Chapter 2

Optimized AC Conductivity Correlated to Structural, Morphological and Thermal Properties of PVDF/PVA/Nafion Polymer Composite

2.1 INTRODUCTION

The polymer science field has drawn an attention for the synthesis of composite, blends and electrolytes (Rajendran et al., 2004; Gnana Kumar et al., 2008). The properties of polymers such as good thermal, electrical and mechanical stability are make it useful for the development of different electrochemical devices such as sensors, fuel cells, supercapacitors and battery applications (Pradeep and Shikha, 2011; Hyeonseok, 2013). In several studies, the properties of polymer were modified by adding different plasticizers, organic/inorganic compound, salts etc.

In the present study the PVDF/PVA/Nafion polymer composite was synthesized. A PVDF polymer is used as a host polymer due to its interesting engineering properties. PVDF is a polymer comes under thermoplastic fluopolymer with highly non-reactive properties. PVDF are also called as plastic material with good strength and easy melt properties. Among all thermoplastic polymers PVDF is having low melting temperature 177°C and low density. A pure PVDF polymer has been used for several applications such as pipes, tubes and plates. PVDF is a semi-crystalline polymer with -35°C glass transition temperature. The PVDF is mainly known for its piezoelectric properties but after poled, it reflects the ferroelectric properties (Xuemei et al., 1997). These properties of PVDF make it useful for sensors and battery applications (Angulakshmi et al., 2011). However, PVA polymer is used for cross-linking agent in the present study. PVA is a polymer obtained by polymerizing vinyl acetate. It is synthetic water soluble polymer. PVA is having several attractive properties such as high hydrophilic, chemical stability, highly emulsifying and good film forming properties (Hassan and Peppas, 2000). For obtaining a fully hydrolysed PVA it should have a melting temperature of 230°C and above. Nafion can be obtained after polymerization of perfluoroalkyl sulfonyl fluoride
with tetrafluoroethylene and used as a dopant in present study. Nafion is having unique ionic properties; due to this it received an attention towards the development of proton exchange membrane fuel cells (Sahu et al., 2009; Molla and Compan, 2011). Nafion is having good thermal and chemical stability but also suffers with a disadvantage of methanol crossover rate (Almeida and Kawano, 1999). In present study, we have carried out with structural, morphological, thermal and electrical properties of PVDF/PVA/Nafion composite. The main objective of this study is to obtain the influence of Nafion (proton conducting nature) on PVDF/PVA polymer blend.

2.2 EXPERIMENTAL

2.2.1 MATERIALS

The polymer composite has been prepared by comprising PVDF, PVA and Nafion. PVDF a fine white powder of molecular weight (MW) 5,34,000 was procured from SD Fine. Chem. Ltd., Mumbai, India. PVA white granules of MW 1,25,000 and LR grade with 86-89% of degree of hydrolysis was procured from SD Fine. Chem. Ltd., Mumbai, India. Nafion is used as a dopant in the present study was procured from E. I. Dupont de Nemours and Co. The polymer composite was prepared by solution casting. Therefore DMF and water were used as solutes. The DMF was procured from Sisco Research Laboratories, Mumbai, India.

2.2.2. PREPARATION OF PVDF/PVA/NAFION COMPOSITE

The PVDF/PVA/Nafion composites were prepared by solution casting. The varying range (70-60 wt% in steps of 5 wt%) of PVDF powder was mixed with DMF and stir (350 rpm) at 70°C for 12 h for proper miscibility with solvent. Simultaneously, PVA (25 wt% constant overall was dissolved in DMF:water::9:1 and stir at 350 rpm for 10 h at 70°C for homogeneous mixing. Afterward a homogeneous solution of PVDF and PVA was mixed together and added 5, 10 and 15 wt% loading of Nafion in volume fraction. The homogeneity and proper miscibility was obtained after consistent stirring (350 rpm) for 10 h at room temperature. The prepared homogeneous solution of PVDF/PVA/Nafion was poured into a glass petrish dish and kept in oven under controlled temperature (60°C) for 12 h. The PVDF/PVA/Nafion composite films of thickness of 50 µm were peeled off
and used for further characterizations. The protocol for the preparation of PVDF/PVA/Nafion polymer composite is shown in Fig. 2.1. The chemical reaction occurs between PVDF, PVA and Nafion is shown in Scheme 2.1.

Fig. 2.1: Protocol to synthesis PVDF/PVA/Nafion polymer composite.
2.3 CHARACTERIZATION

Several characterization techniques of polymer composites have been carried out to claim it for the different electrochemical device applications. The specific application of any polymer composite depends on various parameters such as cost efficiency, environment friendly nature and easy synthesis process. Initially a proper selection of polymer and dopant compound is important for the preparation of polymer composite. After initial selection and synthesis of polymer composite, its chemical, structural, morphological, thermal and electrical properties need to be explored by using different characterization techniques. For determining the properties of synthesized polymer composite at microscopic and macroscopic levels, different types of structural and morphological techniques are used in the present study. In present study, the following characterization techniques were implemented for determining different properties of polymer composite.
2.3.1 X-RAY DIFFRACTION (XRD) TECHNIQUE

The XRD is very vital technique used to determine structural changes and atom/molecular arrangements in material. The XRD data have been used by researchers to obtain several properties such as crystalline size, interlayer spacing and phase equilibrium; all this can also correlate with the order/disorder formation of molecules and atom inside the material and mechanical and morphological properties. However, the amorphous and crystalline nature of polymer composites and electrolytes can be analyzed by calculating degree of crystallinity from XRD analysis. The change in lattice parameter of a material can be evaluated by using Bragg’s law of diffraction. When the x-ray beam comes in a contact with a material it gets diffracted and the concept of diffraction is explained by Bragg’s law \( n\lambda=2dsin\theta \), where \( \lambda \) is a wavelength of X-ray, \( d \) is a interlayer spacing and \( \theta \) is a diffraction angle. The schematic representation of Bragg’s diffraction pattern is shown in Fig. 2.2.

![Bragg's diffraction pattern](image)

Fig. 2.2: Schematic representation of Bragg’s diffraction.

In the present study, the evaluation of interlayer spacing and crystalline size was carried out by using XRD. The structural variation in polymer composite was determined by these parameters. The XRD studies of polymer composite was done by using Cu Kα radiation of wavelength 1.54 Å with a graphite monochromatic diffraction pattern produced by Bruker AXS D8 focus advanced XRD meter (Rigaku, Japan, Tokyo) with ‘Ni- filtered’. The scans in XRD instrument were taken in 2θ range from 10 to 80° with a scanning speed of 1°/mm and step size of 0.01°.
2.3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY TECHNIQUE (FTIR)

To understand the chemical composition and molecular structure arrangement of a material, there are different techniques are used such as NMR, UV-vis., Raman spectroscopy, Infrared spectroscopic. The Fourier transform infrared spectroscopy (FTIR) technique is one of the important characterizations for identifying the presence of different functional group in a material. The FTIR is a modern advancement of Infrared spectroscopy (IR) technique. The FTIR spectroscopy usually records the spectrum of entire sample. The FTIR technique uses a beam of light containing a multiple frequencies instead of monochromatic beam of light. It basically measures the amount of light absorbed or transmitted at particular frequencies. The total amount of absorbed or transmitted data at different combinations of frequencies gets together by computer software and infers the FTIR spectrum containing the absorption or transmittance peak at each wavelength. The schematic representation of the working of FTIR spectrometer is shown in Fig. 2.3.

![Fig. 2.3: Schematic representation of FTIR spectrometer.](image)

In the present study the chemical composition and structural changes with respect to molecular arrangement in polymer composite was performed by using FTIR technique. The FTIR spectrum of present polymer composite was recorded by using Shimadzu IRZ finity-1 spectrometer based FTIR spectroscopy in the wavenumber range of 500-4000 c.m⁻¹ operated in a transmittance mode.
2.3.3 ATOMIC FORCE MICROSCOPY (AFM)

Atomic force microscopy technique (AFM) is a high resolution microscopy instrument used for the morphological characterization of samples. It demonstrates the resolution of nanometer fraction which is much better than optical microscopy. This AFM technique is mainly used to measure the surface roughness and smoothness of a sample. AFM micrograph generally produces the two dimensional as well as three dimensional images of a sample. The cantilever present in AFM is consisting of sharp probe used to scan the surface of a sample. When the cantilever tip brought to the surface of the sample, the force occurs between sample and tip deflects the cantilever which follows the Hooke’s law. The contact mode, tapping mode and non-contact modes are major categories of AFM operation. The schematic representation of AFM microscopy using beam deflection method is shown in Fig. 2.4. In present study the morphological study of polymer composite was carried out by using AFM (Nanosurf Easy Scan 2, Switzerland) operated in the air at 25°C.

![Fig. 2.4: Schematic representation of AFM microscope using beam deflection.](image-url)
2.3.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC is one of the important thermal characterization technique used for polymeric material. This thermal technique is useful to determine the melting temperature ($T_m$), glass transition temperature ($T_g$), heat capacity, heat enthalpy ($\Delta H_m$) and with respect to these information, degree of crystallinity ($\chi_c$) of polymeric material can be measured. The degree of crystallinity of any material can be obtained by using a ratio of change in heat enthalpy ($\chi_c \% = (\Delta H_m / \Delta H_m^0) \times 100$). The difference between the energy flowing through sample and reference material with respect to temperature and time produces the heat enthalpy data from DSC. The model graph of DSC with accordance to data profile is shown in Fig. 2.5.

![Fig. 2.5: Model graph of DSC profile.](image)

In the present study the thermal characterization of polymer composite was carried out by Using DSC technique. The DSC data was recorded by using DSC-60, Shimadju, Japan. All experiments for present polymer composite was performed in the temperature range of 30-300°C with heating rate of 10°C min$^{-1}$ in air atmosphere.
2.3.5 ELECTRICAL CHARACTERIZATION

The electrical properties such as dc conductivity, ac conductivity, dielectric properties and impedance spectroscopy of materials can be obtained by applying external dc voltage across the sample which is kept between the electrodes. There are mainly two types of electrodes: blocking and non-blocking electrodes. The electrical properties of material measured as a function of varying temperature and frequency. The determination of electrical properties depends on the electrical dipole interaction with external electric field. The temperature dependant conductivity is an important property of polymer composites. As the temperature changes the electrons or the ions present in material, gain certain energy and starts moving towards the higher energy level. Therefore, the electrical conductivity of a material decreases with respect to temperature. The model graph shown in Fig. 2.6 represents the change of conductivity with respect to temperature.

![Model graph of conductivity with respect to temperature.](image)

Fig. 2.6: Model graph of conductivity with respect to temperature.

In present study the electrical characterization was carried out by using PSM-1735 impedance analyzer. The sample cut into small size of 15 mm diameter and sandwiched between electrodes and kept inside dry temperature controller. All the samples were done with varying range of temperature (40 to 150°C) at specific frequency of 30 MHz.
2.4 RESULT AND DISCUSSION

2.4.1 XRD ANALYSIS

The XRD analysis is useful to determine the structural properties such as interlayer spacing (d) and crystalline size (D) of the polymer composite. The XRD pattern of pure PVA and PVDF is shown in Fig. 2.7. In XRD pattern, a broad peak at $2\theta = 19.46^\circ$, which is a hollow amorphous region represents the semi-crystalline nature of PVA (Attia and Abd EI-kader, 2013). However, the XRD pattern of PVDF as shown in Fig. 2.7 represents one sharp intense peak and can be easily distinguish from XRD pattern of PVA. The most prominent peaks for PVDF are obtained at $2\theta = 19.13^\circ$. This peak obtained for 002 planes represents the highly intense semi-crystalline nature of PVDF. Another peak of PVDF at $2\theta = 19.40^\circ$ is very small as compared to the sharp peak with lower crystallinity.

![XRD pattern of pure PVA and PVDF](image)

Fig. 2.7: XRD pattern of pure PVA and PVDF.
The XRD pattern of PVA/PVDF/Nafion composite for different loading wt% is shown in Fig. 2.8 (a-d). The addition of Nafion in polymer system causes the decrease in intensity of XRD peaks. In compare to pure polymer XRD pattern, no new peaks have been found in the complex indicating the complete dissociation of Nafion with polymer system (Hema et al., 2009). This result demonstrates the crystalline to amorphous phase transformation. For lower wt% (5 and 10 wt%) loading of Nafion represents almost semi-crystalline peaks with high intensity. However for higher loading wt% (15 and 20 wt%) loading of Nafion, represents the amorphous phase with very less intense peaks. Therefore, we can conclude that the induction of Nafion helps for phase transformation of polymer blend. The evaluated structural parameter gives the more idea and can be direct towards the analysis results.

Fig. 2.8: XRD pattern of PVDF/PVA/Nafion for (a) 70:25:05, (b) 65:25:10, (c) 60:25:15 and (d) 55:25:20 loading wt%.
The interlayer spacing (d) and crystalline size (D) of pure polymer and composite is shown in Table 2.1.

**Table 2.1: Evaluated structural parameters from XRD for different loading wt% of PVDF/PVA/Nafion.**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample Code (wt%)</th>
<th>2θ (degree)</th>
<th>d (nm)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PVA::100</td>
<td>19.36</td>
<td>0.458</td>
<td>2.73</td>
</tr>
<tr>
<td>2.</td>
<td>PVDF::100</td>
<td>19.13</td>
<td>0.463</td>
<td>5.83</td>
</tr>
<tr>
<td>3.</td>
<td>PVDF/PVA/Nafion:: 70:25:05</td>
<td>19.31</td>
<td>0.461</td>
<td>5.17</td>
</tr>
<tr>
<td>4.</td>
<td>PVDF/PVA/Nafion:: 65:25:10</td>
<td>19.19</td>
<td>0.464</td>
<td>4.95</td>
</tr>
<tr>
<td>5.</td>
<td>PVDF/PVA/Nafion:: 60:25:15</td>
<td>19.43</td>
<td>0.456</td>
<td>4.69</td>
</tr>
<tr>
<td>6.</td>
<td>PVDF/PVA/Nafion:: 55:25:20</td>
<td>20.40</td>
<td>0.434</td>
<td>2.66</td>
</tr>
</tbody>
</table>

The interlayer spacing (d) of polymer composite was evaluated from Bragg’s law:

\[ n\lambda = 2d \sin \theta \]

Where, \( \lambda \) is the wavelength of X-ray (1.54 Å), \( \theta \) is the scattering angle, \( n \) is a positive integer and \( d \) represents the interlayer spacing. However, the degree of crystallinity (D) of polymer composite follows the Scherer’s formulae.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

Where, \( D \) represents the degree of crystallinity, \( \beta \) is the FWHM values of the obtained peaks, \( \theta \) is Bragg angle and 0.9 is the value of shape factor. From the above table it is clear that the crystallinity of Nafion inducted polymer composite is decreasing and transforming into amorphous phase. The secondary peak obtained at around \( 2\theta = 40^\circ \) clearly represents the amorphicity nature of composite with respect to loading wt% of Nafion. The interlayer spacing does not show any major changes. The change in phase with respect to loading wt% of Nafion will influence the electrical properties of PVDF/PVA/Nafion composite.
2.4.2 FTIR ANALYSIS

The FTIR studies have been carried out to demonstrate chemical composition between PVDF/PVA and Nafion. The FTIR spectrum of pure PVA and PVDF is shown in Fig. 2.9. The FTIR spectrum of pure PVA represents the transmittance peak at 3419 c.m\(^{-1}\) with respect to intermolecular OH-bending. The peak centered at 3151 c.m\(^{-1}\) and 1625 c.m\(^{-1}\) assigned for OH-vibration and OH-bending of PVA respectively. The C-H stretching and C-H deformation in PVA is obtained a transmittance peak at 2924 c.m\(^{-1}\) and 1400 c.m\(^{-1}\) respectively. However in case of pure PVDF, a major transmittance peaks are obtained at 3010 c.m\(^{-1}\) and 2976 c.m\(^{-1}\) assigned for symmetric and asymmetric stretching vibration of \(-\text{CH}_3\). The transmittance peak of PVDF obtained at 1425 c.m\(^{-1}\) assigned for symmetrical stretching of \(-\text{CF}_2\) group, peak at 902 c.m\(^{-1}\) represents the mixed mode of CH\(_2\) rocking and CF\(_2\) asymmetric stretching in \(\beta\)-phase and at 833 c.m\(^{-1}\) is assigned for in-plane bending or rocking vibration in \(\alpha\) phase (Gang et al., 1994; Benz et al., 2002).

![FTIR spectrum of pure PVA and PVDF](image)

**Fig. 2.9:** FTIR spectrum of pure PVA and PVDF.
The shift in transmittance peaks were obtained after addition of Nafion in PVDF/PVA blend. In presence of Nafion, a broad peak was observed in the wavenumber range of 3500-3000 c.m\(^{-1}\) as shown in Fig. 2.10 (a-c). For 5 wt% loading of Nafion in PVDF/PVA blend the transmittance peak was observed at 3500 c.m\(^{-1}\) assigned for –OH vibration and reveals the presence of PVA in present composite. Similarly, the peak observed at 2932 c.m\(^{-1}\) assigned for C-H stretching represents the presence of PVDF. As the loading wt% of Nafion increases the shift in transmittance peaks has been observed. The peak assigned for OH-stretching was shifted towards the lower wavenumber (3305 c.m\(^{-1}\)). The major peak shifts are observed for CH-stretching from 2953 c.m\(^{-1}\) to 2972 c.m\(^{-1}\). The shift of this wavenumber may be due to intercalation between PVDF, PVA and Nafion. Therefore the FTIR analysis confirms the chemical composition and complex formation of PVDF, PVA and Nafion.

Fig. 2.10: FTIR spectrum of PVDF/PVA/Nafion for (a) 5, (b) 10 and (c) 15 loading wt% of Nafion.
2.4.3 AFM MORPHOLOGICAL STUDIES

Fig. 2.11: AFM topographic images in 2-D and 3-D pattern for (a) 5, (b) 10 and (c) 15 loading wt% of Nafion in PVA/PVDF blend.
The AFM topographical studies of the surface and interface of PVDF/PVA/Nafion composite are shown in Fig. 2.11 (a-c). The AFM is an advance morphological technique to investigate the surface morphology and 3-dimensional topography of the sample. The 2-D and 3-D topography of PVDF/PVA/Nafion represents the surface properties of polymer composite. The AFM images give the information regarding the surface roughness and smoothness of polymer composite. In the present study, the AFM images represent the bright shiny spots on the black background surface. The black dark surface on AFM images represents the rough surface (Rana et al., 2009). Fig. 2.11 (b) represents the AFM images for 10 wt% loading of Nafion in PVDF/PVA blend. The proper homogeneous nature of polymer composite can be easily observed with the better surface smoothness. The 3-D topography of polymer composites also shows the proper arrangement of sharp peaks in well ordered manner. However, as the loading wt% of Nafion increases, the two phase image was observed as shown in Fig. 2.11 (c). The earlier FTIR and XRD reports of polymer composite have shown the presence of α and β phases which are confirmed by AFM micrographs. It is interesting to observe the combination of large and small peaks in 3-D topography at 20 µm resolution for 20 wt% loading of Nafion as shown in Fig. 2.11 (c). This combination reflects the change in surface roughness of the polymer composite. The micrograph also represents the change in crystalline to amorphous behavior of polymer composite. This change in crystallinity behavior can be associated with the presence of Nafion in polymer composite. In polymer composite, the change in behavior of crystallinity influences the electrical properties.

2.4.4 DSC ANALYSIS

DSC analysis of present polymer composite was conducted to examine the effect of Nafion and solvent on melting and glass transition temperature. There are several reports which claim that the crystalline temperature ($T_c$) and melting temperature ($T_m$) of pure PVDF are about 125-128°C and 147-148°C (Dillon et al., 2006; Mago et al., 2008). However, the reports on thermal characterization of pure PVA provide the information regarding the glass transition temperature ($T_g$) and $T_m$. The previous reports gives the information that the DSC curve of PVA represents an endothermic peak around 180-190°C assigned for melting temperature. For melting 100% crystalline PVA, 138.60 J/g
heat is required (Peppas and Merrill, 1976; Guirguis and Moselhey, 2012). The crystallinity values of PVA obtained from DSC is around 48%. In present study the DSC curve of pure PVDF and pure PVA is shown in Fig. 2.12. The evaluated values of $T_m$ for pure polymers in our reports are almost equivalent to the reported results.

![DSC thermograms of pure PVA and PVDF.](image)

For polymer composites the DSC technique was performed to observe the change in melting temperature with respect to loading wt% of Nafion. The DSC curves of PVDF/PVA/Nafion composites are shown in Fig. 2.13. In compare to melting temperature of pure polymer, the shift in melting peaks towards the lower temperature has been observed for polymer composite. The decrease in melting temperature indicates the intermolecular interaction between polymer and Nafion. A melting peak was observed at 138°C for 5 wt% loading of Nafion. The maximum shift in melting temperature was observed for 15 wt% loading of Nafion in PVDF/PVA blend. The drastic change in $T_m$ can be due to the difference in crystalline structure. However, for all composite a single peak has been observed, which is a sign of proper miscibility and single phase behavior in the polymer composites.
In Fig. 2.13 the change in melting was represented by $T_{ma}$, $T_{mb}$ and $T_{mc}$ with respect to loading wt% of Nafion. All the endothermic peaks in DSC curve for polymer composite was observed below the melting temperature of pure polymers. Therefore, the change in melting temperature is mainly due to the presence of Nafion in PVDF/PVA blend. The obtained results from DSC analysis can be correlated with XRD analysis. The change in melting temperature can also refers for the change in crystalline to amorphous phase.

2.4.5 ELECTRICAL CONDUCTIVITY

The electrical characterization of material such as conductivity, dielectric constant etc defines the movements of electrons or ions inside the material. The movement of ions and electrons inside the material occurs mainly due to external condition such as temperature, frequency and dc-bias voltage. Among all the electrical properties, electrical conductivity is an important characterization to define the ability of material to conduct electricity. Electrical conductivity is an important and reliable property to define the
movement of ions/electrons inside the material, which makes the material feasible for electrical device fabrications (Li et al., 2009; Jamail et al., 2013). The conductivity values of polymer composite with respect to varying temperature (40-150°C) are shown in Fig. 2.14. In the present study the conductivity results are directly correlated with AFM morphological as shown in inset Fig. 2.14.

Fig. 2.14: Conductivity vs. temperature for (a) 5, (b) 10 and (c) 15 loading wt% of Nafion in PVA/PVDF blend.

In present polymer composite, the conductivity increases with respect to temperature for 5 wt% loading of Nafion as shown in Fig. 2.14 (a). The evaluated conductivity shows a constant behavior up to 100°C for lower wt% loading of Nafion. The sudden increment in conductivity may be due to increase in mobility of majority charge carriers-electrons. The increase in temperature allows the free movement ions, hence conductivity shows the increment. The increase in conductivity as a function of temperature is a well known concept for polymeric and semiconductor materials (Dutta et al., 2001). The conductivity response for 10 wt% loading of Nafion in PVDF/PVA blend is shown in Fig. 2.14 (b). A sinusoidal curve pattern is observed for conductivity values as a function of temperature for 10 wt% loading of Nafion. The highest conductivity $1.3 \times 10^{-2}$ Sm$^{-1}$ is observed at
80°C, which further decreases with increment in temperature. The highest mobility of electrons represents the highest value of conductivity at 80°C, which can also be called as percolation temperature for a particular composite. The decrease in conductivity after percolation temperature reveals that the movement of electrons has been restricted by vibrating atoms present in the polymer composite. However, a proper movement of electrons towards a particular direction causes the effective conductivity in polymer composites. The electrons get excited with increase in temperature above percolation and become less efficient, which can be another reason for decrease in conductivity. However, a systematic and step wise decrease in conductivity has been observed for 15 wt% loading of Nafion in polymer composite as shown in Fig. 2.14 (c). The decrease in conductivity with respect to temperature defines the self linkage between polymers, which is also a reason for crystalline nature of polymers (NandaPrakash et al., 2013). This variation in crystalline with respect to loading wt% of Nafion is also revealed in XRD. The inset of Fig. 2.14 represents the variation in AFM micrographs which can be directly correlated with the change in conductivity values at particular composition of composites. The change in phase as shown in AFM micrographs is one of the important reason to correlate with conductivity.

Fig. 2.15: Arrhenius plots of (a) 5, (b) 10 and (c) 15 loading wt% of Nafion in PVA/PVDF blend.
The determination of activation energy ($E_a$) is an important phenomenon belongs to electrical characterization. The activation energy of material describes the total amount of energy is required for the movement of electron. It is well known phenomenon that the formation of holes in polymer corresponding to diffusion of large molecules requires a huge amount of energy (Ebrahim et al., 2009). The $E_a$ of present polymer composite was evaluated from linear part of log $\sigma$ versus 1/Temperature curve by using Arrhenius equation as shown in Fig. 2.15. The Arrhenius plot of PVDF/PVA/Nafion polymer composite represents a linear (fitted by using Arrhenius equation) variation of conductivity with respect to temperature. The linear variation in Arrhenius plot describes that the ions transport mechanism occurs in polymer composite due to polymer segmental motion. The apparent activation energy of PVDF/PVA/Nafion polymer composites is tabulated in Table. 2.2. The change in activation represents the increasing trend up to 10 wt% loading of Nafion. The highest $E_a$= 0.67 eV was evaluated for 10 wt% loading of Nafion which is due to diffusion of large molecules with lesser diffusivity.

**Table 2.2: Apparent activation energy ($E_a$) values of PVDF/PVA/Nafion polymer composites.**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample loading (wt%)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PVDF/PVA/Nafion:: 70:25:05</td>
<td>0.33</td>
</tr>
<tr>
<td>2.</td>
<td>PVDF/PVA/Nafion:: 65:25:10</td>
<td>0.67</td>
</tr>
<tr>
<td>3.</td>
<td>PVDF/PVA/Nafion:: 60:25:15</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The variation in $E_a$ values of polymer composite can also be correlated with the XRD results, because the polymer composite with high degree of crystallinity represents the high activation energy value. The decrease in $E_a$ value was observed for higher loading wt% of Nafion in polymer composite. Interplaner separation or two phase separation of PVDF, PVA and Nafion in polymer composite may be the reason for lowering of activation energy.
2.5 CONCLUSION

From all the above results obtained from different characterization techniques, it may be concluded that the PVDF/PVA/Nafion polymer composite in the present studies have a potential application in the field of fuel cells and battery applications. The following conclusions have been drawn from the present studies based on PVDF/PVA/Nafion polymer composite:

- XRD and FTIR results reveal the crystalline to amorphous phase transformation and complex formation between Nafion and PVDF/PVA polymer system.
- The surface morphology and topography images of polymer composite has been obtained from AFM studies, which shows the combination of the bright shiny spots on the black background surface.
- The phase separation images obtained from AFM reveals the presence of \( \alpha \) and \( \beta \) phases, which supports the electrical conductivity.
- The melting temperature of polymer composite was analyzed by differential scanning calorimetry technique, which represents the proper miscibility and single phase behavior in the polymer composites.
- The optimized electrical conductivity for different concentration of Nafion based polymer composite was obtained in the range of \( 10^{-3} - 10^{-2} \) S/m, which also shows the correlation with XRD and AFM results.
- The highest conductivity \( 1.3 \times 10^{-2} \) Sm\(^{-1}\) was observed at 80°C for 10 wt% loading of Nafion, which further decreases with increment in temperature.
- The evaluated activation energy with respect to Arrhenius plot provides the significant results in favour of electrical characterization.