Chapter 3
PART A
Results and Discussion

In this chapter modifications induced in the structural, optical, electrical, thermal and mechanical properties of PVA after incorporation of SiC nanoparticles and Ag nanoparticles have been discussed. Therefore, accordingly this chapter has been divided into two parts. In Part A section 3.1, investigations carried out to obtain structural, electrical and thermal properties of SiC-PVA nanocomposites synthesized using as received SiC nanoparticles have been presented. Section 3.2 illustrates the changes induced in structural, optical, electrical, thermal and mechanical properties of PVA upon incorporation of surface treated SiC (t-SiC) nanoparticles. In section 3.3, alterations in various properties of PVA after inclusion of PVA grafted SiC (PVA-g-SiC) nanoparticles have been described. Part B section 3.4 illustrates the modifications induced in structural, optical, electrical, thermal and mechanical properties of PVA after Ag nanoparticles addition. Finally section 3.5 gives a relative comparison in the modifications induced in various properties of SiC-PVA and Ag-PVA nanocomposites.

3.1 SiC-PVA nanocomposites

SiC-PVA nanocomposites were synthesized by incorporating as received SiC nanoparticles in PVA matrix using solution casting method. Structural and morphological changes occurring in the resulting nanocomposites were analyzed using XRD, TEM and SEM techniques as described in sections 3.1.1 to 3.1.3 respectively. Chemical changes induced in PVA matrix after SiC nanoparticles addition have been studied using FTIR and Raman spectroscopy and are discussed in sections 3.1.4 and 3.1.5 respectively. The electrical properties of the synthesized nanocomposites have been studied by I-V measurements. These results were further analyzed to establish the exact mechanism responsible for charge transport in the
nanocomposites and are discussed under section 3.1.6. Section 3.1.7 illustrates the thermal characterization of the nanocomposites performed using TGA technique and an attempt has been made to understand the changes occurring in the thermal degradation behaviour of PVA after inclusion of SiC nanoparticles. Finally, section 3.1.8 illustrates the important conclusions drawn from the study.

3.1.1 X-Ray Diffraction (XRD)

Structural characterization of the synthesized SiC-PVA nanocomposites was done using XRD technique. XRD patterns of PVA (curve a) and SiC-PVA nanocomposite films, containing 1 wt%, 2 wt% and 3 wt% SiC nanoparticles (curves b-d) are presented in figure 3.1. It can be discerned from figure 3.1 (curve a) that the XRD pattern of PVA does not show any prominent peak. However, the XRD pattern of SiC-PVA nanocomposite films, figure 3.1 (curves b-d) shows a major peak at 2θ value of 35.82° which corresponds to (111) plane and minor peaks at 20 values of 41.61°, 60.30° and 72.04° which corresponds to (200), (220) and (311) planes of SiC nanoparticles [1-6]. These diffraction peaks matched perfectly with standard data available for SiC in Joint committee of powder diffraction standards (JCPDS) file no. 29-1129 [7]. The intensity of the peaks increases with increasing concentration of SiC nanoparticles in PVA matrix and becomes very predominant in the case of SiC-PVA nanocomposite film containing 3 wt% SiC nanoparticles. In the XRD pattern of SiC-PVA nanocomposite film containing 3 wt% SiC nanoparticles, there is also a low intensity peak at 2θ value of 33.9° which is assumed to be due to stacking faults formed during the formation of SiC nanoparticles and is marked as SF [8-10].

XRD pattern was further used to calculate the average size of SiC nanoparticles from the full width at half-maximum (FWHM) of the major peak, using the Debye-Scherer equation number (2) as given in section 2.4.1. Size of SiC nanoparticles dispersed in the PVA matrix calculated using the major peak corresponding to (111) plane comes out to be ~16.8 nm.

The interplanar distance (d) between the crystal planes, at four major peaks corresponding to the (111), (200), (220) and (311) planes, determined using
equation number (1) as given in section 2.4.1, comes out to be 2.52 Å, 2.18 Å, 1.54 Å and 1.31 Å respectively in all the SiC-PVA nanocomposite films.

![XRD spectrum of (a) PVA and SiC-PVA nanocomposite films containing (b) 1 wt% (c) 2 wt% (d) 3 wt% SiC nanoparticles.](image)

**Figure 3.1:** XRD spectrum of (a) PVA and SiC-PVA nanocomposite films containing (b) 1 wt% (c) 2 wt% (d) 3 wt% SiC nanoparticles.

3.1.2 Transmission Electron Microscopy (TEM)

![TEM micrographs of SiC-PVA nanocomposite film containing 3 wt% SiC nanoparticles at different magnifications.](image)

**Figure 3.2:** TEM micrographs of SiC-PVA nanocomposite film containing 3 wt% SiC nanoparticles at different magnifications.
TEM micrographs of synthesized SiC-PVA nanocomposite film were obtained to analyze its morphology. Figure 3.2 depicts the TEM micrograph of SiC-PVA nanocomposite film containing 3 wt% SiC nanoparticles. From the micrograph it can be clearly seen that SiC nanoparticles are not uniformly distributed within the PVA matrix, but tended to agglomerate around white structures (polymer) due to their hydrophobic nature. This inhomogeneous distribution of SiC nanoparticles in PVA can be ascribed to the tendency of SiC nanoparticles to form agglomerates due to van der waals forces amongst them and also due to their poor interfacial adhesion with PVA matrix. Size of SiC nanoparticles obtained using these micrographs is $23 \pm 9$ nm. Size obtained from TEM measurement is consistent with the size obtained from XRD measurement.

### 3.1.3 Scanning Electron Microscopy (SEM)

SEM micrographs were obtained to further study the morphology of SiC-PVA nanocomposite film. Figure 3.3 depicts the morphology and distribution of SiC-PVA nanocomposite film containing 3 wt% SiC nanoparticles. SEM image of nanocomposite film clearly shows the dispersion of spherical SiC nanoparticles within PVA matrix. SEM micrograph further supports the results obtained using TEM and XRD measurements.

![SEM Image](image.png)

**Figure 3.3:** SEM image of SiC-PVA nanocomposite film containing 3 wt% SiC nanoparticles.
3.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

Interaction between PVA and SiC nanoparticles and chemical changes induced in PVA matrix after incorporation of SiC nanoparticles were studied using FTIR spectroscopy. Figure 3.4 shows the FTIR spectra of PVA and SiC-PVA nanocomposite films containing 1 wt%, 2 wt% and 3 wt% SiC nanoparticles. Figure 3.4 (curve a) shows all major peaks associated with various functional groups of PVA. The spectrum of PVA displays peaks at around 3358 cm\(^{-1}\) and at 2931 cm\(^{-1}\) which are attributed to stretching vibrations of O-H bonds and C-H bonds, respectively. The peaks at 1730 cm\(^{-1}\) and 1255 cm\(^{-1}\) have been assigned to the stretching vibrations of C=O and C-O, respectively which are due to the residual acetyl group present in PVA. The vibrational peaks at 1434 cm\(^{-1}\) and 859 cm\(^{-1}\) are assigned to C-H bending and stretching mode of PVA, respectively and at 1097 cm\(^{-1}\) due to C–O stretching vibrations in PVA [11-15]. Presence of these vibrational peaks confirms the monomer structure of PVA. The assignments of the various peaks made in this study are in reasonable agreement with those reported in literature [13-15].

![FTIR spectrum](image)

**Figure 3.4:** FTIR spectrum of (a) PVA and SiC-PVA nanocomposite films containing (b) 1 wt% (c) 2 wt% (d) 3 wt% SiC nanoparticles.
In the FTIR spectra of SiC-PVA nanocomposite films figure 3.4 (curves b-d), major peaks corresponding to various functional groups of PVA were significantly affected by the addition of SiC nanoparticles in the PVA matrix. Incorporation of SiC nanoparticles in PVA matrix results in diminished intensity, broadening and displacement of peaks towards higher wavenumbers. The changes incurred in the FTIR spectra of SiC-PVA nanocomposite films in 1600 to 1800 cm\(^{-1}\) region indicate the structural changes surrounding the C=O group. The peaks related to silicon vibrations are mostly found in the region ranging from 700 to 1500 cm\(^{-1}\) [16, 17], therefore, in nanocomposite films, due to the presence of both SiC nanoparticles and PVA components, there is an overlapping of the peaks in this region as a result the peak shifts towards higher value in nanocomposite films.

The major difference between the spectra of PVA and SiC-PVA nanocomposite films has been observed in the 850 to 950 cm\(^{-1}\) region. In the FTIR spectra of SiC-PVA nanocomposite films it can be clearly seen that the vibrational peak at 862 cm\(^{-1}\) is the most prominent peak. Existence of this peak is ascribed to the stretching vibrations of Si–C bonds of SiC component in the PVA matrix [18-21]. Thus, FTIR spectroscopy confirms the alteration in the structure of PVA after addition of SiC nanoparticles.

### 3.1.5 Raman Spectroscopy

Raman spectroscopy was further used to probe the molecular structure of synthesized nanocomposites. Figure 3.5 shows the Raman spectra of PVA and SiC-PVA nanocomposite films containing 1 wt%, 2 wt% and 3 wt% SiC nanoparticles. Figure 3.5 (curve a) shows all major peaks associated with various functional groups of PVA. The vibrations in the Raman spectra of PVA at 854 cm\(^{-1}\) and 918 cm\(^{-1}\) have been ascribed to the stretching of C-C bonds, peak at 1117 cm\(^{-1}\) correspond to the stretching vibrations of C-O bond. The peaks at 1362 cm\(^{-1}\) and 1462 cm\(^{-1}\) has been ascribed due to the bending vibrations of C-H and O-H bonds and the peak at 2920 cm\(^{-1}\) are due to the stretching vibrations of C-H bond. The assignments of the various peaks made in this study are in reasonable agreement with those reported in literature [22-24].
**Figure 3.5:** Raman spectrum of (a) PVA and SiC-PVA nanocomposite films containing (b) 1 wt% (c) 2 wt% (d) 3 wt% SiC nanoparticles.

Spectra of SiC-PVA nanocomposite films display only four intense bands at 786 cm$^{-1}$, 917 cm$^{-1}$, 1362 cm$^{-1}$ and 1604 cm$^{-1}$. The bands at 786 cm$^{-1}$ and 917 cm$^{-1}$ corresponds to the transverse optical (TO) and longitudinal optical (LO) modes of the SiC nanoparticles [5, 25, 26] while the bands at 1362 cm$^{-1}$ and 1604 cm$^{-1}$ are disorder D bands and graphite like G band [27, 28], respectively. The D-band corresponds to the breathing mode of k-point phonons of $A_{1g}$ symmetry while the G-band represents first-order scattering process of sp$^2$ carbons in $E_{2g}$ stretching mode [29, 30]. Appearance of these bands in the Raman spectra of SiC-PVA nanocomposite films clearly shows that the structure of PVA was significantly affected by the addition of SiC nanoparticles in the PVA matrix. The bands corresponding to vibrations of PVA were completely lost and the spectrum of SiC-PVA nanocomposite films solely shows bands corresponding to SiC nanoparticles. This suggests that the chemical structure of PVA has changed significantly after SiC nanoparticle addition.

### 3.1.6 Electrical Conductivity Behaviour

Figure 3.6(a) shows the current–voltage (I-V) characteristics of PVA and SiC-PVA nanocomposite films containing 1 wt%, 2 wt% and 3 wt% SiC nanoparticles. It is quite evident from figure 3.6(a) (curves b-d) that there is a continuous increase
in conductivity with increasing concentration of SiC nanoparticles in PVA matrix. In the nanocomposite films, SiC nanoparticles act as conductive fillers in the host matrix and provide the continuous conductive pathways for the transfer of charge from one nanoparticle to another as a result the conductivity of nanocomposite films increases. It can also be seen in the figure 3.6(a) that I-V curves are nonlinear in nature.

![Figure 3.6(a): I-V variation of (a) PVA and SiC-PVA nanocomposite films containing (b) 1 wt% (c) 2 wt% (d) 3 wt% SiC nanoparticles.]

The nonlinear nature of I-V curves can be explained on the basis of four different conduction mechanisms: hopping, Schottky emission, Poole-Frenkel emission and space charge-limited conduction (SCLC) as discussed in section 2.4.7. The exact mechanism responsible for conduction in nanocomposite films was determined by comparing the measured I-V curves with curve fits obtained using different conduction mechanism models. For SCLC mechanism to occur slope of log (I) versus log (V) graph should be greater than 2 [31-33] but in the present case the slope is less than 2 so this conduction mechanism was ruled out. Also the results of hopping model were not a perfect fit to the experimental data so this mechanism
was also ruled out. Hence, the conduction mechanism involved in SiC-PVA nanocomposite films can either be Schottky or Poole-Frenkel mechanisms.

To determine the exact charge transport mechanism, graphs between log (I) versus $V^{1/2}$ (for Schottky mechanism) and log (I/V) versus $V^{1/2}$ (for Poole-Frenkel mechanism) were plotted [34-37]. The measured values for Schottky mechanism as shown in figure 3.6(b) were linear when compared to plots obtained from Poole-Frenkel mechanism, and the fitting was reasonably good as the correlation coefficient (R) for the straight lines of the best fit comes out to be 0.99. Hence, it can be concluded that the conduction mechanism which is responsible for the substantial increase in the conductivity of SiC-PVA nanocomposite films is Schottky mechanism.

Figure 3.6(b): Plot of log (I) versus $V^{1/2}$ for (a) PVA and SiC-PVA nanocomposite films containing (b) 1 wt% (c) 2 wt% (d) 3 wt% SiC nanoparticles.
3.1.7 Thermogravimetric Analysis (TGA)

The thermal stability of the synthesized nanocomposite films was studied using TGA. Figure 3.7 present the TGA curves for PVA and SiC-PVA nanocomposite films containing 1 wt%, 2 wt% and 3 wt% SiC nanoparticles.

![TGA curves for PVA and SiC-PVA nanocomposite films](image)

**Figure 3.7:** TGA curves of (a) PVA and SiC-PVA nanocomposite films containing (b) 1 wt% (c) 2 wt% (d) 3 wt% SiC nanoparticles.

It is clear from figure 3.7 that the thermal degradation of SiC-PVA nanocomposite films is different from that of PVA. It can be discerned from figure 3.7 that the maximum decomposition temperature ($T_{\text{max}}$) for PVA film is $\sim275^\circ\text{C}$ and it reduces to $\sim214^\circ\text{C}$ for the nanocomposite film containing 3 wt% SiC nanoparticles. Thus with the introduction of SiC nanoparticles in PVA matrix the onset of thermal decomposition is shifted to lower temperatures. Moreover, all the films show a small weight loss ($\sim5$-$10\%$) for the first decomposition stage ($\sim50$-$210^\circ\text{C}$) and more significant weight loss ($\sim60$-$90\%$) for the second stage ($\sim210$-$500^\circ\text{C}$). The lower value of percentage weight loss in the first stage is presumably due to the evaporation of bound water molecules. At low temperatures ($<400^\circ\text{C}$) PVA displays better thermal stability than SiC-PVA nanocomposite films, as the presence of SiC nanoparticles accelerates the degradation of PVA. This observation
has been reported as the Hofmann elimination reaction, where nanoparticles act as a
catalyzer toward the degradation of the polymer matrix [38, 39]. It is well quoted in
literature that the thermal stability of PVA matrix is highly influenced by the type of
filler being incorporated. For example, sepiolite and HT Sepiolites [40] improve the
thermal stability of PVA, on the other hand magnetite nanoparticles decreases the
thermal stability of PVA [41], whereas in the presence of montmorillonite the
thermal stability of PVA does not change [42].

In the second stage i.e. the temperature range of ~210-500ºC, PVA (Figure 3.7
curve a) decomposes with appreciable weight loss as it vaporizes. At a temperature
of 494ºC a weight loss of 90% is observed for PVA, 82% for 1 wt%, 80% for 2 wt%
and 64% for 3 wt% SiC-PVA nanocomposite film. This decrease in weight loss
with increasing concentration of SiC nanoparticles in PVA matrix is due to the
restriction in mobility of polymer chains. The nanocomposite film with 3 wt% SiC
nanoparticles leaves a residue also known as char of about 30% of initial material;
however, PVA leaves no residue. This enhancement of the char formation can be
ascribed to the high heat resistance exerted by SiC nanoparticles. The increase in
char yield is an indication of the potency of flame retardation of polymers [43-45].
Therefore, higher the amount of residual char after combustion, lower is the amount
of combustible material for perpetuating the flame and greater is the degree of flame
retardency.

3.1.8 Conclusion

It can be concluded that solution casting method has been successfully used to
synthesize SiC-PVA nanocomposite films containing 1 wt%, 2 wt% and 3 wt% SiC
nanoparticles embedded in PVA matrix. XRD, TEM and SEM analysis confirmed
the presence of SiC nanoparticles in PVA matrix. FTIR and Raman spectroscopy
further established that incorporation of varying concentration of SiC nanoparticles
in PVA matrix changes the structure of PVA. I-V studies indicate that the
conductivity of PVA increases with the addition of SiC nanoparticles in PVA matrix
and Schottky mechanism is found to be the dominant conduction mechanism
responsible for the charge transport. TGA studies reveal that the addition of 3 wt %
SiC nanoparticles in PVA shifts the onset of thermal decomposition temperature to
lower values. However, after structural characterization of SiC-PVA nanocomposite
using TEM, it is quite apparent that SiC nanoparticles tend to cluster around PVA matrix and the dispersion was not homogenous. It can be ascribed to the tendency of SiC nanoparticles to form agglomerates due to van der waals forces amongst them and also due to their poor interfacial adhesion with PVA matrix.

The synthesized nanocomposite films of SiC-PVA were dark in colour due to which their optical properties such as optical energy gap, Urbach’s energy, refractive index, dielectric constant and microhardness studies (due to poor visibility of indent) could not be performed.
3.2 Surface treated SiC-PVA (t-SiC-PVA) nanocomposites

This section discusses the results of t-SiC-PVA nanocomposite films fabricated after the incorporation of surface treated SiC (t-SiC) nanoparticles in PVA matrix. Resulting nanocomposite films were structurally characterized using XRD, TEM, SEM, FTIR and Raman spectroscopy as discussed in sections 3.2.1 to 3.2.5 respectively. UV-Vis spectroscopy used to ascertain the optical properties such as optical energy gap, Urbach’s energy, refractive index, dielectric constant of synthesized t-SiC-PVA nanocomposite films has been discussed in section 3.2.6 to 3.2.9 respectively. Section 3.2.10 presents the I-V studies carried out to ascertain the exact charge transport mechanism responsible for increased conductivity of PVA and nanocomposite films. Section 3.2.11 presents the results of TGA studies carried out on t-SiC-PVA nanocomposite films to accomplish their thermal stability. Influence of t-SiC nanoparticles on surface microhardness of PVA matrix has been depicted in section 3.2.12. Finally, section 3.2.13 illustrates the important conclusions drawn from this study.

3.2.1 X-Ray Diffraction (XRD)

XRD technique was used to analyze t-SiC nanoparticles. Figure 3.8(a) (curves a and b) displays the XRD pattern of as received SiC and t-SiC nanoparticles respectively. As shown in figure 3.8(a) (curve a) XRD pattern of as received SiC nanoparticles shows a major peak at 2θ value of 35.2° and minor peaks at 2θ values of 41.03°, 59.7°, 71.6° and 75.1° [1-6]. These peaks correspond to (111), (200), (220), (311) and (222) planes of SiC nanoparticles and are consistent with the peaks of SiC available in JCPDS file no. 29-1129 [7]. From figure 3.8(a) (curve b) it can be discerned that the XRD spectra of t-SiC nanoparticles exhibit peaks at the same 2θ values as displayed by as received SiC nanoparticles.

The value of interplanar spacing at four major peaks corresponding to the (111), (200), (220), (311) and (222) planes determined using equation number (1) as given in section 2.4.1 comes out to be 2.52 Å, 2.18 Å, 1.53 Å, 1.30 Å and 1.25 Å respectively for as received SiC nanoparticles and t-SiC nanoparticles. The average size of as received SiC nanoparticles calculated using the Debye-Scherer equation number (2) as given in section 2.4.1 comes out to be ~ 37 nm and for t-SiC nanoparticles the slight change in size to ~
38 nm was observed which may be due to the surface treatment of SiC nanoparticles [46].

Figure 3.8(a): XRD spectrum of (a) as received SiC nanoparticles and (b) t-SiC nanoparticles.

Figure 3.8(b): XRD spectrum of (a) PVA and (b) t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles.
Figure 3.8(b) (curves a and b) demonstrates the XRD pattern of PVA and t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles. Figure 3.8(b) (curve b) displays that the XRD pattern of SiC-PVA nanocomposite film shows peaks at 2θ values 35.2°, 41.03°, 59.7° and 71.6° with reduced intensity as compared to t-SiC nanoparticles. From these observations it could be implied that the crystalline geometry of SiC nanoparticles has not changed after the surface treatment or after the fabrication of nanocomposite film [47].

### 3.2.2 Transmission Electron Microscopy (TEM)

![TEM micrograph of t-SiC-PVA nanocomposite film containing 0.015 wt% t-SiC nanoparticles.](image)

**Figure 3.9:** TEM micrograph of t-SiC-PVA nanocomposite film containing 0.015 wt% t-SiC nanoparticles.

TEM proved to be very useful in elucidation of morphological changes occurring in PVA after addition of t-SiC nanoparticles. The dispersion of t-SiC nanoparticles in the PVA matrix was analyzed using TEM. Figure 3.9 displays the TEM micrograph of t-SiC-PVA nanocomposite film containing 0.015 wt% t-SiC nanoparticles. It can be discerned from the micrograph that t-SiC nanoparticles are homogeneously distributed in PVA matrix. Average size of t-SiC nanoparticles in PVA matrix obtained using these micrographs came out to be 41 ± 8 nm.
3.2.3 Scanning Electron Microscopy (SEM)

![SEM micrograph of t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles.]

Figure 3.10: SEM micrograph of t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles.

Figure 3.10 shows the SEM micrograph of t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles inside PVA matrix. SEM image of nanocomposite film also depicts the homogenous dispersion of t-SiC nanoparticles within PVA matrix. SEM micrograph further supports the results obtained using TEM.

3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to verify the modification induced in SiC nanoparticles as well as t-SiC-PVA nanocomposite films. Figure 3.11(a) presents the FTIR spectra of as received SiC and t-SiC nanoparticles in the wavenumber range 4000–700 cm\(^{-1}\). In the FTIR spectra of as received SiC nanoparticles (figure 3.11(a) (curve a)) a sharp peak at 785 cm\(^{-1}\) with a shoulder at 910 cm\(^{-1}\) was observed. This peak is assigned to the Si-C stretching vibration of SiC nanoparticles [18-21]. The FTIR spectra of t-SiC nanoparticles is different from that of the as received SiC nanoparticles. In the FTIR spectra of t-SiC nanoparticles (figure
3.11(a) (curve b)) besides the characteristic peak of Si-C vibrations, observed at 785 cm⁻¹, which is of considerably higher intensity in comparison to the peak observed in as received SiC nanoparticles, certain additional peaks were also observed at ~1700 cm⁻¹, 1540 cm⁻¹ and 1184 cm⁻¹ and are assigned to the C=O, C=C and C−O stretching vibrations [11, 12]. The increased intensity of characteristic Si-C peak and the appearance of new peaks indicated that the surface of SiC nanoparticles have been modified after the treatment.

**Figure 3.11(a):** FTIR spectra of (a) as received SiC nanoparticles and (b) t-SiC nanoparticles. Inset: Enlarged view of fingerprint region.

Figure 3.11(b) presents the FTIR spectra of PVA and t-SiC-PVA nanocomposite films containing 0.01 wt%, 0.015 wt% and 0.023 wt% t-SiC nanoparticles. All the peaks present in PVA has been verified in section 3.1.4. Figure 3.11(b) (curves b-d), clearly shows the shifting in the position of the peaks corresponding to various functional groups to lower wavenumbers with respect to PVA. In the FTIR spectra of 0.023 wt% t-SiC-PVA nanocomposite film (figure 3.11(b) (curve d)) the peak corresponding to the O-H stretching vibration shifts from 3311 cm⁻¹ in PVA to 3296 cm⁻¹, peak corresponding to C-H stretching vibrations shifts from 2923 cm⁻¹ to 2916 cm⁻¹, peak corresponding to C=O stretching vibrations shifts from 1721
cm⁻¹ to 1714 cm⁻¹. It can be seen from figure 3.11(b) that in the region between 750-850 cm⁻¹, there is an overlapping of the peak corresponding to the Si-C stretching vibrations and C-H stretching vibrations of PVA which led to the observed shifting of the peak. Hence, the changes observed in the spectra of nanocomposite films are indicative of the presence of molecular interaction between t-SiC and PVA. The strong molecular interactions were mainly attributed to the formation of bonding between the oxygen containing groups (e.g., hydroxyl, carboxyls and epoxides) on the surface of t-SiC nanoparticles and the −OH groups of PVA [48].

![FTIR spectrum of (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.01 wt% t-SiC nanoparticles.](image)

**Figure 3.11 (b):** FTIR spectrum of (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.01 wt% t-SiC nanoparticles.

### 3.2.5 Raman Spectroscopy

Presence of strong molecular interaction between t-SiC nanoparticles and PVA matrix was further verified using Raman spectroscopy. Figure 3.12 presents the Raman spectra of PVA and t-SiC-PVA nanocomposite films containing 0.015 wt% and 0.023 wt% t-SiC nanoparticles.
Raman spectra of PVA displays all the peaks associated with various functional groups of PVA and have been discussed in section 3.1.5 [22-24]. Figure 3.12 (curves b and c) depicts the structural modifications introduced in PVA after incorporation of t-SiC nanoparticles. The peaks corresponding to C-C stretching vibrations at 854 cm$^{-1}$ and 918 cm$^{-1}$, due to the C-O stretching vibrations at 1117 cm$^{-1}$, due to the C-H and O-H bending vibrations at 1362 cm$^{-1}$ and 1462 cm$^{-1}$ of PVA has been considerably reduced in intensity in the Raman spectra of t-SiC-PVA nanocomposite films. The most prominent modification in the Raman spectra is reflected in the peak observed at 2920 cm$^{-1}$ due to the C-H stretching vibrations which has reduced significantly with increased concentration of t-SiC nanoparticles. Thus it is clear that the addition of t-SiC nanoparticles produces significant changes in the molecular structure of PVA. These changes can be associated with the breaking of PVA intra-molecular bonds with simultaneous inclusion of new bonds formed between PVA and t-SiC nanoparticles. Hence, FTIR and Raman spectroscopy results clearly provide the evidence of the presence of molecular interaction between t-SiC nanoparticles and PVA matrix.

**Figure 3.12**: Raman spectra of (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.15wt% (c) 0.023wt% t-SiC nanoparticles.
3.2.6 Determination of optical energy gap

Figure 3.13 shows the variation of \((\alpha h\nu)^{1/2}\) calculated from UV-Visible absorption data with photon energy, \(h\nu\) for PVA and t-SiC-PVA nanocomposite films containing 0.01 wt%, 0.015 wt% and 0.023 wt% t-SiC nanoparticles. From figure 3.13 (curve a) it can be discerned that the spectrum of PVA is characterized by an absorption peak at 4.38 eV energy (or wavelength 283 nm) and no absorption peaks are observed at lower energies. This absorption peak can be attributed to the absorption by carbonyl groups present in the polymer [49-51]. In the absorption spectra of t-SiC-PVA nanocomposite films figure 3.13 (curves b-d), the absorption edge shifts to lower energies (higher wavelength) with increasing concentration of t-SiC nanoparticles. Moreover, overall absorption increases with increasing concentration of t-SiC nanoparticles in PVA matrix. These alterations in absorptions may be attributed to the formation of structural defects in PVA matrix after incorporation of t-SiC nanoparticles [52].

![Plot of (αhν)^{1/2} versus (hν)](image)

**Figure 3.13:** Plots of \((\alpha h\nu)^{1/2}\) versus \((h\nu)\) to determine optical energy gap in (a) PVA and t-SiC-PVA nanocomposite film containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.

Optical energy gap of PVA and t-SiC-PVA nanocomposite films was calculated using equation number (11) given in section 2.4.6. Optical energy gap \(E_g\)
has been determined by the extrapolation of best fit line between \((a\nu)^{1/2}\) and \(h\nu\) to intercept the \(h\nu\) axis \((\alpha = 0)\) [53-55]. The values of optical energy gap so obtained are listed in table 1. It is clear from table 1 that the value of \(E_g\) decreases from 4.1 eV for PVA to 3.0 eV for 0.023 wt% t-SiC-PVA nanocomposite film. The decrease in optical energy gap of PVA by incorporation of t-SiC nanoparticles may be ascribed to the formation of localized states within the Highest occupied molecular orbital–Lowest unoccupied molecular orbital (HOMO-LUMO) gap of PVA. As the t-SiC nanoparticles concentration is increased, these nanoparticles start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby, assist in transfer of charge carriers between the two localized states [56, 57].

3.2.7 Determination of Urbach’s energy

![Figure 3.14: Plots of ln(\(\alpha\)) versus (\(h\nu\)) used to determine the Urbach’s energy in (a) PVA and t-SiC-PVA nanocomposite film containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.](image)

Urbach’s energy of PVA and t-SiC-PVA nanocomposite films was calculated using equation number (12) given in section 2.4.6. Figure 3.14 shows the variation...
of ln(α) with photon energy, hv for PVA and t-SiC-PVA nanocomposite films. Urbach’s energy $E_u$ which is a measure of disorder, has been determined by taking the reciprocal of slope of best fit line between ln(α) and hv and the values obtained has been listed in table 1. From table 1 a sharp increase in the value of Urbach’s energy from 0.55 eV for PVA to 1.16 eV for nanocomposite film containing 0.023 wt% t-SiC nanoparticles has been observed. As Urbach’s energy is a measure of disorder content, therefore, it can be inferred that disorder in the form of localized states within the HOMO-LUMO gap of PVA matrix increases with increasing concentration of t-SiC nanoparticles [58, 59].

**Table 1:** Optical parameters for PVA and t-SiC-PVA nanocomposite films.

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<th>Optical energy gap</th>
<th>Urbach’s energy</th>
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<tr>
<td></td>
<td>$E_g$ (eV)</td>
<td>$E_u$ (eV)</td>
</tr>
<tr>
<td>PVA</td>
<td>4.1</td>
<td>0.55</td>
</tr>
<tr>
<td>0.01 wt%</td>
<td>3.9</td>
<td>0.59</td>
</tr>
<tr>
<td>0.015 wt%</td>
<td>3.4</td>
<td>0.92</td>
</tr>
<tr>
<td>0.023 wt%</td>
<td>3.0</td>
<td>1.16</td>
</tr>
</tbody>
</table>

**3.2.8 Determination of refractive index**

The evaluation of refractive indices of nanocomposites is of considerable importance for applications in integrated optical devices such as switches, filters, modulators etc., where the refractive index of a material is the key parameter in the design of a device. The refractive index ‘n’ was estimated using equation number (15) given in section 2.4.6. Figure 3.15 shows the variation of the refractive index of PVA and t-SiC-PVA nanocomposite films containing 0.01wt%, 0.015wt% and 0.023wt% t-SiC nanoparticles with wavelength. From figure 3.15 it is clear that the refractive index increases from 1.7 for PVA to 2.2 for nanocomposite film containing 0.023 wt% t-SiC nanoparticles at 550 nm wavelength. It is known that the high value of refractive index is an indication of higher density of
nanocomposite films [52, 60, 61]. Increasing the concentration of t-SiC nanoparticles in PVA leads to an increase in the degree of disorder and consequently the refractive index increases.

**Figure 3.15:** Refractive index variations of (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.

**Refractive index dispersion**

The optical properties of any solid material is characterized by the complex refractive index ($n^* = n + ik$). The real part of the refractive index ($n$) gives the dispersion and the imaginary part of the refractive index ($k$) gives the absorption of the electromagnetic wave. Refractive index dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion. From figure 3.15 it can be seen that for PVA refractive index shows normal dispersion i.e decreases with increasing wavelength however, in case of t-SiC-PVA nanocomposite films, in the region from 300 nm to 500 nm refractive index displays an anomalous behaviour i.e it increases with increasing wavelength. The normal dispersion region in t-SiC-PVA nanocomposites starts from 500 nm and extends upto 650 nm.
In the normal dispersion region, the refractive index was analyzed using single oscillator model described in section 2.4.6. Refractive index \( n \), at frequency, \( \nu \) is related to the energy parameter \( E_d \), and single oscillator energy \( E_0 \) according to equation number (17) given in section 2.4.6. The values of \( E_d \) and \( E_0 \) has been obtained from the intercept and slope of the linear fitted lines by plotting \( (n^2 - 1)^{-1} \) versus \((h\nu)^2 \) [62-64] as shown in figure 3.16. Values of \( E_d \) and \( E_0 \) are tabulated in table 2.

The values of long wavelength refractive index, \( n_\infty \), average interband oscillator wavelength, \( \lambda_0 \) and average oscillator strength \( S_0 \) were determined using equation numbers (18)-(20). There values were obtained from the slope and intercept of linear fitted lines by plotting \((n^2 - 1)^{-1} \) versus \( \lambda^{-2} \) as illustrated in figure 3.16 and are tabulated in table 2.

**Figure 3.16:** Plot of \((n^2 - 1)^{-1} \) versus \((h\nu)^2 \) and \( \lambda^{-2} \) for (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.
3.2.9 Determination of dielectric constant

The dielectric constant of nanocomposite films was calculated from the complex refractive index as discussed in section 2.4.6. The real part of the dielectric constant is a measure of storage of energy within a material and the imaginary part is a measure of the loss of energy within a material. Together, the real and imaginary parts of dielectric constant describe the interaction of the material with the electromagnetic field. Real and imaginary parts of the dielectric constant were calculated using equation number (23) and (24) given in section 2.4.6. Figure 3.17(a) and (b) shows the variations of real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric constant with energy for PVA and t-SiC-PVA nanocomposite films having different concentration of t-SiC nanoparticles. It can be discerned from figure 3.17(a) and (b) that the real as well as imaginary parts of dielectric constant increases with increase in concentration moreover, the values of real part of dielectric constant are higher than imaginary part. Real and imaginary parts of the dielectric constant are directly related to the defect density within the forbidden gap of the nanocomposite films [65-67]. Higher values of real part of dielectric constant indicates enhancement in energy storage capacity of prepared nanocomposites.

![Graph showing variations of real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric constant with energy for PVA and t-SiC-PVA nanocomposite films.]

**Figure 3.17(a):** Variation of real ($\varepsilon_1$) part of dielectric constant with energy for (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.
Figure 3.17 (b): Variation of imaginary ($\epsilon_2$) part of dielectric constant with energy for (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.

Table 2: Values of Optical parameters with respect to t-SiC nanoparticle content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$n_o$</th>
<th>$\lambda_o$ (nm)</th>
<th>$S_o \times 10^{-5}$ (nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>5.2</td>
<td>8.5</td>
<td>1.61</td>
<td>236</td>
<td>2.9</td>
</tr>
<tr>
<td>0.01wt%</td>
<td>5.8</td>
<td>13.6</td>
<td>1.82</td>
<td>211</td>
<td>5.2</td>
</tr>
<tr>
<td>0.015wt%</td>
<td>5.4</td>
<td>16.0</td>
<td>1.91</td>
<td>206</td>
<td>6.3</td>
</tr>
<tr>
<td>0.023wt%</td>
<td>11.0</td>
<td>40.8</td>
<td>2.16</td>
<td>112</td>
<td>29.4</td>
</tr>
</tbody>
</table>

The oscillator energy $E_o$ and the dispersion energy $E_d$ increases with increasing concentration of t-SiC nanoparticles. These variations in the value of optical constants may be attributed to the formation of charge transfer complexes as localized electronic states between HOMO-LUMO gap of the PVA matrix. These charge transfer complexes makes the lower energy transitions feasible and lead to the observed changes in optical parameters [56, 57, 60, 61].
3.2.10 Electrical Conductivity Behaviour

Figure 3.18 depicts the dependence of current I on applied voltage V with increasing concentration of t-SiC in PVA matrix. It is clear from figure 3.18 that there is a continuous increase in conductivity with increasing concentration of t-SiC nanoparticles in PVA matrix (curves b-d).

![Figure 3.18: I-V variation of (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.](image)

According to percolation theory when t-SiC nanoparticles are added in an insulating (PVA) matrix, the nanoparticles attach with each other to form a continuous conducting network. Thus, they act as conductive fillers in the host matrix and provide the continuous conductive pathways for the transfer of charge from one nanoparticle to another as a result the conductivity of nanocomposite films increases. It is also evident from figure 3.18 that the I-V curves are nonlinear in nature. Such nonlinear characteristics can arise from a number of nonohmic charge transport processes as discussed in section 2.4.7. In order to determine the exact mechanism responsible for nonlinear variation of current with voltage, a detailed analysis of the I-V characteristics was carried out.
The I-V characteristics was plotted on a log-log scale for low as well as for high voltage regions, however it did not yield the slope \( n > 2 \) as expected for SCLC to occur [31-33] so this mechanism for conduction was ruled out. Also the results of hopping model were not a perfect fit to the experimental data so this mechanism was also ruled out. Charge transport in these regions may therefore be associated either with Poole-Frenkel or Schottky conduction mechanism.

The linear fittings of the log (I) versus \((V)^{1/2}\) graph were used to determine whether the controlling conduction mechanism is Schottky emission or the Pool-Frenkel effect. Figure 3.19 shows a plot of log (I) versus \((V)^{1/2}\) [34-37] for PVA and t-SiC-PVA nanocomposite films. It is quite clear from figure 3.19 that the entire voltage region can be divided into three different voltage regions with altered slopes for which the plot of log (I) versus \((V)^{1/2}\) has an approximate linear relationship. These regions are classified as low voltage (1st) region \((0 < V < 10 \text{ V})\), medium voltage (2nd) region \((10 < V < 30 \text{ V})\) and high voltage (3rd) region \((36 < V < 100 \text{ V})\). Since the field lowering coefficient \(\beta\) is a vital factor that determines the magnitude of the coulombic field, the \(\beta_s\) and \(\beta_{PF}\) values were theoretically calculated using equation number (27) and (29) discussed in section 2.4.7 [68, 69]. The theoretically calculated values of \(\beta_s\) and \(\beta_{PF}\) are \(3.1 \times 10^{-5}\) and \(6.2 \times 10^{-5}\) eV \(V^{-1/2}\) \(\text{m}^{1/2}\), respectively (taking the high frequency dielectric constant as 1.5).

The values for \(\beta_s\) and \(\beta_{PF}\) were also experimentally determined from the slope of linear fittings by plotting log (I) versus \(V^{1/2}\) at low, medium as well as high voltage regions as shown in figure 3.19. The experimental as well as the theoretical values of \(\beta_s\) and \(\beta_{PF}\) so obtained are tabulated in table 3.

The experimental value of \(\beta\) is found to be near to \(\beta_{PF}\) values in low voltage region. Hence, it is suggested that the dominant conduction mechanism is of Poole–Frenkel type in low voltage region. However, at the medium as well as high voltage regions experimental value of \(\beta\) becomes closer to \(\beta_s\). Hence, the dominant conduction mechanism at medium and high voltage regions is Schottky conduction mechanism. There is a transition of the conduction mechanism from Poole-Frenkel to Schottky in the high voltage regions. Thus it can be inferred from this observation that at sufficiently higher voltages conduction takes place through an electrode limited process.
Figure 3.19: Plot of log (I) versus $V^{1/2}$ for (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.01 wt% (c) 0.015 wt% (d) 0.023 wt% t-SiC nanoparticles.

Table 3:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical $\beta_{PF}$ (eV $V^{-1/2}m^{1/2}$)</th>
<th>Theoretical $\beta_s$ (eV $V^{-1/2}m^{1/2}$)</th>
<th>Experimental $\beta_{exp}$ ($10^{-5}$) (eV $V^{-1/2}m^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1^{st}$ region</td>
</tr>
<tr>
<td>PVA</td>
<td></td>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td>0.01 wt%</td>
<td>$6 \times 10^{-5}$</td>
<td>$3 \times 10^{-5}$</td>
<td>5.0</td>
</tr>
<tr>
<td>0.015 wt%</td>
<td></td>
<td></td>
<td>5.2</td>
</tr>
<tr>
<td>0.023 wt%</td>
<td></td>
<td></td>
<td>5.4</td>
</tr>
</tbody>
</table>

3.2.11 Thermogravimetric Analysis (TGA)

The evaluation of thermal performance of surface modified nanofiller is vital as it significantly affects the properties of the resulting nanocomposite films. TGA is a versatile technique for thermal characterization of nanocomposites. Hence, TGA analysis
was carried out to observe the thermal response of t-SiC nanoparticles. Figure 3.20(a) shows the TGA curves for as received and t-SiC nanoparticles. From the thermogram in figure 3.20(a) (curve a) it can be seen that initially the as received SiC nanoparticles shows a slight weight loss at 100°C which is assigned to the loss of water and after ~100°C, main oxidation process started which resulted in the weight increase [70]. The weight loss for as received SiC nanoparticles began at ~620°C and is attributed to the oxidation of carbon [71]. From figure 3.20(a) (curve b) it can be discerned that the thermal degradation of t-SiC nanoparticles is quite different from as received SiC nanoparticles. For t-SiC nanoparticles, thermal degradation takes place in single stage i.e increasing the temperature from ~50°C to 700°C resulted in ~8.5% weight loss of t-SiC nanoparticles. This increase in weight loss after surface treatment could be due to the oxidation of outer layer of t-SiC nanoparticles. Such oxidation of outer layer was also evident from XRD measurement. However, such type of thermal degradation behavior has not been reported in literature to the best of our knowledge.

Figure 3.20(a): TGA curves of (a) as received SiC nanoparticles and (b) t-SiC nanoparticles.
The thermal response of PVA after inclusion of t-SiC nanoparticles was also studied using TGA. Figures 3.20(b) shows the TGA curves for PVA and t-SiC-PVA nanocomposite films containing 0.015 wt% and 0.023 wt% t-SiC nanoparticles.

**Figure 3.20(b):** TGA curves of (a) PVA and t-SiC-PVA nanocomposite films containing (b) 0.015 wt% (c) 0.023 wt% t-SiC nanoparticles.

It can be discerned from figure 3.20(b) (curve a) that the maximum decomposition temperature ($T_{\text{max}}$) for PVA film is ~285°C and it is only slightly reduced to ~283°C for the t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles. Thus the introduction of t-SiC nanoparticles in PVA matrix has not affected the onset of thermal decomposition of PVA substantially. From figure 3.20(b) it can be seen that PVA as well as t-SiC-PVA nanocomposite films in the first decomposition stage i.e. ~50-140°C show a small weight loss of ~4-6%. This can be attributed to the evaporation of bound water molecules [72]. In the second stage i.e. the temperature range of ~240-470°C, PVA (Figure 3.20(b) curve a) decomposes with ~90% weight loss as it vaporizes, a weight loss of 86% is observed for 0.015 wt% (Figure 3.20(b) curve b) and 81% for 0.023 wt% (Figure 3.20(b) curve c) t-SiC nanoparticle concentration in PVA matrix. This decrease in weight loss with increase in concentration of t-SiC nanoparticles in PVA matrix is due to the
restriction in mobility of polymer chains [43]. It can also be seen from figure 3.20(b) (curve c) that for the nanocomposite film with 0.023 wt% SiC nanoparticles char yield is more (~8%) as compared to PVA which is due to the high heat resistance exerted by t-SiC nanoparticles. The increase in char yield is an indication of greater degree of flame retardancy [44, 45].

### 3.2.12 Surface Hardness Analysis

![Graph showing variation of hardness and penetration depth with respect to different concentration of t-SiC nanoparticles in PVA at 9.8 mN load.]

**Figure 3.21:** Variation of hardness and penetration depth with respect to different concentration of t-SiC nanoparticles in PVA at 9.8 mN load.

Figure 3.21 depicts the variation in Knoop microhardness and penetration depth of t-SiC-PVA nanocomposite films at 9.8 mN load. The Knoop microhardness number (KHN) for PVA as well as the nanocomposite films was calculated using equation number (31) given in section 2.4.9. It can be discerned from figure 3.21 that the microhardness of PVA is 2.4 Kgf/mm² and it increases to a value of 3.8 Kgf/mm² for PVA containing 0.01 wt% t-SiC nanoparticles. When the concentration of t-SiC nanoparticles in PVA matrix is increased to 0.015 wt% the microhardness is 4.1 Kgf/mm² and with further increase in concentration to 0.023 wt% t-SiC nanoparticles microhardness reaches 4.6 Kgf/mm². Thus the surface hardness of PVA is enhanced by addition of t-SiC nanoparticles and it increases...
with increasing concentration of t-SiC nanoparticles in PVA matrix. Figure 3.21 also shows the decreasing penetration depth with increase in t-SiC nanoparticles concentration inside PVA matrix. Decreasing penetration depth with increasing concentration is also an indication of increased microhardness.

The increase in microhardness may be attributed to higher microhardness of SiC nanoparticles [73] as compared to PVA. Moreover, the increase in hardness after the nanoparticles addition may be due to the relatively uniform distribution of t-SiC nanoparticles within the PVA matrix as can be seen from TEM image also. In general, the addition of nanoparticles to polymer matrices significantly increases the mechanical properties, particularly modulus and hardness of the nanocomposites if the nanoparticles are strongly bonded to the polymer matrix [74]. The treatment of SiC nanoparticles have introduced the functional groups on its surface (verified using FTIR and Raman spectroscopy) which has improved its dispersion and interaction with the PVA matrix by providing a mode to bond with PVA and hence contributed towards the enhancement in microhardness of the t-SiC-PVA nanocomposite films. Also increasing t-SiC nanoparticles concentration leads to decrease in inter-particle distance and hence nanoparticles are much closer to each other and will resist more strongly the penetration of indenter in the matrix [75].

3.2.13 Conclusion

In summary, it can be concluded that the surface treatment of SiC nanoparticles had improved its dispersion in PVA matrix as a result nanocomposites of PVA reinforced with t-SiC nanoparticles were fabricated successfully by solution casting method. XRD measurements have shown that the surface treatment has not affected the crystalline geometry of SiC nanoparticles. FTIR confirmed the formation of active sites such as C=O, C-O bonds on the surface of SiC nanoparticles which has improved its bonding with PVA. Formation of bonding between t-SiC nanoparticles and PVA matrix was also verified using Raman spectroscopy. Optical energy gap decreased from 4.1 eV for PVA to 3.0 eV for t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles and Urbach’s energy was increased from 0.54 eV for PVA to 1.16 eV for t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles. The refractive index increased from 1.7 for PVA to 2.2 for t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles.
at 550 nm. Real and imaginary parts of dielectric constants increased with increasing concentration. The conductivity of t-SiC-PVA nanocomposite films was observed to depend on the concentration of t-SiC nanoparticles in PVA matrix and the carrier transport was shown to consist of a combination of transport mechanism. Schottky mechanism was the main conduction mechanism in medium and high voltage regions and Poole Frenkel in low voltage regions. Addition of t-SiC nanoparticles did not have a substantial effect on the onset of thermal decomposition temperature. The knoop microhardness number of nanocomposites was found to increase from 2.4 Kgf/mm² for PVA to 4.6 kgf/mm² for t-SiC-PVA nanocomposite film containing 0.023 wt% t-SiC nanoparticles.
3.3 PVA grafted SiC/PVA (PVA-g-SiC/PVA) nanocomposites

This section discusses the results of PVA-g-SiC/PVA nanocomposites synthesized by embedding PVA grafted SiC nanoparticles (PVA-g-SiC) into PVA matrix. The success of the grafting process and structural characterization of PVA-g-SiC/PVA nanocomposite film has been accomplished using XRD, TEM, SEM, FTIR and Raman spectroscopy as discussed in sections 3.3.1 to 3.3.5 respectively. UV-Vis absorption spectroscopy, utilized to ascertain the optical properties such as optical energy gap, Urbach’s energy, refractive index, dielectric constant of PVA and PVA-g-SiC/PVA nanocomposite film has been discussed in section 3.3.6 to 3.3.9 respectively. Section 3.3.10 presents the I-V studies carried out to ascertain the charge transport mechanism responsible for increased conductivity of PVA and nanocomposite film. The thermal stability of the synthesized nanocomposites was studied using TGA and has been described in section 3.3.11. Influence of PVA-g-SiC nanoparticles on surface microhardness of PVA matrix has been depicted in section 3.3.12. Finally, Section 3.3.13 illustrates the important conclusions drawn from this study.

3.3.1 X-Ray Diffraction (XRD)

XRD studies were performed on as received SiC nanoparticles and PVA-g-SiC nanoparticles to ascertain the grafting of PVA on the surface of SiC nanoparticles. Figure 3.22(a) (curves a and b) presents the XRD pattern of as received SiC nanoparticles and PVA-g-SiC nanoparticles. In the XRD spectra of as received SiC and PVA-g-SiC nanoparticles, peaks are observed at 20 values of 35.2°, 41.0°, 59.7°, 71.6° and 75.1° and are due to diffraction from (111), (200), (220), (311) and (222) planes of SiC respectively [1-6]. These peaks are consistent with the peaks of SiC available in JCPDS file no. 29-1129 [7]. Occurrence of peaks at the same 20 values after the grafting of SiC nanoparticles with PVA clearly shows that the presence of PVA layer on the SiC nanoparticles does not affect the crystalline geometry of SiC nanoparticles.
Figure 3.22(a): XRD spectrum of (a) as received SiC nanoparticles and (b) PVA-g-SiC nanoparticles.

Figure 3.22(b): XRD spectrum of (a) PVA and (b) PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.
Figure 3.22(b) (curves a and b) presents the XRD pattern of PVA and PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles. Figure 3.22(b) (curve b) shows that the XRD pattern of nanocomposite film contains peaks at 20 values 35.2°, 41.03°, 59.7°, 71.6° and 75.1° corresponding to SiC nanoparticles as verified in as received as well as in PVA-g-SiC nanoparticles. However, compared to nanoparticles the intensity of these peaks has been reduced significantly after incorporation in PVA matrix. From these observations it could be implied that the crystalline geometry of SiC nanoparticles has not changed after the grafting procedure or after the fabrication of nanocomposite film [47].

The value of interplanar spacing at four major peaks corresponding to the (111), (200), (220), (311) and (222) planes determined using equation number (1) as given in section 2.4.1 comes out to be 2.52 Å, 2.18 Å, 1.54 Å, 1.31 Å and 1.25 Å respectively. Size of SiC nanoparticles before and after PVA grafting was calculated from the major peak corresponding to (111) plane using the Debye-Scherer equation number (2) as given in section 2.4.1. In case of as received SiC nanoparticles the size comes out to be ~37 nm, however for PVA-g-SiC nanoparticles, the size slightly increases to ~40 nm suggesting the presence of PVA on the surface of SiC nanoparticles.

3.3.2 Transmission Electron Microscopy (TEM)

![TEM image of PVA-g-SiC nanoparticles.](image)

**Figure 3.23:** TEM image of PVA-g-SiC nanoparticles.
Chapter-3 Results and Discussion

TEM was used to ascertain the presence of PVA layer on the surface of SiC nanoparticles. Figure 3.23 shows the TEM micrograph of PVA-g-SiC nanoparticles. It is clear from TEM micrograph that PVA has been successfully grafted on the surface of SiC nanoparticles.

3.3.3 Scanning Electron Microscopy (SEM)

Morphological characterization was further carried out using SEM. Figure 3.24(a) and (b) shows the SEM images of as received SiC nanoparticles and PVA-g-SiC nanoparticles respectively. SEM images clearly show a uniform distribution of PVA over SiC nanoparticles. Hence, from TEM and SEM micrographs it can be deduced that the surface of SiC nanoparticles has been grafted by PVA.

![SEM images of (a) as received SiC nanoparticles and (b) PVA-g-SiC nanoparticles.](image)

**Figure 3.24:** SEM images of (a) as received SiC nanoparticles and (b) PVA-g-SiC nanoparticles.

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to analyze the change in chemical bonding of the SiC nanoparticles before and after the grafting process. Figure 3.25(a) shows the FTIR spectra of as received SiC nanoparticles and PVA-g-SiC nanoparticles.
Figure 3.25(a): FTIR spectra of (a) as received SiC nanoparticles and (b) PVA-g-SiC nanoparticles. Inset: Enlarged view of fingerprint region.

In the FTIR spectra of as received SiC nanoparticles (figure 3.25(a) curve a), a sharp peak at 785 cm⁻¹ with a shoulder at 910 cm⁻¹ was observed which is related to the Si-C stretching vibration of SiC nanoparticles [19-21]. However, the spectrum of PVA-g-SiC nanoparticles is different from that of the as received nanoparticles. The characteristic peak of Si-C vibration in PVA-g-SiC nanoparticles at 785 cm⁻¹, is of considerably higher intensity as compared to SiC nanoparticles. Beside the increased intensity of peaks, some additional peaks also appear in the spectra of PVA-g-SiC nanoparticles.

In PVA-g-SiC nanoparticles (figure 3.25(a) curve b), peaks appearing at 1750 cm⁻¹ and 1140 cm⁻¹ corresponds to the C=O and C-O stretching vibrations. In the region from ~ 3000 to 3600 cm⁻¹ there is a slight appearance of a wide ranging band which is attributed to O-H stretching vibrations. The peaks appearing at 2940 and 2845 cm⁻¹ represents the C-H asymmetric and symmetric stretching vibrations, respectively [11-14]. Hence, the increase in the intensity of characteristic Si-C peak and the formation of new peaks in the FTIR spectra of PVA-g-SiC nanoparticles indicates that the surface of SiC nanoparticles have been successfully grafted with PVA.
Figure 3.25(b) shows the FTIR spectra of PVA (curve a) and PVA-g-SiC/PVA nanocomposite film (curve b). All the peaks present in PVA has been verified in section 3.1.4. The assignments of the various peaks made in this study are in reasonable agreement with those reported in the literature [11-15]. From figure 3.25(b) (curve b), it can be clearly seen that the peak due to O-H stretching vibration has been shifted from 3504 cm\(^{-1}\) in the PVA to the lower wavenumber 3261 cm\(^{-1}\) in nanocomposite film and the peak due to C-H stretching vibration has been shifted from 2961 cm\(^{-1}\) in PVA to 2917 cm\(^{-1}\) in the nanocomposite film. Moreover, in the FTIR spectra of nanocomposite film, stretching vibrations of the Si–C bonds at 781 cm\(^{-1}\) was also observed. Hence, the presence of vibrations corresponding to PVA as well as SiC nanoparticles is indicative of the strong molecular interactions between the PVA and PVA-g-SiC nanoparticles.

**3.3.5 Raman Spectroscopy**

In order to further confirm the presence of PVA on the surface of SiC nanoparticles Raman spectroscopy was carried out. Figure 3.26(a) shows the Raman
spectra for as received SiC and PVA-g-SiC nanoparticles. In the Raman spectra of as received SiC nanoparticles, peaks at 786 cm$^{-1}$ and 954 cm$^{-1}$ corresponds to the transverse optical (TO) and longitudinal optical (LO) modes of SiC nanoparticles [5, 25, 26]. However, in the Raman spectra of PVA-g-SiC nanoparticles, these modes are shifted to lower wavenumber i.e 766 cm$^{-1}$ and 913 cm$^{-1}$ respectively. Also, the FWHMs of these observed peaks lie in the ranges of 30–50 cm$^{-1}$ for the TO mode and 40–50 cm$^{-1}$ for the LO mode, which are quite large as compared to the values obtained for as received SiC nanoparticles.

The bands appearing at 1356 cm$^{-1}$ and 1582 cm$^{-1}$ in the spectra of as received SiC nanoparticles corresponds to the disorder D band and graphite like G band [27, 28] which are of very low intensity, however in case of PVA-g-SiC nanoparticles these D and G bands became more pronounced and are displaced towards lower wavenumber i.e 1331 cm$^{-1}$ and 1557 cm$^{-1}$ respectively. Modifications observed in the D and G bands provide the information about the chemical and structural changes in SiC nanoparticles after grafting with PVA. The ratio between the intensity of the D band and the intensity of the G band, denoted as I$_D$/I$_G$, is considered as an indicator of the degree of disorder in the PVA-g-SiC nanoparticles and is presented in table 4. An increase in this ratio for PVA-g-SiC nanoparticles indicates a high proportion of sp$^3$ carbon, which is generally attributed to the presence of structural defects [76].

Table 4:

<table>
<thead>
<tr>
<th>SiC nanoparticles</th>
<th>D peak</th>
<th>G peak</th>
<th>I$_D$/I$_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>1356</td>
<td>1582</td>
<td>0.9</td>
</tr>
<tr>
<td>PVA-g-SiC</td>
<td>1331</td>
<td>1557</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Hence, the changes observed in Raman as well as in FTIR spectra of PVA-g-SiC nanoparticles show that the SiC nanoparticles have been successfully grafted with PVA.
Figure 3.26(a): Raman spectra of (a) as received SiC nanoparticles and (b) PVA-g-SiC nanoparticles.

Figure 3.26(b) presents the Raman spectra of PVA and PVA-g-SiC/PVA nanocomposite film. Presence of all the peaks in the Raman spectra of PVA has been verified in section 3.1.5 [22-24]. The induced structural changes in PVA after incorporation of PVA-g-SiC nanoparticles can be clearly seen in figure 3.26(b) (curve b).

It can be discerned from the Raman spectra of PVA-g-SiC/PVA nanocomposite film that most of the peaks corresponding to PVA vibrations has been lost and the peaks at the wavenumber 1335 cm\(^{-1}\) and 1586 cm\(^{-1}\) which corresponds to the disorder D band and graphite like G band are observed. Moreover, the peak observed at 2920 cm\(^{-1}\) corresponding to C–H stretching vibrations are of considerably reduced intensity in the Raman spectra of PVA-g-SiC/PVA nanocomposite film as compared to peak observed in PVA, which suggests that molecular structure of PVA has been significantly modified after the addition of PVA-g-SiC nanoparticles. This result might be indicative of the formation of inter-molecular complexes between PVA-g-SiC nanoparticles and PVA matrix [22]. Hence, FTIR and Raman spectroscopy results clearly provide the evidence of the presence of strong molecular interaction between PVA-g-SiC nanoparticles and PVA matrix.
Figure 3.26(b): Raman spectra of PVA and PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.

### 3.3.6 Determination of optical energy gap

Optical energy gap of PVA and PVA-g-SiC/PVA nanocomposite film was calculated using equation number (11) given in section 2.4.6. Optical energy gap $E_g$ has been determined by the extrapolation of best fit line between $(\alpha h\nu)^{1/2}$ and $h\nu$ to intercept the $h\nu$ axis $(\alpha = 0)$ [53-55]. Figure 3.27 shows the variation of $(\alpha h\nu)^{1/2}$ calculated from UV-Visible absorption data with photon energy, $h\nu$. The values of optical energy gap so obtained are listed in table 5. It is clear from table 5 that the value of $E_g$ decreases from 4.1 eV for PVA to 3.4 eV for PVA-g-SiC/PVA nanocomposite film. The decrease in optical energy gap of PVA by incorporation of PVA-g-SiC nanoparticles may be ascribed to the formation of charge transfer complexes as localized states in the HOMO-LUMO gap of PVA. Presence of these localized states reduces the gap separating the two localized states within the PVA matrix thus lowering the potential barrier between them, thereby, providing a path for charge carriers to travel between the two localized states [56, 57].
3.3.7 Determination of Urbach’s energy

Figure 3.28 shows the variation of ln(α) with photon energy, hν for PVA and nanocomposite film. Urbach’s energy $E_u$ which is a measure of disorder, has been determined using equation number (12) given in section 2.4.6. The values of $E_u$ was obtained by taking the reciprocal of slope of best fit line between ln(α) and hν and have been listed in table 5. From table 5 a sharp increase in the value of Urbach’s energy from 0.55 eV for PVA to 1.06 eV for nanocomposite film has been observed. Urbach’s energy is a measure of disorder content, hence disorder in the form of localized states within the HOMO-LUMO gap of PVA matrix has been formed after the incorporation of PVA-g-SiC nanoparticles which has also led to the decrease in the optical energy gap [58, 59].

Figure 3.27: Plots of $(αhν)^{1/2}$ versus hν to determine optical energy gap in (a) PVA and PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.
Figure 3.28: Plots of ln(α) versus (hν) used to determine the Urbach’s energy in (a) PVA and PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.

Table 5: Optical parameters for PVA and PVA-g-SiC/PVA nanocomposite film.

<table>
<thead>
<tr>
<th></th>
<th>Optical energy gap</th>
<th>Urbach’s energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_g (eV)</td>
<td>E_u (eV)</td>
</tr>
<tr>
<td>PVA</td>
<td>4.1</td>
<td>0.55</td>
</tr>
<tr>
<td>0.015 wt%</td>
<td>3.4</td>
<td>1.01</td>
</tr>
</tbody>
</table>

3.3.8 Determination of refractive index

Figure 3.29 shows the variation of refractive index of PVA and PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles with wavelength. From figure 3.29 it is clear that the refractive index increases from 1.7 for PVA to 2.0 for PVA-g-SiC/PVA nanocomposite film at 550 nm wavelength. The increase in refractive index indicates increased density within the
nanocomposite film [52, 60, 61], which in turn leads to a reduction in the inter-atomic spacing.

**Figure 3.29:** Refractive index variations of (a) PVA and (b) PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.

**Refractive index dispersion**

From figure 3.29 it can be seen that for PVA refractive index decreases with increasing wavelength showing normal dispersion but in case of nanocomposite film, it decreases in the wavelength region 500 nm to 650 nm displaying normal dispersion however it increases in the region from 300 nm to 500 nm displaying an anomalous behaviour i.e, increases with increasing wavelength.

Dispersion parameters $E_d$ and $E_0$ were calculated using equation number (17) given in section 2.4.6. Figure 3.30 presents the plots of $(n^2 - 1)^{-1}$ against $(hv)^2$ and the values of $E_d$ and $E_0$ can be obtained from the intercept and slope of the linear fitted lines [62-64] and are tabulated in table 6.
The values of \( n_\infty, \lambda_0, \text{ and } S_0 \) were determined from the slope and intercept of linear fitted lines by plotting \((n^2 - 1)^{-1}\) versus \(\lambda^{-2}\) as illustrated in figure 3.30 and are tabulated in table 6.

![Figure 3.30](image)

**Figure 3.30**: Plot of \((n^2 - 1)^{-1}\) versus \((h\nu)^2\) and \(\lambda^{-2}\) for (a) PVA and (b) PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.

### 3.3.9 Determination of dielectric constant

Figure 3.31(a) and (b) show the variations of real \((\varepsilon_1)\) and imaginary \((\varepsilon_2)\) parts of the dielectric constant with energy for PVA and PVA-g-SiC/PVA nanocomposite film. From figure 3.31 it can be clearly seen that values of both real \((\varepsilon_1)\) as well as imaginary \((\varepsilon_2)\) parts of the dielectric constant has increased with respect to PVA and the values of real part of dielectric constant are higher than imaginary part. Higher value of real part of dielectric constant indicates high energy storage capacity of prepared nanocomposite [65-67].
Chapter 3 Results and Discussion

Figure 3.31(a): Variation of real ($\varepsilon_1$) part of dielectric constant with energy for (a) PVA and (b) PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.

Figure 3.31(b): Variation of imaginary ($\varepsilon_2$) part of dielectric constant with energy for (a) PVA and (b) PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.
Table 6: Values of Optical parameters for PVA and PVA-g-SiC/PVA nanocomposite film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$n_\infty$</th>
<th>$\Lambda_0$ (nm)</th>
<th>$S_0 \times 10^5$ (nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>4.8</td>
<td>5.2</td>
<td>1.45</td>
<td>260</td>
<td>1.6</td>
</tr>
<tr>
<td>Nanocomposite film</td>
<td>9.7</td>
<td>28.9</td>
<td>1.99</td>
<td>127</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Table 6 shows that oscillator energy $E_o$ and the dispersion energy $E_d$ increases with respect to PVA. These variations in the value of optical constants may be attributed to the formation of charge transport complexes in the form of localized states between HOMO-LUMO gap in the PVA matrix. These charge transfer complexes makes the lower energy transitions feasible and lead to the observed changes in optical parameters [56, 57, 60, 61].

### 3.3.10 Electrical Conductivity Behaviour

Figure 3.32 (a) show the dependence of current $I$ on applied voltage $V$ for PVA and PVA-g-SiC/PVA nanocomposite film. It is clear from figure 3.32 that the conductivity of PVA increases after incorporation of PVA-g-SiC nanoparticles in PVA matrix. The increase in conductivity of PVA matrix can be due to the formation of continuous conducting network in the nanocomposites film after the addition of PVA-g-SiC nanoparticles in an insulating (PVA) matrix. Thus, PVA-g-SiC nanoparticles act as conductive fillers in the PVA matrix, which provide the continuous conductive pathways for the transfer of charge from one nanoparticle to another.

It is also evident from figure 3.32(a) that the I-V curves are nonlinear in nature. Such nonlinear characteristics can be explained by considering nonohmic charge transport processes such as hopping, Schottky emission (SE), Poole Frenkel effect (PF), space charge limited conduction (SCLC), etc as discussed in section 2.4.7.
The I-V characteristics was plotted on a log-log scale for low as well as high voltage regions, however it did not yield the slope \( n > 2 \) as expected for SCLC to occur [32, 33] so this mechanism for conduction was ruled out. Also the results of hopping model were not a perfect fit to the experimental data so this mechanism was also ruled out. Charge transport in these regions may therefore be associated either with Poole-Frenkel or Schottky conduction mechanism.

In order to find out whether the conduction mechanism is Schottky emission or the Pool-Frenkel, the graph between log (I) versus \( V^{1/2} \) [34-37] were plotted. Figure 3.32(b) shows a plot of log (I) versus \( V^{1/2} \) for PVA and SiC-PVA nanocomposite film. In figure 3.32(b) three different voltage region can be plotted observed viz. low voltage (1st) region (0 < V < 10 V), medium voltage (2nd) region (10 < V < 30 V) and high voltage (3rd) region (36 < V < 100 V) having altered slopes for which the plot of log (I) versus \( V^{1/2} \) has linear relationship. The \( \beta_s \) and \( \beta_{PF} \) values were theoretically calculated using equation number (27) and (29) discussed in section 2.4.7 The theoretically calculated values of \( \beta_s \) and \( \beta_{PF} \) are 3.1 \( \times 10^{-5} \) and 6.2 \( \times 10^{-5} \) eV \( V^{-1/2} \) \( m^{-1/2} \), respectively (taking the high frequency dielectric constant as 1.5). The values for \( \beta_s \) and \( \beta_{PF} \) were also experimentally determined from the slope of linear

---

**Figure 3.32(a):** I-V characteristics of (a) PVA and (b) PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.
fitting by plotting log (I) versus $V^{1/2}$ at low, medium and high voltage regions. The experimental as well as the theoretical values of $\beta_s$ and $\beta_{PF}$ so obtained are tabulated in table 3.

Figure 3.32(b): Plot of log (I) versus $V^{1/2}$ for (a) PVA and (b) PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.

Table 7:

<table>
<thead>
<tr>
<th></th>
<th>Theoretical $\beta_{PF}$ (eV $V^{-1/2}m^{1/2}$)</th>
<th>Theoretical $\beta_s$ (eV $V^{-1/2}m^{1/2}$)</th>
<th>Experimental $\beta_{exp}$ ($10^{-5}$ (eV $V^{-1/2}m^{1/2}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$6 \times 10^{-5}$</td>
<td>$3 \times 10^{-5}$</td>
<td>$1^\text{st}$ region $2^\text{nd}$ region $3^\text{rd}$ region</td>
</tr>
<tr>
<td>PVA</td>
<td>$4.6$</td>
<td>$2.8$</td>
<td>$1.4$</td>
</tr>
<tr>
<td>Nanocomposite film</td>
<td>$5.2$</td>
<td>$2.8$</td>
<td>$1.7$</td>
</tr>
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</table>

The experimental value of $\beta$ is found to be near to $\beta_{PF}$ values for low voltage region. Hence, it is suggested that the dominant conduction mechanism is of Poole–
Frenkel type in low voltage region. However, at the medium as well as high voltage region experimental value of $\beta$ becomes closer to $\beta_s$. Hence, the dominant conduction mechanism at medium and high voltage regions is Schottky conduction mechanism. There is a transition of the conduction mechanism from Poole-Frenkel to Schottky in the high voltage regions. Thus it can be inferred from this observation that at higher voltage regions conduction is through an electrode limited process.

### 3.3.11 Thermogravimetric Analysis (TGA)

After the affirmation of PVA grafting onto SiC nanoparticles, TGA analysis was carried out to observe the thermal response of PVA-g-SiC nanoparticles and to measure the degree of PVA grafting on SiC nanoparticles surface. Figure 3.33(a) shows the TGA curve for as received SiC nanoparticles and PVA-g-SiC nanoparticles. From figure 3.33(a) (curve a), it can be seen that TGA shows a slight weight loss at 100 °C for as received SiC nanoparticles, which was assigned to the loss of water and after 100 °C, main oxidation process started which resulted in the weight increase [70]. The weight loss began at ~620°C in air and is attributed to the oxidation of carbon [71]. However, the thermal degradation of PVA-g-SiC nanoparticles is different from that of as received SiC nanoparticles. The thermal degradation of PVA-g-SiC nanoparticles consists of two stages of degradation. TGA shows initial weight loss upto 100°C and main weight loss from ~141°C to 413°C. This loss could be caused by the thermal degradation of the grafted polymer on the surface of SiC nanoparticles. The grafting degree is highly dependent on the initial quantity of polymer used and the reaction time [77]. On comparison of the thermal degradation processes of as received SiC nanoparticles and PVA-g-SiC nanoparticles, it can also be deduced that the amount of PVA grafted on surface of SiC is very small.

Grafting degree can be determined by using the following equation [78]:

$$
\eta_{gr} = \frac{W_g - W_o}{W_o} \times 100
$$

(1)

where $W_g$ and $W_o$ are the weights of the PVA-g-SiC and as received SiC nanoparticles, respectively. Using the above equation (1) the total amount of PVA grafted on the surface of SiC nanoparticles comes out to be ~1.2 %. 

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Figure 3.33(a): TGA curves of (a) as received SiC nanoparticles and (b) PVA-g-SiC nanoparticles.

The thermal stability of PVA-g-SiC/PVA nanocomposite film was studied using TGA. Figure 3.33(b) shows the comparison of thermal stability curves for PVA and PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles. It can be discerned from figure 3.33(b) (curve a) that the maximum decomposition temperature ($T_{\text{max}}$) for PVA film is ~260°C and it is slightly increased to ~274°C for the nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles. Thus the introduction of PVA-g-SiC nanoparticles in PVA matrix increased the onset of thermal decomposition of PVA. From figure 3.33(b) it can be seen that PVA as well as PVA-g-SiC/PVA nanocomposite film in the first decomposition stage i.e. ~50-130°C show a small weight loss of ~5-8%. This can be attributed to the evaporation of bound water molecules [76]. In the second stage i.e. the temperature range of ~250-464°C, PVA (Figure 3.33(b) curve a) decomposes with ~90% weight loss as it vaporizes and a weight loss of 86% is observed for PVA-g-SiC/PVA nanocomposite film (Figure 3.33(b) curve b). This slight decrease in weight loss is due to the restriction in mobility of polymer chains [43]. It can also be seen from figure 3.33(b) (curve b) that the nanocomposite film with 0.015 wt% PVA-g-SiC nanoparticles does not leave significant char at the end of degradation. The enhancement in thermal stability of PVA-g-SiC/PVA nanocomposite than the PVA...
is due to the strong interfacial interactions between the components in the nanocomposites. Similar kind of enhancement was also observed after addition of PVA grafted graphene oxide (PVA-g-GO) in PVA matrix where PVA-g-GO/PVA nanocomposite show better thermal stabilities than GO/PVA nanocomposites due to the stronger interfacial interaction between the components [48]. Hence, it can be inferred from this observation that addition of PVA-g-SiC nanoparticles increases the onset of thermal decomposition temperature of PVA matrix as opposed to that observed in case of as received SiC nanoparticles where the thermal decomposition temperature decreases.

![Graph](image_url)

**Figure 3.33 (b):** TGA curves of (a) PVA and (b) SiC-PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles.

### 3.3.12 Surface Hardness Analysis

Figure 3.34 depicts the variation in Knoop microhardness and penetration depth of PVA and PVA-g-SiC/PVA nanocomposite film at 9.8 mN load. The Knoop microhardness number (KHN) for PVA as well as the nanocomposite film was calculated using the equation number (31) given in section 2.4.9. It can be discerned from figure 3.34 that the microhardness of PVA is 2.4 Kgf/mm² and it increases to a value of 4.9 Kgf/mm² for PVA containing 0.015 wt% PVA-g-SiC nanoparticles.
nanoparticles. Hence, the surface hardness of PVA is enhanced by addition of PVA-g-SiC nanoparticles. Figure 3.34 also shows the decreased penetration depth with addition of PVA-g-SiC nanoparticles inside PVA matrix. Decreased penetration depth is also an indication of increased microhardness. This increase in hardness of PVA-g-SiC/PVA nanocomposite as compared to PVA may be attributed to the higher hardness exerted by SiC nanoparticles and due to the uniform distribution of PVA-g-SiC nanoparticles inside the PVA matrix [73-75].

Figure 3.34: Variation of hardness and penetration depth with respect to different concentration of PVA-g-SiC nanoparticles in PVA at 9.8 mN load.

3.3.13 Conclusion

It can be concluded that PVA was successfully grafted onto the surface of SiC nanoparticles. XRD measurements ascertain the increase in size of SiC nanoparticles after grafting as compared to as received SiC nanoparticles calculated using Scherer's equation, hence confirms the presence of PVA on SiC nanoparticles surface. XRD pattern also confirms that the grafting procedure did not alter the crystalline geometry of SiC nanoparticles. TEM and SEM images clearly reveal that the surface of SiC nanoparticles has been grafted with PVA. FTIR and Raman spectroscopy validates the chemical attachment of PVA onto the surface of SiC nanoparticles by introducing
functional groups. Optical energy gap decreased from 4.1 eV for PVA to 3.4 eV for PVA-g-SiC/PVA nanocomposite film and Urbach’s energy increased from 0.55 eV for PVA to 1.06 eV for PVA-g-SiC/PVA nanocomposite film. The refractive index increased from 1.7 for PVA to 2.04 for PVA-g-SiC/PVA nanocomposite film. Real and imaginary parts of dielectric constant increased with respect to PVA. The analysis of I-V curves shows that the charge transport consists of a combination of transport mechanism. Schottky mechanism was the main conduction mechanism at medium and high voltage regions whereas Poole Frenkel was the chief conduction mechanism at low voltage regions. Thermal stability curves of as received SiC nanoparticles and PVA-g-SiC nanoparticles shows different decomposition behavior and the amount of PVA grated on surface of SiC nanoparticles was found to be dependent on the initial quantity of PVA used. PVA-g-SiC nanoparticles enhanced the thermal stability of PVA by shifting the onset of thermal decomposition temperature to higher value. Knoop microhardness studies reveal increased microhardness of PVA-g-SiC/PVA nanocomposite film as compared to PVA.
PART B

3.4 Ag-PVA nanocomposites

This part discusses the modifications induced in various properties of PVA after incorporation of Ag nanoparticles. Resulting nanocomposite films were structurally characterized using XRD, TEM, SEM, FTIR and Raman spectroscopy as discussed in sections 3.4.1 to 3.4.5 respectively. UV-Vis spectroscopy was used to study the variations induced in absorption, refractive index and dielectric constant of PVA after Ag nanoparticle addition and is described in section 3.4.6 to 3.4.8 respectively. Further, section 3.4.9 presents the I-V studies carried out to ascertain the charge transport mechanism responsible for increased conductivity of PVA and Ag-PVA nanocomposite films. Section 3.4.10 presents the results of TGA studies carried out on Ag-PVA nanocomposite films to accomplish their thermal stability. Influence of Ag nanoparticles on surface microhardness of PVA matrix has been depicted in section 3.4.11. Finally, section 3.4.12 illustrates the important conclusions drawn from the study.

3.4.1 X-Ray Diffraction (XRD)

The formation of Ag-PVA nanocomposite was confirmed using XRD analysis. Figure 3.35 presents the XRD spectra of Ag-PVA nanocomposite film containing 0.056 wt% Ag nanoparticles. Figure 3.35 clearly reveals all the prominent peaks at 2θ values of 38.1°, 44.3°, 64.5° and 77.6° which represents the (111), (200), (220) and (311) planes of silver and are consistent with peaks of Ag available in JCPDS file no. 4-0783 [79-84]. Presence of these Ag peaks after incorporating in PVA matrix confirms the formation of Ag-PVA nanocomposite. The value of interplanar spacing corresponding to the (111), (200), (220) and (311) planes calculated using equation number (1) given in section 2.4.1 comes out to be 2.36 Å, 2.04 Å, 1.44 Å and 1.23 Å respectively. The average size of Ag nanoparticles in Ag-PVA nanocomposite films calculated using Debye Scherer equation number (2) as given in section 2.4.1 comes out to be ~15 nm.
Chapter 3 Results and Discussion

**Figure 3.35:** XRD spectrum of Ag-PVA nanocomposite film containing 0.056 wt% Ag nanoparticles.

### 3.4.2 Transmission Electron Microscopy (TEM)

**Figure 3.36:** TEM micrograph of (a) Ag nanoparticles and (b) Ag-PVA nanocomposite film containing 0.056 wt% Ag nanoparticles.

Figure 3.36(a) and (b) displays the TEM micrograph of Ag nanoparticles and Ag-PVA nanocomposite film containing 0.056 wt% Ag nanoparticles respectively. It can be
discerned from TEM micrograph of Ag nanoparticles (Figure 3.36(a)) that they are almost spherical in shape. In TEM micrograph of Ag-PVA nanocomposite film (Figure 3.36(b)) it was observed that Ag nanoparticles are uniformly dispersed inside PVA matrix however, the observed nanoparticles are slightly deviated from spherical symmetry which may be due to the interaction of Ag nanoparticles with PVA matrix. TEM micrograph reveals that Ag nanoparticles of average size 15±9 nm are present in the PVA matrix which is consistent with the size obtained using XRD.

3.4.3 Scanning Electron Microscopy (SEM)

Morphology and distribution of Ag nanoparticles in PVA matrix was further characterized using SEM. Figure 3.37 depicts the SEM image of Ag-PVA nanocomposite film containing 0.056 wt% Ag nanoparticles. SEM image clearly shows the presence of almost spherical Ag nanoparticles within PVA matrix. These results are in good agreement with those obtained using TEM.

Figure 3.37: SEM image of Ag-PVA nanocomposite film containing 0.056 wt% Ag nanoparticles.

3.4.4 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.38 presents the FTIR spectra of PVA and Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles. All the peaks present in PVA has been verified
in the previous section 3.1.4 [11-15]. It can be clearly seen from figure 3.38 (curve b) that after the addition of Ag nanoparticle in PVA matrix most of the peaks are diminished in intensity and are slightly displaced towards higher wavenumber. The peak observed at 3332 cm\(^{-1}\) assigned to –OH stretching vibration, at 2938 cm\(^{-1}\) due to the C-H stretching vibration and at 1731 cm\(^{-1}\) due to C=O stretching vibrations has been shifted to 3341 cm\(^{-1}\), 2948 cm\(^{-1}\) and 1739 cm\(^{-1}\) respectively in the FTIR spectra of Ag-PVA nanocomposite film. Peak at 1142 cm\(^{-1}\) due to the symmetric C-C stretching mode, representing the crystalline regions in PVA disappear upon incorporation of Ag nanoparticles, indicating reduction in the crystalline phase of PVA [85].

Another change in the FTIR spectra of Ag-PVA nanocomposite has been observed for the peaks at 1375 cm\(^{-1}\) and 1430 cm\(^{-1}\). In alcohols, the peak at 1375 cm\(^{-1}\) is the result of the coupling of the O-H in-plane vibrations at 1420 cm\(^{-1}\) with the C-H wagging vibration (CH-OH). The decrease in the ratio between the intensities of this peak and the peak at 1430 cm\(^{-1}\) upon incorporation of Ag nanoparticles indicates the decoupling between O-H and C-H vibrations due to bonding interaction between O-H group of PVA and Ag nanoparticles. Thus, it can be inferred that the addition of Ag nanoparticles leads to the structural rearrangement in PVA matrix [86].

Figure 3.38: FTIR spectra of (a) PVA and (b) Ag-PVA nanocomposite film containing 0.062 wt % Ag nanoparticles.
3.4.5 Raman Spectroscopy

Figure 3.39: Raman spectrum of (A) (a) PVA and (b) Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles (B) Enlarged view.

Figure 3.39(A) presents the Raman spectra of PVA and Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles. All the peaks present in PVA has been verified in section 3.1.5 and are in good agreement with the literature [22-24]. It can be clearly seen from figure 3.39(A) that peaks corresponding to various functional groups of PVA has been displaced and reduced in intensity after the addition of Ag nanoparticles in PVA matrix. Peaks at 856 cm\(^{-1}\) and 918 cm\(^{-1}\) due to C-C stretching vibrations have been shifted to 848 cm\(^{-1}\) and 910 cm\(^{-1}\) respectively. Moreover peaks at 1118 cm\(^{-1}\) due to C–O stretching vibrations and at 2920 cm\(^{-1}\) due to C–H stretching vibrations has been considerably reduced in intensity upon incorporation of Ag nanoparticles. The most significant difference in the Raman spectra of Ag-PVA nanocomposite film can be observed in 1300-1600 cm\(^{-1}\) region (Figure 3.39(B) enlarged view). Peaks observed in the Raman spectra of Ag-PVA nanocomposite film at 1331 and 1597 cm\(^{-1}\) corresponding to the disorder D band and graphite like G bands respectively [27, 28] has been enhanced significantly which is attributed to the surface enhanced raman scattering (SERS) effect of Ag nanoparticles [87]. Metal nanostructures have proven to be effective SERS active substrates. According to the electromagnetic theory of SERS, enhancements depend on the excitation of the localized surface plasmon resonance,
which is influenced by several significant parameters such as size, shape and nature of the nanoparticles [88].

### 3.4.6 UV-Visible Absorption Spectroscopy

Figure 3.40(a): Absorption spectra of colloidal Ag nanoparticles

Figure 3.40(a) and (b) presents the UV-Visible absorption spectra of colloidal Ag nanoparticles and Ag-PVA nanocomposite films with varying concentration of Ag nanoparticles. Figure 3.40(a) clearly shows the presence of SPR peak at around 395 nm for Ag nanoparticle colloids however, for Ag-PVA nanocomposite films the SPR peak was observed at around 405 nm [Figure 3.40(b)]. The absorption spectrum of nanocomposite films is broader and peak is red shifted as compared to Ag nanoparticle in colloidal solution. Similar observations were made earlier also for silver, copper and gold nanoparticles [89-92]. This red shift in the SPR peak obtained for Ag-PVA nanocomposite film may be attributed to the increase in the particle size and/or due to wider size distribution of the nanoparticles within the polymer because the band width, intensity and position of the SPR wavelength of these metallic nanoparticles vary with particle size and shape and with their surrounding matrix [93, 94]. From figure 3.40(b) (curves b-f) it is clear that with increasing concentration of Ag nanoparticles in the polymer matrix SPR intensity increases.
Figure 3.40(b): Absorption spectra of (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt % (c) 0.04 wt % (d) 0.048 wt % (e) 0.056 wt % (f) 0.062 wt % Ag nanoparticles.

3.4.7 Determination of refractive index

Figure 3.41 shows the wavelength dependence of refractive index for PVA and Ag-PVA nanocomposite films. It can be discerned from figure 3.41 that the refractive index of Ag-PVA nanocomposite films increases with increasing concentration of Ag nanoparticles in PVA matrix. It increases from 1.5 for PVA to 1.6 for 0.02 wt% Ag nanoparticles and to 1.96 for Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles at 550 nm wavelength. The increase in refractive index is an indication of high density of nanocomposite films. Addition of Ag nanoparticles in PVA matrix may be responsible for the formation of localized electronic states in the HOMO–LUMO gap. These localized electronic states govern the optical and electrical properties of host material vis-à-vis their role as trapping and recombination centres, thus enhancing the low energy transitions leading to the observed change in refractive index [60, 61].
Figure 3.41: Refractive index variation of (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt % (c) 0.04 wt % (d) 0.048 wt % (e) 0.056 wt % (f) 0.062 wt % Ag nanoparticles.

**Refractive index dispersion**

It is highly imperative to analyze the dispersion of refractive index in order to use a device for opto-electronic applications. It is clear from figure 3.41 that for PVA refractive index decreases with increasing wavelength showing normal dispersion but in case of Ag-PVA nanocomposite films, it decreases in the wavelength region 310 nm to 400 nm displaying normal dispersion. Beyond 400 nm, it starts exhibiting an anomalous behaviour as it increases with increasing wavelength.

In the normal dispersion region (the transparent region), the refractive index has been analyzed using the single oscillator model developed by Wemple and DiDomenico as discussed in section 2.4.6.

The values of $E_d$ and $E_o$ were obtained from the intercept and slope of the linear fitted lines by plotting $(n^2 - 1)^{-1}$ versus $(hv)^2$ [62-64] as shown in figure 3.42. Values of $E_d$ and $E_o$ obtained are tabulated in table 8. It can be discerned from table 8 that values of $E_d$ and $E_o$ decreases with increasing concentration of Ag nanoparticles in PVA matrix. Wemple and DiDomenico noted that the refractive index dispersion is approximately inversely
related to $E_d$ and $E_o$. Hence, dispersion of refractive index is controlled by the combined effects of $E_d$ and $E_o$.

Further, the long wavelength refractive index ($n_\infty$), average interband oscillator wavelength ($\lambda_o$) together with the average oscillator strength ($S_o$) for PVA and Ag-PVA nanocomposite films were determined from the slope and intercept of linear fitted lines by plotting $(n^2 - 1)^{-1}$ versus $\lambda^{-2}$ as illustrated in figure 3.42 and the values so obtained are tabulated in table 8. The quantitative measurements of these parameters may help in tailoring and modelling the properties of such nanocomposites for their use in optical devices.

**Figure 3.42:** Plot of $(n^2-1)^{-1}$ versus $(hv)^2$ and $\lambda^{-2}$ for (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt% (c) 0.04 wt% (d) 0.048 wt% (e) 0.056 wt% (f) 0.062 wt% Ag nanoparticles.
3.4.8 Determination of dielectric constant

Figure 3.43(a) and (b) shows the variation in real and imaginary parts of the dielectric constant with energy for Ag-PVA nanocomposite films having different concentration of Ag nanoparticles. It can be discerned from figure 3.43(a) and (b) that the real as well as imaginary parts of dielectric constant increases with increase in concentration moreover, the values of real part of dielectric constant are higher than imaginary part. Real and imaginary parts of the dielectric constant are directly related to the defect density within the forbidden gap of the nanocomposite films [65-67]. Increase in the value of real part of dielectric constant enhances the energy storage capacity of the prepared nanocomposites.

Figure 3.43(a): Variation of real part of dielectric constant with energy for (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt% (c) 0.04 wt% (d) 0.048 wt% (e) 0.056 wt% (f) 0.062 wt% Ag nanoparticles.
Figure 3.43(b): Variation of imaginary part of dielectric constant with energy for (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt% (c) 0.04 wt% (d) 0.048 wt% (e) 0.056 wt% (f) 0.062 wt% Ag nanoparticles.

Table 8. Values of Optical parameters with respect to Ag nanoparticle content in PVA matrix.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$n_\infty$</th>
<th>$\lambda_\infty$ (nm)</th>
<th>$S_o \times 10^{-5}$ (nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>12.3</td>
<td>15.2</td>
<td>2.24</td>
<td>101</td>
<td>12.2</td>
</tr>
<tr>
<td>0.02 wt%</td>
<td>5.77</td>
<td>6.67</td>
<td>2.15</td>
<td>215</td>
<td>2.50</td>
</tr>
<tr>
<td>0.04 wt%</td>
<td>5.50</td>
<td>6.55</td>
<td>2.19</td>
<td>226</td>
<td>2.34</td>
</tr>
<tr>
<td>0.048 wt%</td>
<td>5.27</td>
<td>7.35</td>
<td>2.39</td>
<td>235</td>
<td>2.52</td>
</tr>
<tr>
<td>0.056 wt%</td>
<td>4.81</td>
<td>6.50</td>
<td>2.35</td>
<td>258</td>
<td>2.03</td>
</tr>
<tr>
<td>0.062 wt%</td>
<td>5.04</td>
<td>6.40</td>
<td>2.26</td>
<td>246</td>
<td>2.10</td>
</tr>
</tbody>
</table>
Chapter 3 Results and Discussion

3.4.9 Electrical Conductivity Behaviour

Figure 3.44(a) and (b) shows the dependence of current I on the applied voltage V for PVA and Ag-PVA nanocomposite films containing different concentration of Ag nanoparticles. It can be discerned from figure 3.44(a) that with the addition of Ag nanoparticles in PVA matrix resistivity increases with increasing concentration of Ag nanoparticles as compared to PVA. When the concentration of Ag nanoparticles is 0.056 wt% the trend reverses i.e resistivity decreases (conductivity increases) with increasing concentration of Ag nanoparticles as depicted in figure 3.44(b).

The initial increase in resistivity of Ag-PVA nanocomposite can be explained on the basis of Coulomb blockade effect. According to the Coulomb blockade effect, when we add metal nanoparticles of proper quantities into polymer and disperse evenly with proper space distribution, many tunnelling knots may be formed [95]. While Coulomb blockade condition \( e^2/2C \gg k_B T \) is satisfied, Coulomb blockade phenomenon or single electron effect will occur, preventing electrons (or charge carrier) from moving directionally in a certain electric field. When Ag nanoparticles are dispersed uniformly in PVA, they may be considered as many tunnelling knots, preventing charge carrier from moving at a voltage. In macroscopic view, it will enhance insulating property of dielectrics [96].

![Figure 3.44(a): I-V characteristics of (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt% (c) 0.04 wt% (d) 0.048 wt% Ag nanoparticles](image-url)
Figure 3.44(b): I-V characteristics of (a) PVA and Ag-PVA nanocomposite films containing (b) 0.056 wt% (c) 0.062 wt% Ag nanoparticles.

Figure 3.44(a) and (b) depicts the nonlinear nature of I-V curves for PVA and Ag-PVA nanocomposite films. Such nonlinear characteristics can arise from a number of nonohmic charge transport processes such as Schottky emission (SE), Poole Frenkel effect (PF), space charge limited conduction (SCLC) etc as discussed in section 2.4.7. In order to determine the exact mechanism of charge transport, a detailed analysis of I-V characteristics was carried out. The I-V characteristics plotted on a log-log scale did not yield the slope $n > 2$ as expected for SCLC [32, 33] so this mechanism of conduction is ruled out. The plots of hopping mechanism were also not the perfect fit to the data so this mechanism was also ruled out. Hence, the conduction mechanism could be either Poole Frenkel or Schottky mechanism.

To determine the exact mechanism of charge transport, value of $\beta$ is calculated as described in previous sections. The calculated values of $\beta_s$ and $\beta_{PF}$ are $3.1 \times 10^{-5}$ and $6.2 \times 10^{-5}$ eV V$^{-1/2}$ m$^{1/2}$, respectively. But the experimental value of $\beta$ determined from the slopes of linear fits of log (I) versus (V)$^{1/2}$ curve (see figure 3.45) is found to be near to $\beta_{PF}$ values. That is, the experimental value of $\beta$ is closer to the calculated $\beta_{PF}$ value. Hence, it is suggested that the dominant conduction mechanism is Poole–Frenkel mechanism.
Figure 3.45: Plot of log (I) versus $V^{1/2}$ for (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt% (c) 0.04 wt% (d) 0.048 wt% (e) 0.056 wt% (f) 0.062 wt% Ag nanoparticles.

Figure 3.46: Plot of log (I/V) versus $V^{1/2}$ for (a) PVA and Ag-PVA nanocomposite films containing (b) 0.02 wt% (c) 0.04 wt% (d) 0.048 wt% (e) 0.056 wt% (f) 0.062 wt% Ag nanoparticles.
From another point of view, the interpretation of the conduction mechanism from the experimental data may be done by using the measured slope of $\log(I/V)$ versus $V^{1/2}$ [36, 37] as shown in figure 3.46. If the measured values of figure 3.46 are linear, the conduction mechanism is considered to be Poole–Frenkel process which is indeed the case and the correlation coefficient (R) of the best fit lines comes out to be 0.99, hence, the dominant conduction mechanism is Poole–Frenkel mechanism in this voltage region.

### 3.4.10 Thermogravimetric Analysis (TGA)

The thermal stability of the synthesized Ag-PVA nanocomposite films was studied using TGA. Figures 3.47 present the TGA thermograms for PVA and Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles.

![TGA curves](image)

**Figure 3.47:** TGA curves of (a) PVA and (b) Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles.

It can be seen from figure 3.47 that the thermal degradation behavior of the Ag-PVA nanocomposite is different from that of the PVA. From figure 3.47 (curve a) it can be discerned that the decomposition of PVA starts from ~50°C to 140°C which show a small weight loss of ~5% and is due to the evaporation of bound water molecules. In the temperature range of ~240-464°C, PVA (figure 3.47 curve a) decomposes with ~90%
weight loss as it vaporizes. However, Ag-PVA nanocomposite film (figure 3.47 curve b) does not show any appreciable weight loss up to 217°C and after that major decomposition takes place. The maximum decomposition temperature ($T_{\text{max}}$) for PVA film is ~288°C and it is reduced to ~222°C for the Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles. Thus, the introduction of Ag nanoparticles in PVA matrix shifts the onset of the thermal decomposition toward lower temperatures when TGA was performed in air atmosphere. However, there is a slight increase in the residual weight of the Ag-PVA nanocomposites compared to the PVA. The results observed in this study are somewhat different as compared to previous studies on thermal stability of PVA after Ag nanoparticles addition. For example, Mbhele et al. [86] and Khanna et al. [89] performed TGA in nitrogen atmosphere and showed improvement in thermal stability by shifting of onset of thermal decomposition to higher temperatures with an increase in residual weight of PVA after Ag nanoparticle addition. However, there are reports on decreasing decomposition temperature upon Ag nanoparticle addition. Manna et al. [97] studied Ag-poly(vinylidene fluoride) (PVDF) nanocomposites and showed reduced thermal stability of PVDF matrix in the presence of Ag nanoparticles but with no significant changes in residual weight at the end of degradation. Bozani et al. [98] have also shown a decrease in decomposition temperature upon Ag nanoparticle addition in starch matrix. A decrease in thermal stability can most likely be attributed to catalyzing behaviour of metal nanoparticles towards degradation of polymeric matrix [76].

### 3.4.11 Surface Hardness Analysis

Figure 3.48 depicts the variation in Knoop microhardness and penetration depth of Ag-PVA nanocomposites at an applied load of 9.8 mN. The Knoop microhardness number (KHN) for PVA as well as the Ag-PVA nanocomposite films was calculated using the equation number (31) given in section 2.4.9. It can be discerned from figure 3.48 that the microhardness of PVA is 2.4 Kgf/mm² and it increases to a value of 2.9 Kgf/mm² for 0.02 wt% Ag nanoparticles. With further increase in concentration of Ag nanoparticles to 0.062 wt% microhardness value reaches to 12.1 Kgf/mm². Thus it can be inferred that the surface hardness of PVA is enhanced by the addition of Ag nanoparticles and it increases with increasing concentration of Ag nanoparticles in PVA matrix. From figure 3.48 it can also be
seen that penetration depth decreases with increase in Ag nanoparticles concentration inside PVA matrix. Decreasing penetration depth with increasing concentration is also an indication of increased microhardness. This increase in microhardness value might be attributed to the increasing size of Ag nanoparticles in PVA matrix with the increasing concentration as for a given volume nanoparticles are much closer to each other and resists more strongly the penetration of indenter [74].

![Figure 3.48: Variation of hardness and penetration depth with respect to different concentration of Ag nanoparticles in PVA at 9.8 mN load.](image)

**3.4.12 Conclusion**

In summary, it can be concluded that Ag-PVA nanocomposite films were prepared successfully without using any additional stabilizing agent. The synthesized Ag-PVA nanocomposite films were structurally characterized using XRD, TEM, SEM, FTIR and Raman spectroscopy. XRD analysis revealed that Ag nanoparticles of size ~15 nm are uniformly distributed within polymer matrix. TEM and SEM images clearly reveal the dispersion of spherical Ag nanoparticles within the PVA matrix. Appearance of characteristic SPR peak of Ag nanoparticles at 405 nm in UV-Visible absorption spectra of Ag-PVA nanocomposite films confirms the formation of nanocomposite. The
refractive index increased from 1.5 for PVA to 1.96 for Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles. Real and imaginary parts of dielectric constant increased with increasing concentration of Ag nanoparticles in PVA. Detailed analysis of I-V characteristics predict that when the concentration of Ag nanoparticles in PVA matrix is low, insulating properties of PVA are enhanced. This enhancing of insulating properties of PVA matrix was explained on the basis of Coulomb blockade effect. When the concentration of Ag nanoparticles in PVA matrix is further increased the conductivity increases. It is perceived from I-V studies that the main conduction mechanism was Poole-Frenkel mechanism. TGA studies showed that the addition of Ag nanoparticles decreases the onset of thermal decomposition temperature to lower values. The knoop microhardness number of nanocomposites was found to increase from 2.4 Kgf/mm$^2$ for PVA to 12.1 kgf/mm$^2$ for Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles.

Due to the experimental limitations optical energy gap and Urbach’s energy for Ag-PVA nanocomposite films could not be calculated.
3.5 Comparative study of SiC-PVA nanocomposites and Ag-PVA nanocomposites

Surface plasmon resonance

Surface plasmon resonance (SPR) peak which is a characteristic peak of Ag nanoparticle was observed at around 395 nm for Ag nanoparticle colloids and at around 405 nm for Ag-PVA nanocomposite films. In case of SiC-PVA nanocomposites no such resonance could be observed in the visible region.

Optical energy gap and Urbach’s energy

Addition of t-SiC and PVA-g-SiC nanoparticles in PVA matrix has led to the decrease in the optical energy gap. For the t-SiC-PVA nanocomposite it decreased from 4.1 eV for PVA to 3.4 eV for 0.015 wt% t-SiC nanoparticles and to 3.0 eV for 0.023 wt% t-SiC nanoparticles. For PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles it decreased from 4.1 eV for PVA to 3.4 eV.

Sharp increase in the value of Urbach’s energy for t-SiC-PVA and PVA-g-SiC/PVA nanocomposite films had been observed. It increased from 0.55 eV for PVA to 0.92 eV for t-SiC-PVA nanocomposite containing 0.015 wt% t-SiC nanoparticles and to 1.16 eV for nanocomposite film containing 0.023 wt% t-SiC nanoparticles. For PVA-g-SiC/PVA nanocomposite film, it increased from 0.55 eV for PVA to 1.06 eV for nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles. Formation of localized electronic states within the HOMO-LUMO gap of PVA after the addition of nanoparticles is responsible for the decrease in the optical energy gap and increase in the Urbach’s energy [56-59]. Both t-SiC-PVA as well as PVA-g-SiC/PVA nanocomposite showed almost similar effect on the optical behaviour which shows that the modification of SiC nanoparticles surface did not alter the optical response after incorporation in a matrix.

Refractive index

t-SiC-PVA, PVA-g-SiC/PVA nanocomposites as well as Ag-PVA nanocomposites show improvement in the refractive indices as compared to PVA matrix. SiC-PVA nanocomposite films synthesized using 0.015 wt% t-SiC nanoparticles and 0.015 wt% PVA-g-SiC nanoparticles shows almost similar increase in refractive index i.e. from ~1.7 for PVA to ~2.0 for SiC-PVA nanocomposite films at 550 nm wavelength. However, the increase in refractive index of PVA after Ag nanoparticles incorporation was not much as
compared to t-SiC and PVA-g-SiC nanoparticles. It increases from 1.5 for PVA to 1.6 for 0.02 wt% Ag nanoparticles and to 1.96 for Ag-PVA nanocomposite film containing 0.062 wt% Ag nanoparticles at 550 nm wavelength. The increase in refractive index is an indication of high density of nanocomposite films [52, 60, 61]. Hence it can be discerned from this observation that t-SiC-PVA nanocomposite films and PVA-g-SiC/PVA nanocomposite films have higher density than Ag-PVA nanocomposite films.

**Electrical Conductivity Behaviour**

For the comparative purpose, I-V curves for SiC-PVA nanocomposite films synthesized using 0.015 wt% as received, t-SiC and PVA-g-SiC nanoparticles were plotted as shown in figure 3.49.

![I-V curves for SiC-PVA nanocomposite films](image)

**Figure 3.49:** I-V curves for SiC-PVA nanocomposite films synthesized using 0.015 wt% (a) as received (b) PVA-g-SiC and (c) t-SiC nanoparticles.

It can be discerned from figure 3.49 that the electrical conductivity of t-SiC-PVA and PVA-g-SiC/PVA nanocomposite films is more as compared to as received SiC-PVA nanocomposite films. This enhancement in conductivity properties of PVA after addition of t-SiC and PVA-g-SiC nanoparticles is perceived to be due to homogenous distribution of nanoparticles in the PVA matrix. However, detailed analysis of I-V data indicates that the conduction mechanism responsible for increase in conductivity of all the nanocomposite films is voltage dependent and Schottky
mechanism is the dominant conduction mechanism at high voltage regions and Poole Frenkel mechanism at low voltage regions. Thus it can be inferred from this observation that modification of surface of SiC nanoparticles has improved the conductivity of PVA nanocomposites which is ought to be due to the improved interfacial interaction of modified SiC nanoparticles with PVA matrix.

I-V behaviour of Ag-PVA nanocomposites was dissimilar from SiC-PVA nanocomposites. For Ag-PVA nanocomposites, analysis of I-V data predicts that when the concentration of Ag nanoparticles in PVA matrix is low ~0.048 wt%, insulating properties of PVA are enhanced. This enhancing of insulating properties of PVA matrix was due to the Coulomb blockade effect [95]. When the concentration of Ag nanoparticles in PVA matrix was further increased to 0.056 wt% the conductivity increases. The conductivity rises with increasing concentration as the conductive nanoparticles begin to aggregate to produce chains of particles in intimate contact, providing conductive paths across the sample.

Hence, it can be implied that higher concentrations of Ag nanoparticles are needed to increase the conductivity of PVA matrix as compared to SiC nanoparticles.

**Thermogravimetric Analysis (TGA)**

Analysis of TGA curves obtained in air atmosphere shows that PVA-g-SiC/PVA nanocomposite shows better thermal stability than t-SiC-PVA, SiC-PVA and Ag-PVA nanocomposites. Addition of 3 wt% as received SiC nanoparticles and 0.062 wt% Ag nanoparticles into PVA matrix shifts the onset of thermal decomposition to lower temperature. Addition of 0.023 wt% t-SiC did not alter the thermal decomposition temperature. However, 0.015 wt% PVA-g-SiC slightly increases the onset of thermal decomposition temperature. The main reason for this improvement can be attributed to the better chemical attachment of PVA-g-SiC nanoparticles with PVA matrix. Hence, it can be perceived that incorporation of PVA-g-SiC nanoparticles do not degrades the thermal stability of PVA matrix as opposed to the catalyzing behaviour of as received SiC nanoparticles and Ag nanoparticles towards the decomposition of PVA [76].
Surface Hardness Analysis

Enhancement in surface hardness is more in case of PVA-g-SiC/PVA nanocomposite films as compared to t-SiC-PVA nanocomposite films and Ag-PVA nanocomposites at 9.8 mN load. Knoop microhardness values were increased from 2.4 Kgf/mm$^2$ for PVA to 4.1 Kgf/mm$^2$ for t-SiC-PVA nanocomposite film containing 0.015 wt% t-SiC nanoparticle and to 4.6 for 0.023 wt% t-SiC nanoparticles. For PVA-g-SiC/PVA nanocomposite film containing 0.015 wt% PVA-g-SiC nanoparticles it increased from 2.4 Kgf/mm$^2$ to ~5 Kgf/mm$^2$. For Ag-PVA nanocomposites it increased from 2.4 Kgf/mm$^2$ for PVA to 2.9 Kgf/mm$^2$ for 0.02 wt% Ag nanoparticles and to 12.1 Kgf/mm$^2$ for 0.062 wt% Ag nanoparticles. Microhardness is highly dependent upon the uniform distribution and interfacial interaction of nanoparticles with the polymeric matrix [75] hence, from the above observation it can be deduced that the PVA-g-SiC/PVA nanocomposites shows better dispersion and interaction with the PVA matrix and are much more effective in enhancing the microhardness of PVA matrix even better than Ag nanoparticles at similar concentrations.