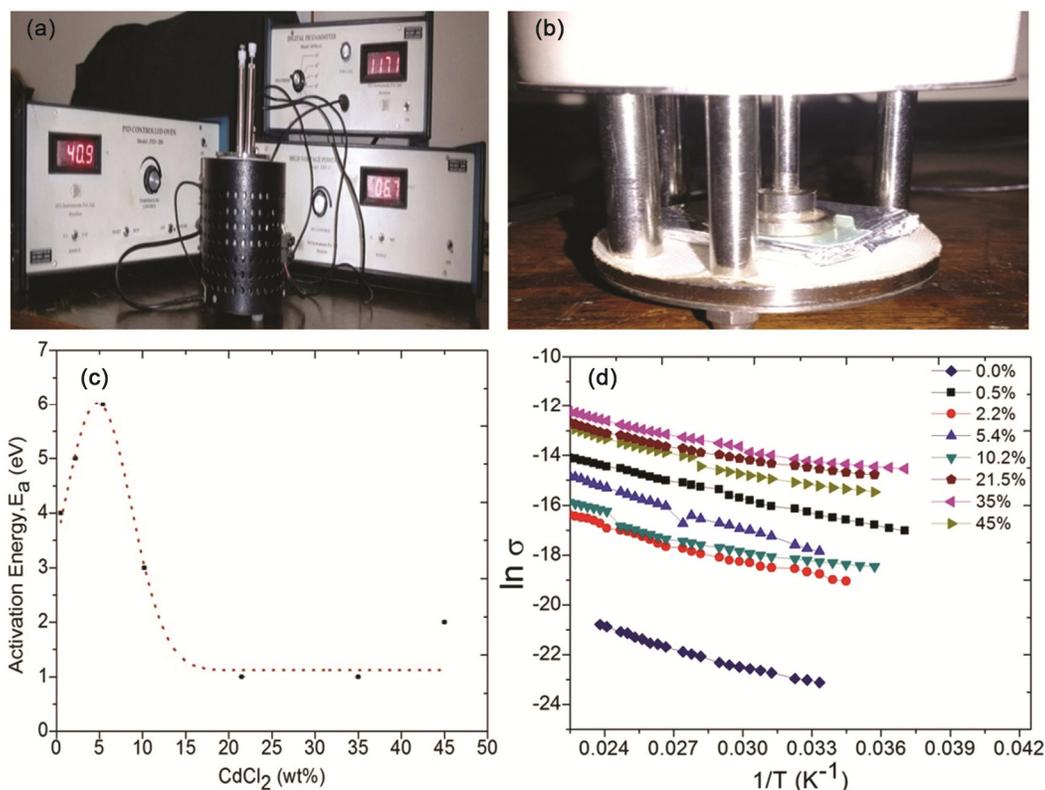


Fig. 4 — (a) DC two-probe electrical experimental set up, (b) sample sandwiched between two metal electrodes, (c) variation of activation energy, (d) Variation of electrical conductivity (σ) relative to reciprocal temperature of PVA-PVP blends doped with different concentrations of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$.

endotherm at 300 °C is due to the first stage of degradation of the sample. Multiple endotherms at lower dopant (up to 10.2 wt%) level PVA-PVP blend samples indicate the presence of crystalline domains having varying thickness, which could have been induced by the formation of nano- crystals in the host polymer material.

4 Conclusions

The analysis of PVA-PVP blends doped with $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ show modified optical, electrical and thermal properties at different dopant levels (from 0.5 wt% up to 45 wt%). Self-grown, crystalline nano-regions of cadmium have been achieved by introducing CdCl_2 in PVA-PVP matrix in the dopant range 0.5 wt% up to 5.4 wt%. These nano-rods have uniform distribution and neat arrangement throughout the samples resulting in enhanced degree of crystallinity. Increased surface roughness at lower dopant (from 0.5 wt% up to 5.4 wt %) region and enhanced amorphousness at higher dopant concentration (from 10.2wt% up to 45 wt%) have been observed from AFM and XRD spectra respectively.

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