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Thermal and Conductivity Studies of VO^{2+} Doped Methacrylic Acid - Ethyl Acrylate (MAA:EA) Copolymer Films

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New polymer electrolyte films of Methacrylic Acid - Ethyl Acrylate (MAA:EA) copolymer embedded with different concentrations of VO^{2+} ions were prepared by solution casting technique. Thermal properties of these films were investigated employing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Electrical conductivity of the films was measured with impedance analyzer in the frequency range of 1 Hz to 1 MHz and in the temperature range of 30 - 70 ºC. It was observed that the magnitude of conductivity increased with the increase in the salt concentration as well as the temperature.

Keywords: *MAA:EA copolymer, solution casting technique, TGA, DSC, Ionic conductivity*

1. Introduction

Copolymers represent a class of materials of long-standing interest to materials scientists, physicists, and chemists. One of their most noteworthy features, microphase separation, occurs when two (or more) covalently tethered and chemically distinct blocks become immiscible [1-4]. Copolymers are hybrid macromolecules that have captured the attention of scientists and technologists over the last several decades. Copolymer films are used for a number of technological and scientific applications due to their optical, thermal, mechanical, electronic and electrical properties. In recent years, there has been considerable interest in the preparation and characterization of copolymer films for their possible use as light stable color filters [5], solar cells and optical sensors [6]. If the properties of the copolymer are tuned in right direction by adding suitable dopants, these copolymers could be best candidates for space applications [7]. Methacrylic Acid-Ethyl Acrylate (MAA:EA) copolymer has drawn special attention amongst the copolymers because of its good environmental stability, easy process, and transparency. MAA:EA copolymer is a potential material having good charge capacity and dopant dependent electrical and optical properties. The chemical structure of MAA:EA copolymer is shown in Figure (1).

Based on the importance and relevance of the MAA: EA copolymer as a suitable matrix, transition metal ions can be used as a filler to modify the electric conduction and optical absorption of the polymer matrix. It should be noted that the formation of transition metal particles inside the polymer system is also of interest for potential application such as storage of optical data, shielding of electromagnetic radiation flexible elements for resistive heating, laser systems, optical lenses and integrated waveguides. The VO^{2+} ion introduces more packing efficiency to the host, which in turn influences the thermal properties of the polymer [8]. Moreover, so far no work has been reported on VO^{2+} ions doped MAA:EA films. Hence, the authors have aimed at the present investigation.

2. Materials and Methods

Methacrylic Acid - Ethyl Acrylate (1:1) dispersion 30 percent copolymer with molecular weight 250,000 g/mol was purchased from Merck Millipore India Ltd. MAA:EA copolymer films(14µm thickness)doped with VO^{2+} in various concentrations were prepared at room temperature by solution casting method. The desired concentrations of VO^{2+} solution (1.5, 3.5, 5, 7.5 and 10 mol%) were prepared by using distilled water. 5ml of MAA:EA copolymer was dissolved in distilled water separately. Different amounts of (1.5, 3.5, 5, 7.5 and 10 mol%) VO^{2+} ions were added into the copolymer solution. The solution was magnetically stirred for 10-12 hours to get homogeneous mixture and then cast onto plastic dishes. The solution was slowly evaporated at room temperature to obtain free standing copolymer film at the bottom of the dishes.

In order to investigate the nature of the copolymer films, differential scanning calorimetry (DSC) measurement was carried out by an SEIKO calorimeter (DSC - 220) at a continuous heat rate of 10 °C/min under nitrogen atmosphere from 40 to 400 ºC. The thermo gravimetric data was recorded using the SEIKO thermal analysis system (TGA - 20) in the presence of nitrogen flow from 40 to 600 ºC at the heating rate of 10 °C/min. The electrical properties of the polymer electrolyte films were measured by a computer controlled impedance analyzer (PSM 1735, Newton 4th Ltd, UK) over the frequency range 1 Hz-1 MHz with a signal level of 10 mV. The prepared samples were cut into circular pieces and dried at 50 °C under vacuum for 1 h to reduce the environmental moisture effect before the electrical measurements. The

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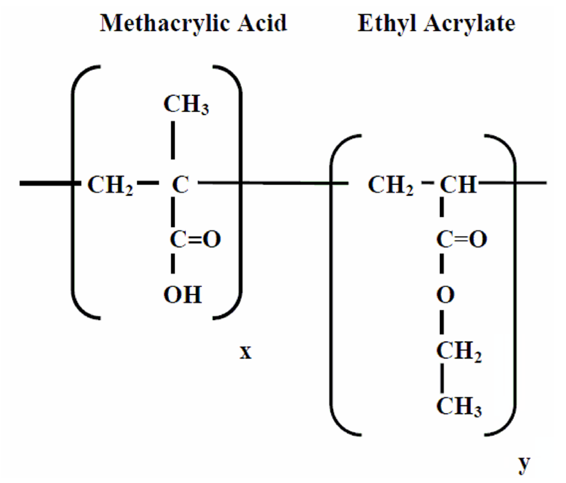

Figure 1. Chemical structure of MAA:EA copolymer.

measurements were carried out by sandwiching the polymer electrolyte film between two stainless steel electrodes in the temperature range of 30 - 70 ºC.

3. Results & Discussion

3.1. Thermal studies

3.1.1. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is used to measure the changes that occur in a sample as a function of temperature. Using this technique, the glass transition temperature (T_g) as well as melting temperature (T_m) of the material can be identified [9]. Figure (2) shows the DSC curves of pure MAA:EA copolymer and MAA:EA doped with VO^{2+} ions in different concentrations (1.5, 3.5, 5, 7.5 and 10 mol%). From the Figure, T_m and T_g of pure MAA:EA copolymer films are observed to be 210 and 75ºC respectively. DSC analysis made on the pure and VO^{2+} ions doped MAA: EA copolymer samples having only one T_g indicates homogeneous behavior of the copolymer films.

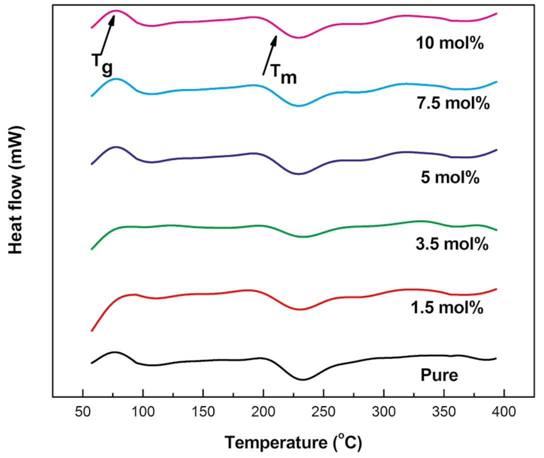

Figure 2. DSC curves of MAA:EA copolymer films containing VO^{2+}(a) pure (b) 1.5 mol% (c) 3.5 mol% (d) 5 mol% (e) 7.5 mol% (f) 10 mol%.

An endothermic peak is observed at around 210 ºC which corresponds to the melting point of MAA:EA copolymer. A slight shift of T_m towards lower temperature on the addition of VO^{2+} to the host polymer reveals the transition from semi - crystalline to an amorphous phase. The lowering of T_m upon dopant addition is quite common [10] and has been related to the decrease in spherulite sizes [11] and their surface free energy. This clearly indicates the suppression of crystallites, thereby increasing the amorphous content in the polymer. As a result of more flexible amorphous environment getting trapped in or adjacent to the crystalline matrix, the suppressed crystalline portion of the VO^{2+} doped MAA:EA copolymer melts probably at lower temperatures.

3.1.2 Thermogravimetric analysis

Figure (3) shows the dTGA curves of pure and VO^{2+} ions doped MAA:EA copolymer films at different concentrations (1.5, 3.5, 5, 7.5 and 10 mol %). It can be clearly seen that the samples start complete decomposition at around 400 ºC. This indicates that the samples are stable up to that temperature. Analysis of dTGA curves of pure and VO^{2+} ions doped copolymers reveals that there are three distinct steps of weight loss. The first step of weight loss in the range of 50 - 210 ºC may be attributed to the elimination of side products in the process of anhydride formation as indicated by an endothermic transition in the same temperature range as noticed from DSC scans. The 4 -5% weight loss below 170 ºC is attributed to the loss of absorbed water [11, 12]. The second and third steps observed in the temperature range 210- 400 ºC and above 400 ºC are the regions of major weight loss which are due to the extensive degradation of the polymer backbone. According to Zain et al. [10] the decomposition occurred at 210 ºC is attributed to the elimination of evaporated molecules in the side groups of MAA:EA copolymer and the decomposition above 400 ºC is due to quantized graft chain degradation.

3.2. Conductivity studies

3.2.1. Impedance analysis

AC impedance spectroscopy has become a powerful tool for the investigation of ionic conductivity of solid electrolyte films. Figure (4) shows the typical impedance plot of pure and various concentration of VO^{2+} doped MAA:EA copolymer at room temperatures in the frequency range of 1Hz-1MHz. It has been found that the idealized impedance plane plots of Z'' as a function of Z', i.e. Cole-Cole plots of the films (Z' and Z'' denote the real and imaginary parts of the complex impedance Z^*), contain a semi circular arc and inclined spike, which together are characteristic behavior of ionically conducting solids with blocking electrodes [13]. The semicircle is due to the parallel combination of bulk

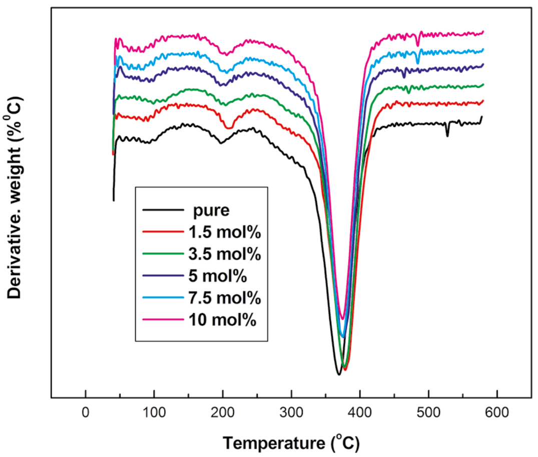

Figure 3. dTGA curves of pure and VO^{2+} doped MAA:EA copolymer films.

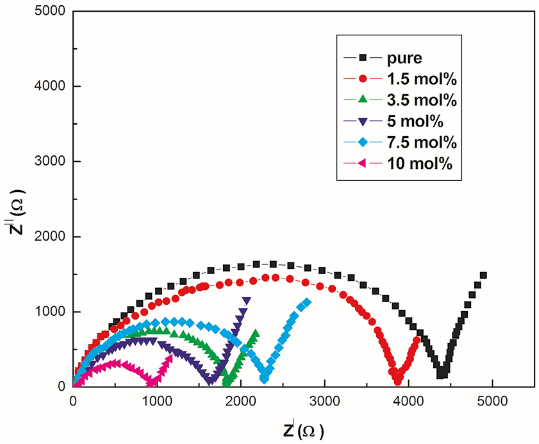

Figure 4. Room-temperature Nyquist impedance plots of pure and VO^{2+} doped MAA:EA copolymer electrolyte films.

resistance (due to the migration of ions) and bulk capacitance (due to the immobile polymer chains). Hence the frequency response of the given sample could be represented by an equivalent circuit consisting of a parallel combination of the circuit elements R (resistance) and C (capacitance). In impedence analysis, the semi circles are due to the bulk properties and the spike are to interfacial process in polymer electrolyte. The bulk resistance decreases with increasing dopant concentration. The decrease in the bulk resistance of the polymer electrolyte is due to enhancement of the ionic mobility and the number of carrier ions with concentration of the dopant, resultantly semi - circular form is lost similar trend was observed by Pavani et. al [9]. The presence of the depressed semi circle reveals the non-Debye nature of the sample [14] due to the potential well for each site, through which the ion transport takes place, not being equal. The inclined spike represents formation of double layer capacitance at the electrode-electrolyte interface due to the migration of ions at low frequency. The capacitance values are in the range of pF, which represents the bulk response of the sample[15]. The electrode double layer at each interface possesses increasing impedance against ion transfer with decrease in frequency, which in the Nyquist plot of impedance spectra, was represented by an inclined spike [16]. Furthermore the inclination of the spike at an angle less than 90° to the real axis is due to the roughness of the electrode-electrolyte interface [17]. The ionic conductivity of pure and VO^{2+} MAA:EA copolymer electrolytes is calculated from the relation $\sigma = I/R_bA$ where I, is the thickness of the film, A, the area of the film and R_b, the bulk resistance of the film material which is obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance [18]

3.2.2. Composition dependence of conductivity

The variation of conductivity (σ), as a function of VO^{2+} concentration in pure at different temperatures is shown in Figure (5). From the figure, it is seen that the conductivity of pure MAA:EA is about 8.25×10^{-9} Scm^{-1} at room temperature and increases to 1.14×10^{-7} Scm^{-1} for 10 mol% of VO^{2+} ions. The increase in ionic conductivity with the addition of VO^{2+} is attributed to a reduction in crystallinity of copolymer electrolyte and also the increase in number of mobile charge carriers. The coordination interactions of the ether oxygen atoms of MAA:EA with VO^{2+} cations, which result in a reduction in crystallinity of MAA:EA copolymer, are responsible for the increase in ionic conductivity. The maximum conductivity shows the maximum and effective interaction between oxygen atoms and VO^{2+} cations in the electrolytes [19]. VO^{2+} ions dissociation is an additional factor in enhancement of ionic conductivity. The dissociation of dopant will promote more free VO^{2+} ions transfer into the electrolyte. The increment in conductivity with salt concentration due to the rise in the number of charge carriers is shown in Figure (5). The conductivity data of pure and VO^{2+} doped MAA:EA copolymer at room temperature are presented in Table 1.

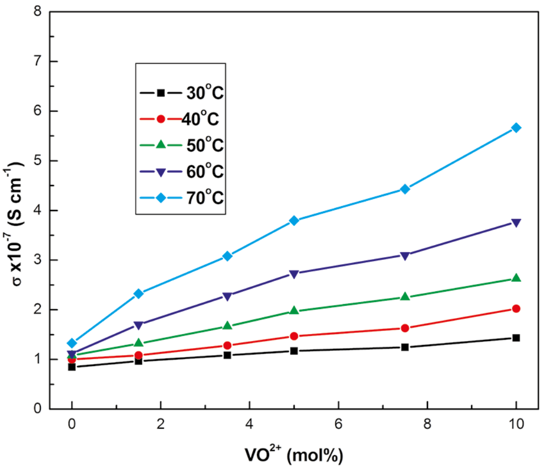

Figure 5. Ionic conductivity as a function of VO^{2+} concentration for the MAA:EA copolymer electrolyte system at different temperatures.

Table 1. Conductivity and energy values of pure and VO^{2+} doped MAA:EA copolymer films

Concentration Mol% VO^{2+}/ MAA:EA	Conductivity at 303 K (S cm^{-1})	Activation energy E_a(eV)
Pure	8.25×10^{-9}	0.53
1.5	3.26×10^{-8}	0.50
3.5	5.78×10^{-8}	0.48
5	6.25×10^{-8}	0.46
7.5	0.22×10^{-7}	0.43
10	1.14×10^{-7}	0.41

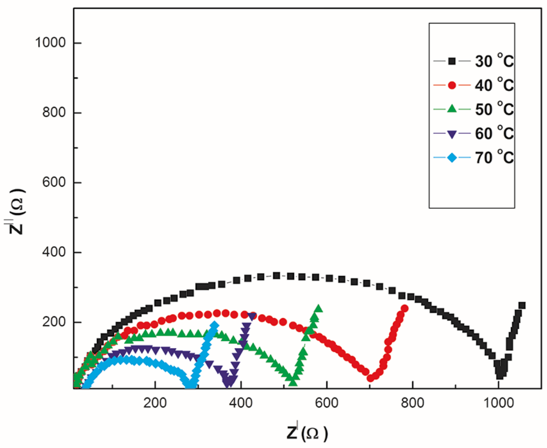

Figure 6. Nyquist impedance plots of the 10 mol% of VO^{2+} doped MAA:EA copolymer electrolyte film at different temperatures.

Figure (6) shows typical Nyquist impedance plots of the 10 mol% of VO^{2+} doped MAA:EA copolymer electrolyte film at different temperatures in the frequency and temperature ranges 1 Hz - 1 MHz and 30 - 70 ºC, respectively. The plots exhibit the general behavior of ionic solids with blocking electrode i.e., a semi-circle with an inclined spike. The diameter of the semi-circle shrinks with raising temperature, indicating a negative temperature coefficient for resistance or a positive temperature coefficient for conductivity. Moreover, with increasing temperature, the spikes/lines slightly get parallel to the imaginary axis, which is an indication of better contact of the copolymer electrolyte film with the electrode.

3.2.3. Temperature dependence of conductivity

The bulk conductivity has been calculated from the impedance plot, and logarithms of conductivity were plotted against the inverse of temperature to observe the temperature dependence of conductivity. Figure (7) shows the linear dependence of log σ on inverse temperature (1000/T) for pure and VO^{2+} doped MAA:EA copolymer films. The linear variation in log σ vs. 1000/T plot suggests an Arrhenius-type thermally activated process represented by

$$\sigma_{dc} = \sigma_0 \exp(-E_a/kT) \qquad (1)$$

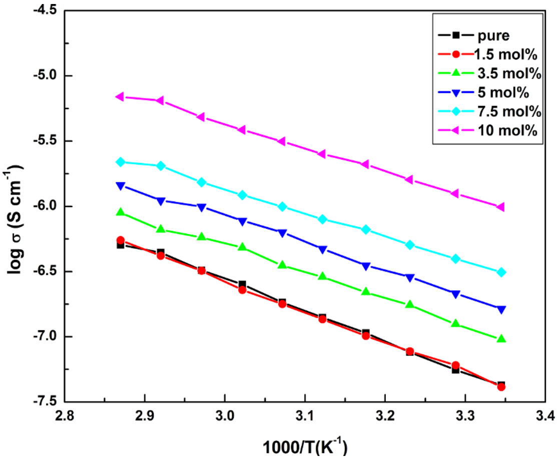

Figure 7. linear dependence of log σ on inverse temperature (1000/T) for pure and VO^{2+} doped MAA:EA copolymer films.

where σ_o is the pre-exponential factor, E_a the activation energy, k the Boltzmann constant and T the absolute temperature. The magnitude of ionic conductivity was found to increase with increase in temperature in all compositions of the polymer blend electrolyte system including pure film. This may be explained on the basis of an increase in either ionic mobility or the concentration of carrier ions [20].In polymer electrolytes, change of conductivity with temperature is due to segmental motion, which results in an increase in the free volume of the system [21]. When temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur [21]. Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity increases. The increase of temperature causes the increase in conductivity due to the increased free volume and their respective ionic and segmental mobilities. This increase in free volume would facilitate the motion of ionic charges [22].

3.2.4. Activation energy

The activation energies were calculated from the slope of the Arrhenius plots and the values are shown in Table 1. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration that can be evaluated by linear fitting of the log σ vs 1000/T plots [23, 24]. Therefore, it can be suggested that the activation energy is due to the energy that is required to provide a conductive condition for the migration of ions. From the table it was found that the activation energy values decreased with increasing concentration of VO^{2+}. This may be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice [25]. These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice, resulting in a decrease of activation energy.

4. Conclusions

Polymer electrolytes based on MAA:EA copolymer with VO^{2+} as the dopant at different concentrations were prepared using solution casting technique. The DSC measurements of VO^{2+} ions doped MAA:EA copolymer films show that the melting temperature shifted towards the lower temperature with increasing dopant concentration. The dTGA curves in the pure and VO^{2+} doped copolymers reveal that there are three distinct steps of weight loss. This is due to loss of absorbed water, elimination of side chains and main chain decomposition. The first step of weight loss in dTGA supports an endothermic transition in DSC. The impedance study showed that the addition of VO^{2+} ions to the polymer electrolyte enhanced the ionic conductivity. The increase in the conductivity with an increase in concentration of VO^{2+} was attributed to an increase in the amorphosity.

5. References

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