6.1 Overview of the Present Study

Nanocomposites are the new class of materials, in which the dimensions of one of the constituents occur at the nanometer scale. When metal nanoparticles are dispersed in polymer matrix, the unique combination, named as polymer-metal nanocomposite, syndicates the excellent inherent properties, such as easy processability, light weight, flexibility and mouldability, etc., of polymers (Darraud et al., 1997; Ruck et al., 1997; Hong et al., 2001; Lee et al., 2001; Thompson, 2001; Liu et al., 2002; Singh, 2002; Fink, 2004; Singh et al., 2005; Kondyurin & Bilek, 2008; Hadjichristov et al., 2009) with the exclusive and interesting optical & electrical properties of metal nanoparticles (Yu et al., 1997; Link & El-Sayed, 1999; Mohamed et al., 2000; Peng et al., 2000; Jin et al., 2001; Hao et al., 2002; Jin et al., 2003; Chen et al., 2009; Hubenthal, 2011; Zhang et al., 2011). Due to such exceptional properties, the Polymer-Metal nanocomposite materials are proved to be promising candidates from both scientific and technological point of view (Mayer, 2001; Sih and Wolf, 2005; Corbierre et al., 2005; Zhu and Zhu, 2006; Avasthi et al., 2007; Meng et al. 2008; Ramesh et al. 2009; Harisparashad and Radhakrishnan 2010; Ramesh et al. 2011; Christopher et al., 2012; Harikrishnan et al., 2012; Liu et al., 2013; Qi et al., 2013; Sandeep et al., 2013). Moreover, properties of such combination highly rely on the choice of polymer as well as size, shape, nature and concentration of embedded nanoparticles. Any small variation in the concentration as well as in size and shape of the metal nanoparticles can lead to dramatic changes in the optical and electrical behaviour of these nanocomposites (Schurmann et al., 2005; Son et al., 2006). Therefore, in order to fabricate such nanocomposites of technological importance; size, shape, concentration and dispersion of nanoparticles in polymer matrix must be controlled carefully. This is a key challenge due to the easy aggregation of nanoparticles arising from their highly reactive nature (Lee et al., 2006, Sangermano et al., 2007).

Further, the properties of polymer-metal nanocomposites can be regulated through various treatments, like thermal annealing, chemical doping, irradiation with electromagnetic radiations, swift heavy ions (Abyanesh et al., 2007; Bernard et al., 2011; Puiso et al., 2011; Sharma et al., 2011), etc. When the polymer nanocomposites are subjected to UV, gamma or heavy ions irradiation, due to the transfer of energy
from the incident radiation, the size, shape, concentration and dispersion of the embedded nanoparticles can be tuned \((\text{Clemenson et al., 2007, Klimmer et al., 2009})\). This may be attributed due to the chain-scissioning, cross-linking etc. within the polymer matrix \((\text{Tripathy et al., 2001, Saqan et al., 2007})\) and the enhancement in the surface and interface energies of the embedded nanoparticles \((\text{Grigorev et al., 2004; Singh et al., 2008})\). This leads to the synthesis of functional materials with unique properties for their utilization in device fabrication and other technological applications \((\text{Fernandez et al., 2003, Lu et al., 2006, Njuguna et al., 2007; Meng et al. 2008; Ramesh et al. 2009; Harisparashad and Radhakrishnan 2010; Ramesh et al. 2011; Christopher et al., 2012; Harikrishnan et al., 2012; Liu et al., 2013; Qi et al., 2013; Sandeep et al., 2013})\). Although, sufficient literature is available related to the synthesis and characterization of polymer-metal nanocomposites but the studies related to irradiation induced effects on their optical, electrical, thermal and structural behaviour are scarce.

Motivated with the feasibility of tuning the properties of polymer-metal nanocomposites as a result of irradiation, in the present work, we have concentrated on a comprehensive study related to the effect of gamma, ultraviolet and swift heavy ion irradiation on the optical, electrical and structural behaviour of PVA–Ag nanocomposites. The observed changes in the optical and electrical properties have been tried to be correlated with the induced structural changes, revealed through X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and Raman Spectroscopy. The selection of PVA in PVA–Ag nanocomposites is due to its high dielectric strength, good charge storage capacity, dopant-dependent electrical and optical properties and capability to act as good stabilizing and capping agent for embedded metal nanoparticles \((\text{Khanna et al., 2005; Bhajanti et al., 2007; Mahendra et al., 2010; Voue et al., 2011})\) while silver nanoparticles provide interesting optical and electrical properties.

### 6.2 Objectives

The following were the specific objectives of the present study:

1. To synthesize PVA–Ag nanocomposites by in-situ chemical reduction method and preparation of their films by solution casting method.
2. To reveal the size distribution and dispersion of embedded nanoparticles through Transmission Electron Microscopy.

3. To study the optical, electrical and structural behaviour of prepared PVA–Ag nanocomposite films using UV–Visible spectroscopy, I–V measurements, FTIR and Raman Spectroscopic techniques and XRD analysis.

4. To analyze the variation in optical, electrical and structural properties of prepared PVA–Ag nanocomposite films as a result of gamma, UV and swift heavy ion irradiation at different doses.

5. To understand the irradiation induced changes in optical and electrical behaviour of PVA–Ag nanocomposite films in terms of induced structural changes.

6.3 Important Results

The PVA–Ag nanocomposite films have been prepared by in-situ chemical reduction of silver nitrate in polymeric PVA solution followed by solution casting.

1. The UV-Visible absorption spectrum recorded for the prepared PVA–Ag nanocomposite film revealed the characteristic surface plasmon resonance (SPR) band at 425 nm, which is the signature of the formation of Ag nanoparticles inside PVA matrix.

2. The TEM images indicated that the embedded Ag nanoparticles in PVA matrix are almost spherical in shape, with their average diameter 13 ± 5 nm.

3. The observed changes in optical and electrical properties of prepared PVA–Ag nanocomposites on exposure to gamma radiation are summarized below.

   (i) A continuous increase in intensity and decrease in FWHM of SPR band have been observed with gamma irradiation dose signifying the increase in concentration and decrease in size of embedded nanoparticles.

   (ii) The average size of the nanoparticles is reduced to 7 ± 3 nm after gamma irradiation dose of 50 kGy, as compared to 13 ± 5 nm for unirradiated sample.

   (iii) The value of optical energy gap reduces, from 4.57 eV to 3.71 eV for gamma irradiation dose of 50 kGy, while refractive index increases consistently with irradiation dose in the complete visible range. The value
of refractive index, which was found to be 1.68 for PVA–Ag nanocomposite without irradiation, has been increased to 1.79 at 632 nm after irradiation at the dose of 50 kGy.

(iv) A significant increase in DC conductivity by ~1 order of magnitude has been observed at gamma irradiation dose of 50 kGy. Further, the dominant charge conduction mechanism for these nanocomposites has been found to be ohmic in nature both before and after gamma irradiation.

4. The UV radiation exposure causes significant modifications in the properties of prepared nanocomposites, described as follows.

(i) The intensity of SPR band enhances whereas FWHM reduces consistently on increasing UV exposure time. This variation in SPR band is attributed to increase in number density and decrease in diameter of embedded nanoparticles.

(ii) Reduction in average size from 13 ± 5 nm to 6 ± 2 nm has been observed on UV-ray exposure for 300 minutes.

(iii) A continuous reduction in optical energy gap value and enhancement in refractive index have been resulted with increase in UV exposure time. The value of optical energy gap reduces from 4.57 eV to 4.10 eV after UV exposure for 300 minutes, whereas that of refractive index increases from 1.68 to 1.90 at wavelength 632 nm.

(iv) DC conductivity has been observed to increase considerably after UV exposure, i.e. by about one order after UV exposure for 300 minutes.

5. PVA–Ag nanocomposites irradiated to SHI (Si^{12+}) at doses 1x10^{11}, 3x10^{11} and 1x10^{12} ions/cm^2, resulted in the alteration of the following properties of these nanocomposites.

(i) A continuous variation in SPR band; increase in intensity while decrease in FWHM, with increasing ion irradiation dose has been observed. These variations are as a result of increased concentration with decreased size of embedded nanoparticles.

(ii) The average size of the embedded nanoparticles has been found to decrease from 13 ± 5 nm to 6 ± 1 nm after ion beam irradiation at the dose of 1x10^{12} ions/cm^2.
(iii) The optical energy gap has been observed to decrease from 4.57 eV to 2.25 eV after exposure to SHI at a dose of $1 \times 10^{12}$ ions/cm$^2$ whereas refractive index increases from 1.68 (before irradiation) to 1.86 at wavelength 632 nm, after irradiation at the same dose.

(iv) A continuous increase in DC conductivity has been observed with increasing ion dose with maximum upto about 2 orders of magnitude after irradiation at $1 \times 10^{12}$ ions/cm$^2$. Also, the charge conduction mechanism shifts from ohmic to SCLC after SHI irradiation.

6. The irradiation induced structural rearrangements in PVA–Ag nanocomposites are revealed through XRD, FTIR and Raman analysis. Further, the Raman spectroscopy shows the presence of intense D and G bands indicating the formation of carbonaceous cluster after irradiation of these nanocomposite films.

Finally it can be concluded that the optical parameters e.g. optical energy gap, refractive index and electrical properties like conductivity of PVA–Ag nanocomposites can be tuned to desired extent after gamma, UV and ion beam irradiation through the proper choice of the type of irradiation and the related parameters. However, the effects are more pronounced for heavy ion irradiation as compared to gamma and UV exposure upto the doses ensuring the sample stability during exposure.

6.4 Future Projections

Some of the future projections related to the present study are:

- The present work may be extended towards the study of mechanical, thermal and magnetic behaviour of PVA–Ag nanocomposites.

- The present work may be extended to effect of irradiation of other heavy ions on the properties of these nanocomposites.

- The similar studies may be carried out for other combinations of metal nanoparticles and host polymeric matrix.

- The metal nanoparticles may be replaced by semiconducting nanoparticles for further study.
References


