Thermal, Optical, and Dielectric Studies of VO^{2+} Doped PVC Films

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ABSTRACT

Pure and VO^{2+} doped poly(vinyl chloride) (PVC) films were prepared by using the solution casting method. Various techniques including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis) and electron paramagnetic resonance (EPR) were employed in the characterization of the samples. The thermal properties of these films were investigated by employing DSC and TGA. Using the DSC thermograms, glass transition temperature (T_g) and melting temperature (T_m) of the PVC films were measured. Thermogravimetric curves of pure and VO^{2+} doped PVC films showed three distinct steps of weight loss. The FTIR results showed that the addition of VO^{2+} reduces the crystallinity of PVC due to the interaction of vanadium ions with the CH stretching modes of the CH_2 groups. Optical absorption edge and indirect band gap showed a decreasing trend with increasing the VO^{2+} concentration. From the EPR spectra, the Spin – Hamiltonian parameters (g and A) were evaluated. For dielectric studies the films were studied in the frequency range from 10 KHz to 2 MHz at room temperature. It was observed that with the increase in frequency, the value of dielectric constant decreases up to100 kHz, thereafter it becomes almost constant for all the samples.

1-Introduction

Polymer electrolytes (PES) have attracted considerable interest in terms of their technical applications like computers, communication devices, industrial controls, laboratory equipment, spaceships, electronic vehicles, etc. [1]. Moreover they are directly required in the probable electronic market like solar cells, fuel cells, supercapacitors, sensors, and other electrochemical devices. Polymer electrolytes have many advantages such as no leakage, high performance, safety, volumetric stability, cost efficiency, size and efficiency of the whole battery system as its electrolyte. These polymer electrolytes have a potential to meet the requirements of a solid system such as mechanical stability and no leakage, yet at the same time, they exhibit high ionic conductivity [2]. Other electrolytes have also been reported containing salts of sodium, magnesium and zinc metals besides lithium salt complexes [3, 5]. Presently, the worldwide attention has focused on an environment-friendly material of high-performance energy storage devices. Mostly, lithium ion conducting polymer electrolytes are employed due to their high capacity and excellent chemical stability. On the other hand, lithium-ion batteries are relatively expensive

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and suffer from safety limitations because of their explosive nature. Poly(vinyl chloride) (PVC) has a wide range of applications. PVC is an amorphous, thermoplastic and substantially linear polymer, with a huge commercial market interest due to the accessibility to the basic raw materials. It is used as thermoplastic due to its many valuable features like low price, good process ability, chemical resistance, good mechanical strength, thermal stability, and low flammability. Currently, PVC is one of the world's leading synthetic polymers with global consumption of approximately 40 million tonnes per annum [6, 7].

The combination of polymers with metal compounds is quite popular as it yields excellent performance through taking advantage of the component. Among the polymers, PVC attracts most attention because it has good electronic properties and low cost for its infinite abundance. Moreover, it has better thermal stability and favorable properties of thin film, and can be easily synthesized by chemical or electrochemical methods[8]. PVC supports for metal catalysts (Co, Ni, Cr, Fe, Mo, Bi, and V) has several advantages, such as high flexibility, high conductivity, controllable morphologies and high dispersive ability to prevent the agglomeration of the active catalyst. Among the transition metal ions, VO^{2+} has been extensively used as a probe to study the symmetry of the crystalline electric field. Vanadium oxides are also promising optical switching materials on the basis of their electrochromic properties [9-12]. To the best of our knowledge, no one has reported the thermal, optical and dielectric studies on VO^{2+} doped PVC films. In this paper, we prepared VO^{2+} doped PVC polymer electrolyte for application of solid state batteries. The objective of this work is to study the effect of VO^{2+} dopant on the ionic conductivity, thermal behavior and optical properties of VO^{2+} doped PVC solid polymer electrolytes. Both DSC and TGA were used to analyze the thermal properties of VO^{2+} doped PVC polymer electrolyte system.

2- Experimental procedure

Poly(vinyl chloride) (PVC) obtained from M/S Sigma-Aldrich has a mean relative molecular mass of about 534,000 g/mol. PVC polymer films doped with VO^{2+} in various concentrations were prepared at room temperature by the solution casting method. The desired concentration of $VOSO_4$ solution (1-5mol%) was prepared by using distilled water. 1g/mol of PVC polymer was dissolved in tetra hydro furan (THF) separately. Different amounts of $VOSO_4$ solution (1-5 mol%) were poured into the polymer solution. The mixture was magnetically stirred for 10-12 hours to obtain a homogeneous mixture and then cast into glass dishes. The film was slowly evaporated at room temperature to obtain free-standing polymer films at the bottom of the dishes.

In order to investigate the nature of the polymer films, differential scanning calorimetry (DSC) measurement was carried out by a SEIKO calorimeter (DSC–220) with a continuous heating rate of 10 °C/min under a nitrogen atmosphere from 50 to 400 °C. The thermogravimetric analysis (TGA) was done using the SEIKO thermal analysis (TGA–20) system in the presence of nitrogen flow from 50 to 400 °C, at a heating rate of 10 °C/min. FTIR spectra of these films were recorded using the NICOLET 5700 FTIR spectrophotometer. The spectra were taken over a wavenumber range of 400-4000 cm^{-1}. The EPR spectra were recorded at room temperature on a JEOL FEIX ESR spectrometer operating in the X-band frequency of 9.86 GHz with a field modulation of 100 KHz. The magnetic field was scanned from 0 to 5000 gauss. UV-Vis absorption spectra of the prepared samples were recorded in the range of 200-900 nm at room temperature using JASCO UV-VIS-NIR spectrophotometer (model V.700). In order to investigate the nature of the polymer films, the electrical conductivity of polymer complexes was studied by using Hioki 3532-50 LCR Hi-Tester interfaced to a computer in the frequency range 100 Hz -2 MHz and the temperature range of 303- 363K.

3-Results and discussion

3-1-Differential scanning calorimetry

DSC measurements were carried out to understand the thermal history and stability of the present polymer sample. Using the DSC thermograms, glass transition temperature (T_g), the percentage of relative crystallinity and melting temperature (T_m) of polymer films were measured. The DSC thermograms of pure and VO^{2+} doped PVC films at different concentrations (1-5 mol%) in the temperature range of 50 - 400 °C are shown in Fig.e 1. The pure PVC film shows glass transition temperature around 51 °C. The glass transition temperature of the polymer is influenced by its molecular weight and mobility of chain segments. Earlier, Reddy et al. [13] reported glass transition temperature of 81 °C for pure PVC films and Ramesh and Arof [14] reported around 54 °C. In the present study the thermograms showed a glass transition temperature around 51 °C. Furthermore, the T_g value is found to shift towards higher temperature with the increase in VO^{2+} concentration. This effect is a result of the increase in the cohesive forces of attraction among polymer chains due to the penetration of the VO^{2+} ions into the polymer matrix. This establishes polar attractive forces between the VO^{2+} ions and the chain segments, thereby decreasing the segmental mobility.

It can be seen that all the samples exhibit only one T_g which indicates the homogeneous behavior of the polymer films [14] and should be arisen from the chain movement of this block. It can be seen that high T_g polymers are achieved due to their aromatic backbone.

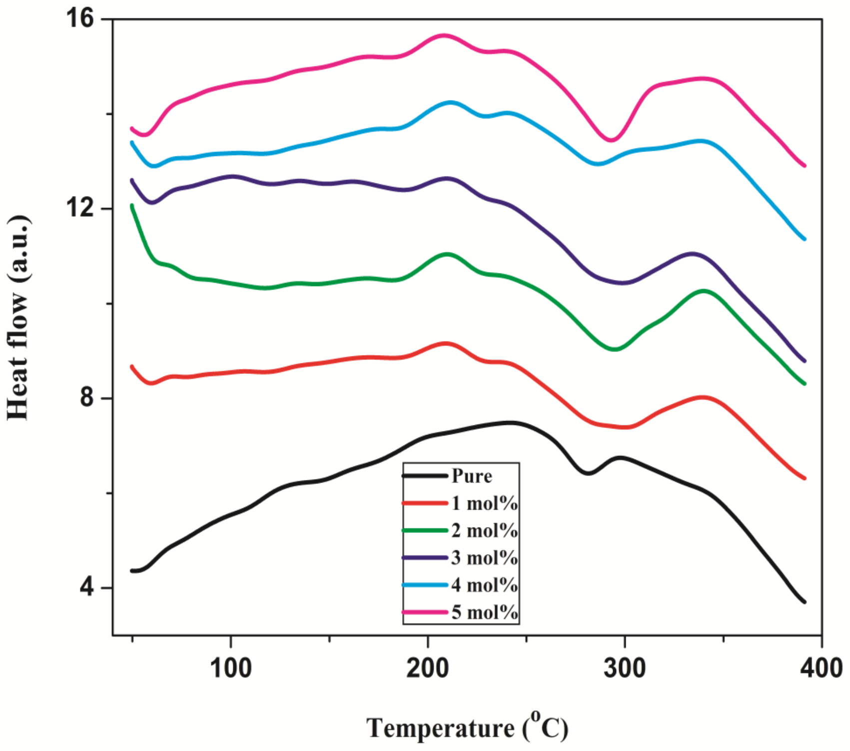

Fig. 1. DSC curves of pure and VO^{2+} doped PVC polymer films

As can be seen in Fig. 1, the two observed peaks are due to the melting of primary crystallites and melting of secondary crystallites. The first endothermic peak observed at 180 °C and 200 °C for pure and VO^{2+} doped polymer films respectively corresponds to the melting of primary crystals. The second endothermic peak has been observed around 280 °C and 300 °C for pure and VO^{2+} doped PVC films respectively which is due to the dehydrochlorination of PVC or melting temperature of last melted crystallites. The endothermic peak increased with the increasing content of VO^{2+} segment. After the attachment of vanadium ions, the endothermic peak shifts to higher temperatures because of the chain confinement by the ion clusters [15]. A slight shift of T_m towards higher temperature on the addition of VO^{2+} to the polymer reveals the variation of crystallinity of the polymer [16]. On increasing the dopant concentration the crystallinity increases which leads to the increase in the decomposition temperature. The DSC curves in Fig. 1 show two exothermic peaks, the first exothermic peak at 200 ˚C contributes to the combustion of organic residuals and the other strong peak at 350 ˚C corresponds to the decomposition temperature of PVC which is well above the heating temperature employed in the present work [18]. The decomposition temperature increases with increasing metal ion concentration which is related to the increase of the polymeric chains rigidity, as a result of the metal inclusion into the molecular structure of the polymeric chains [19].

3-2-Thermogravimetric analysis

Thermogravimetric analysis (TGA) provides complementary and supplementary characterization information to the most commonly used thermal technique, DSC. It is based on the measurement of the mass loss of the material as a function of temperature or time in a controlled atmosphere. In the thermogravimetric method, a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at a constant temperature.

The TGA thermographs of pure and VO^{2+} doped PVC polymer films at different concentrations (1-5 mol%) are shown in Fig. 2. Thermal stability is represented by the weight loss of the sample after heating over the temperature range of 40-400 ˚C. It is found that there are three temperature regions that can be identified over which most of the weight changes occur. The first weight loss occurs between 60 to 70 ˚C with a weight loss of 5% which may be due to the evaporation of THF.

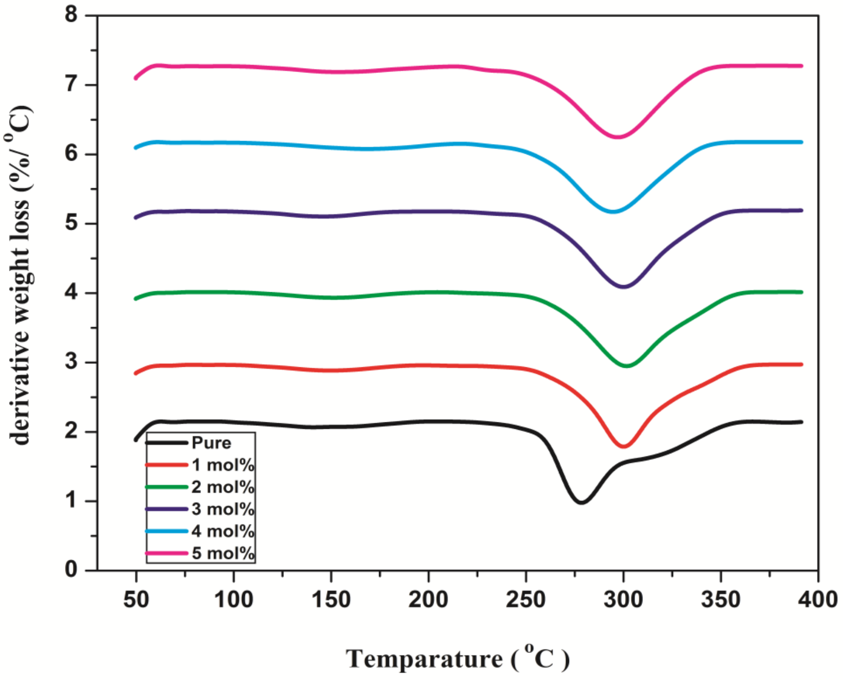

Fig. 2. DTG curves of pure and VO^{2+} doped PVC polymer films

The second weight loss occurs between 260 and 310˚C and is attributed to dehydrochlorination with a weight loss of 20% [20, 21]. The third degradation higher than 310˚C corresponds to the decomposition of PVC main backbone chain [22]. In Table 1, the weight losses are presented at different temperature regions. These results indicate that in the presence of VO^{2+}, the decomposition route is different from that of undoped PVC. Probably the presence of vanadium strengthens the van der waals interactions between the PVC chains, leading to increased decomposition temperature. The DSC and TGA results clearly indicate the increase in the melting temperature, which in turn indicates the higher crystallinity of the doped sample.

Table 1. Thermal degradation of pure and VO^{2+} doped PVC films

Temperature (°C)	**Weight loss (%)**					
	Pure	1 mol%	2mol%	3 mol%	4 mol%	5 mol%
0-70	5.38	6.37	6.37	5.79	4.13	6.01
90-310						
310-400	63.85	63.08	63.08	64.19	62.81	68.15
Residue left at						
400	82.22	78.5	78.5	75.48	74.94	81.93
Max.	17.78	21.50	21.50	24.52	25.06	18.07
decomposition						
temperature	337	329	328	323	331	329

3-3-Fourier Transform Infrared Spectroscopy

The FTIR spectra were recorded in the range 500 – 4000 cm^{-1} in the transmittance mode and the spectra of pure and VO^{2+} (1- 5 mol%) doped PVC polymer films are shown in Fig. 3. The FTIR spectrum of pure PVC exhibits several bands characteristic of stretching and bending vibrations of C – Cl, C – H, C = C and O – H groups. From Fig. 3, the characteristic bands of pure PVC can be classified into three regions. The first is called the C – Cl stretching region in the range of 600 – 700 cm^{-1}. The second region is called C – C stretching in the range from 900 – 1200 cm^{-1}. The third region is 1250 – 2970 cm^{-1} in PVC (numerous CH modes) [23]. The following changes in spectral feature have been observed after comparing the spectrum of pure PVC with VO^{2+} doped PVC. The C – Cl stretching mode for pure PVC is observed at 834 cm^{-1} [24]. When VO^{2+} is added to PVC, there is a broadening of the peak at 1 mol%, thereafter the peak intensity is reduced and the neighboring peaks disappear. This may be due to ionic association through redistribution of charge accompanying formation of ionic pairs and aggregation.

The absorption peak appearing at 1450 cm^{-1} in the pure PVC is shifted to the higher frequency region for the VO^{2+} doped films. By increasing the dopant concentration, the bands are broadened with increasing intensity. These shifts may be due to the addition of VO^{2+} and this is consistent with the earlier observations. It suggests that VO^{2+} may be located on the vinyl chloride of the polymer chain [25]. The strong broad absorption band appearing in the 2769 – 3088 cm^{-1} region in pure PVC corresponds to symmetric and asymmetric CH stretching modes of the CH_2 groups. With increasing dopant concentration, the intensity of these bands in PVC is found to decrease and with further increasing of the dopant concentration the band disappears.

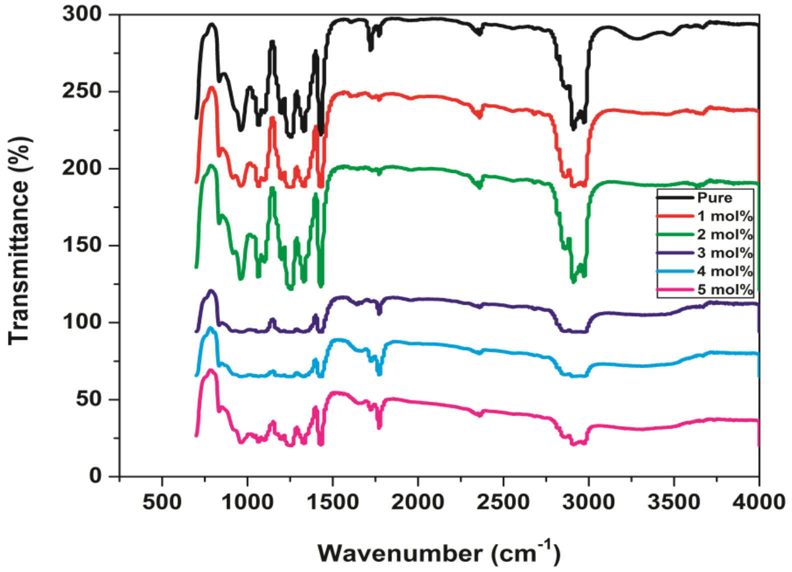

Fig. 3. FTIR spectra of pure and VO^{2+} doped PVC polymer films

The vibrational peaks are observed at 2647, 2539, 1455, 1210 and 890 cm^{-1} of PVC are found to be absent in the doped films. The disappearance of bands in the doped film suggests the coordination or complexation of VO^{2+} to the chlorine of PVC. The change in the intensity of the peaks indicates the complexation between the VO^{2+} ions and polymer. These observations indicate a clear interaction between PVC and VO^{2+} [26].

3-4- Optical studies

UV – Vis absorption spectroscopy is a technique by which the absorption of the electromagnetic wave is measured as a function of frequency or wavelength. UV-Vis absorption is a commonly used analytical tool for studying the interactions between electrons and radiation.The absorption process induces an interaction between VO^{2+} and the polymer [27] which can be understood through variations in the absorption spectra. An absorption spectrum is a fingerprint of a molecule or polymer material.

The optical absorption spectra of pure and VO^{2+} (1- 5 mol%) doped PVC polymer films are shown in Fig. 4. The spectrum of pure PVC film shows a peak lying at about 290 nm which is assigned to the carbonyl group of PVC. In the doped films, the intensity of this peak is increased as the absorption coefficient increases as the doping level increases. This may be due to the string interaction between PVC and VO^{2+} [28].

The absorption coefficient α can be determined from the spectra using the formula.

$$\alpha = \left(\frac{A}{d}\right) \times 2.303 \tag{1}$$

Where A is the absorbance and d is the thickness of the sample. From the position of the absorption edge in the linear portions of α vs. hυ curve (as shown in Fig. 5) when an direct band gap exists, the absorption coefficient has the following dependence on the energy of the incident photon [29].

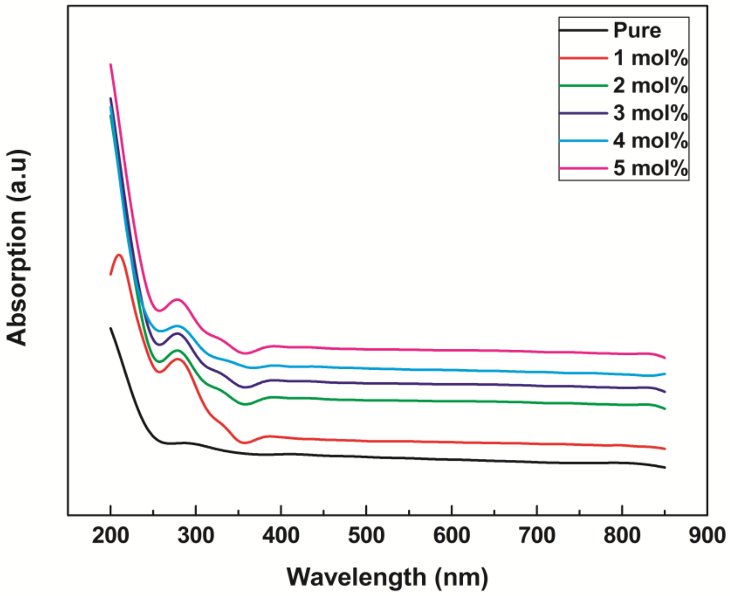

Fig. 4. UV-Vis absorption spectra of pure and VO^{2+} doped PVC polymer films

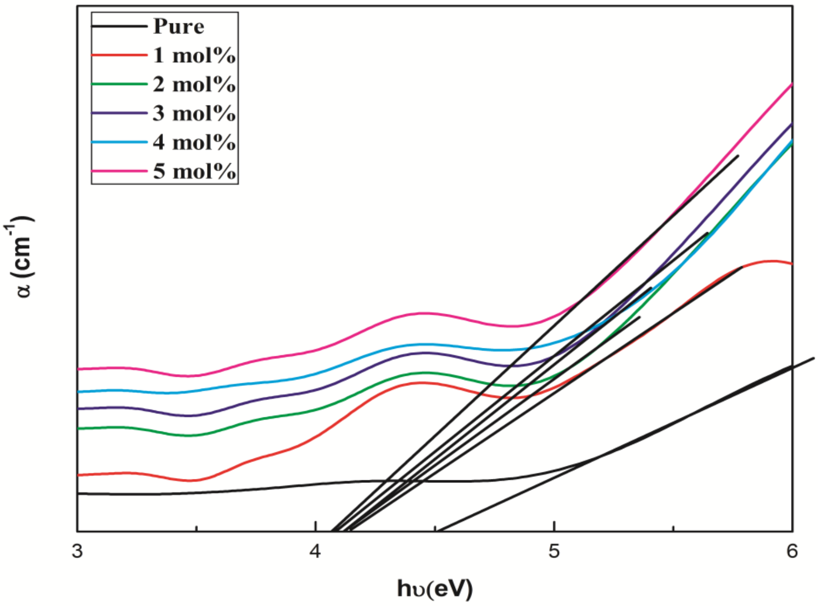

Fig. 5. The α vs. hυ plots of pure and VO^{2+} doped PVC polymer films

For pure PVC film the absorption edge lies at 4.49 eV while for the samples (1-5mol%), it lies at 4.13, 4.11, 4.09, 4.06 and 4.04 eV, respectively. When an indirect band gap exists, the absorption coefficient has the following dependence on the energy of the incident photon [30].

$$\alpha = \frac{c\left(h\upsilon - E_g\right)^m}{h\upsilon} \quad (2)$$

where E_g is the optical band gap and c is band tailing parameter related to constant. At the fundamental edge of semiconductor materials, two types of optical transitions can take place. In both types of optical transitions, the photon interacts with the electron in the valence band and rises it to the conduction band. There is no interaction with the lattice in the direct transition, and the photon interacts with the lattice in indirect transition. In the given equation m decides the transition; for m= ½ the transition is directly allowed, m = 2 for the indirectly allowed transition. After applying all values of m, the samples m = 2 (indirect transition) is found most suitable to calculate band gap.

Table 2. Absorption edge and indirect band gap values of pure and doped with VO^{2+} polymer films

PVC: VO^{2+} Concentration (mol %)	**Absorption edge (eV)**	**Band gap energy (eV)**
		Indirect
Pure	4.49	4.16
1	4.13	3.97
2	4.11	3.94
3	4.09	3.90
4	4.06	3.84
5	4.04	3.71

The indirect band gaps were obtained from the plots of $(\alpha h\upsilon)^{1/2}$ vs. hυ (Fi. 6). For pure PVC polymer film the indirect band gap lies at 4.16 eV while for the doped films the values decrease which vary from 3.97 to 3.71 eV (Table 2). From Table 2, absorption edge and indirect band gap showeda decreasing trend with increasing the VO^{2+} concentration, which is favorable for increasing conductivity. The conductivity of pure PVC at room temperature is about 4.87 x 10^{-8} Scm^{-1} and the highest conductivity has been found for PVC- 5 mol% VO^{2+} polymer electrolyte at room temperature to be 2.86 x 10^{-6} Scm^{-1}. The increase in ionic conductivity with the addition of VO^{2+} is attributed to the reduction in crystallinity of the polymer electrolyte and also the increase in the number of mobile charge carriers [31].

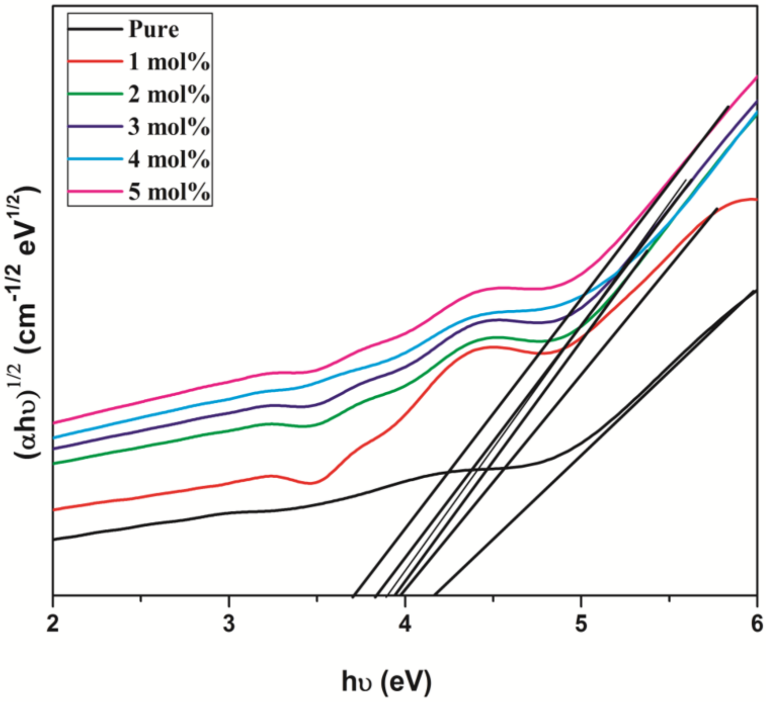

Fig. 6. $(\alpha h\upsilon)^{1/2}$ vs hυ plots of pure and VO^{2+} doped PVC polymer films

3-5-Electron paramagnetic resonance studies The EPR spectra (recorded at room temperature) of pure to VO^{2+} doped (1-5 mol%) PVC polymer films are shown in Fi. 7. The spectra are observed to be complex made up of resolved hyperfine components arising from the unpaired $3d^1$ electron of the ^{51}V isotope whose spin is 7/2 [32]. As the concentration of VO^{2+} is increased, an increasing degree of resolution and signal intensity were observed. The well-resolved hyperfine structure of the ESR spectra obtained for the PVC containing VO^{2+} is typical of isolated V^{4+} in a ligand field of C_{4v} symmetry that is present as VO^{2+} species. The variations of the resolution and the line width of the ESR signal are obviously due to the variations in the concentration of V^{4+} and also due to the structural and microstructural modifications, which can produce fluctuations in the degree of distortion or even of the coordination geometry of V^{4+} sites. The spectra indicate that VO^{2+} exists in the polymer network in an octahedral site with tetragonal compression since $g_{\parallel} < g_{\perp} < g_e$ (Table 3) indicates tetragonal distortion around vanadyl ions increases with increasing the concentration of VO^{2+} [33]. The broadening of the ESR signal with increasing the concentration of VO^{2+} is apparently due to the presence of a larger concentration of V^{4+} and may also be due to exchange coupling between V^{3+} (if any) and V^{4+} [34]. The values of $g_{\parallel}$ and $g_{\perp}$ (obtained from these spectra) are given in Table 3.

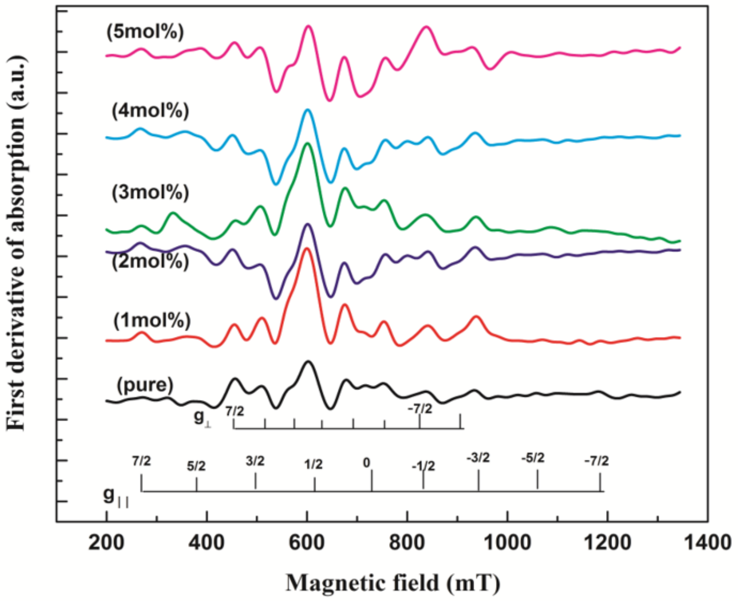

Fig. 7. EPR spectra of pure and VO^{2+} doped PVC polymer films at room temperature

Table 3. The g-factor values of VO^{2+} doped PVC films

VO^{2+} content (mol%)	$g_{\parallel}$	$g_{\perp}$
1	1.921	1.976
2	1.937	1.963
3	1.927	1.956
4	1.930	1.958
5	1.932	1.953

3-6-Dielectric studies

The electrical permittivity describes behavior the of material in the electric field and consists of a two parts real part, $\varepsilon^{/}$, called the dielectric constant, and an imaginary part, $\varepsilon^{//}$, called the dielectric loss factor. Thus, the permittivity is expressed as:

$\varepsilon^{*} = \varepsilon^{/} - j\,\varepsilon^{//}$

where the dielectric constant represents the ability of a material to store electric energy and the dielectric loss factor describes the loss of electric field energy in the material.

The dielectric properties of PVC films were studied in the frequency range of 10 KHz to 2 MHz at room temperature. Fig. 8 show the variation of the dielectric constant as a function of frequency at room temperature for all samples. It is observed that with the increase in frequency, the value of dielectric constant decreases up to100 kHz, thereafter it becomes almost constant for all the samples. The presence of all types of polarizations (dipolar, electronic, ionic and space charge) may be primarily responsible for this type of trend at very low frequencies for the samples. The value of $\varepsilon^{/}$ increases with increase in space charge polarization, which in turn may be due to a large concentration of defects [35]. But on increasing frequency, the above polarizations slowly vanish which results in the rapid decrease in the dielectric constant. The decrease is rapid at lower frequency and slower at higher frequency. The decrease of dielectric constant with increasing frequency is a normal dielectric behavior which is also observed by other researchers [36, 37]. In other words, higher values of dielectric constant at low frequencies may be due to the presence of all the four polarizations namely space charge, oriental, electronic and ionic polarization and its low values at high frequencies might be due to the less of importance of these polarizations [38]. The dielectric constant is higher for 5 mol% when compared with pure and the other VO^{2+} doped samples. This suggests that the electric loss is strongly dependent on the frequency of the applied field and very low electric loss indicates the high purity of the PVC samples. Also, the decrease in $\varepsilon^{/}$ values with the increase in VO^{2+} doping concentration into matrix was observed, which may be due to the more electron exchange between PVC and VO^{2+} at all frequencies [39]. It is observed that with the increase in the doped concentration the value of dielectric constant decreases rapidly with increasing frequency due to the electrode polarization effects. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the value of dielectric constant [40]. At high frequency, the dominant mechanism contributing to dielectric constant is the hopping mechanism in their respective interstice under the influence of alternating current. The frequency of hopping between ions could not follow the frequency of applied field and hence it lags behind. Therefore, the values of dielectric constant become reduced at higher frequency [41]. A low loss factor is desirable for a dielectric material so that the dissipated electric power to the insulator is minimized. This type of consideration is very important for high power circuits operating at high speed.

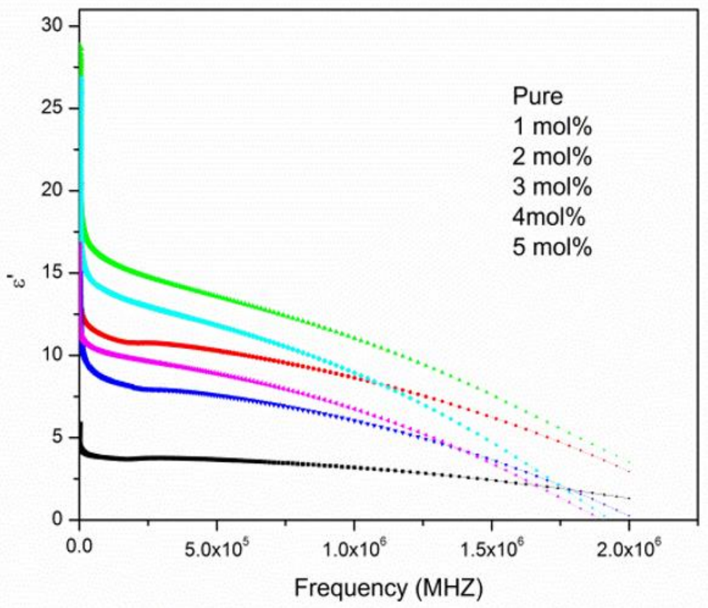

Fig. 8. Dielectric constant vs frequency measured at Room temperature of pure and VO^{2+} doped PVC polymer films

4-Conclusion

Pure and VO^{2+} doped PVC polymer films were prepared using the solution cast technique. Using the DSC thermograms, glass transition temperature (T_g) and melting temperature (T_m) of the PVC films were measured. The pure PVC film shows T_g around 51°C, and the T_g value is found to shift towards higher temperature with the increase in VO^{2+} concentration. Thermogravimetric curves of pure and VO^{2+} doped PVC films showed three distinct steps of weight loss. The DSC and TGA results clearly indicate the increase in the melting temperature, which in turn indicate the higher crystallinity for the doped sample. The FTIR spectrum exhibits a number of bands, which are attributed to C−Cl, C−H, C═C and C−H, CH, CH_2 groups of the stretching and bending vibrations. The absorption edge and indirect band gap showed a decreasing trend with increasing the VO^{2+} concentration which is favorable for increasing conductivity and dielectric constant. The EPR spectra confirmed that the vanadyl ions were present in the PVC polymer films as VO^{2+} in an octa hedral site with a tetragonal coordination. These data revealed that the present electrolyte system is a credible candidate for electrochemical device applications. The dielectric properties of PVC films were studied in the frequency range of 10 to 2 MHz at room temperature. It was observed that with the increase in frequency, the value of dielectric constant decreases up to100 kHz, thereafter it becomes almost constant for all the samples. The dielectric constant is higher for 5 mol%. The VO2+ doped PVC films were compared with all the samples, and it was found that the highest conductivity was related to the 5 mol% VO^{2+} doped polymer electrolyte.

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