

Modified Optical And Dc Conductivity Properties of Gamma Ray Irradiated PVA_xPS_(1-x) Films

Prabha.K.^{1*}, H.S. Jayanna²

^{1,2}Department Of Physics, Kuvempu University, Shankaraghatta, Shimoga – 577 451, Karnataka, India

ABSTRACT: In the present work influence of different doses gamma irradiation on the optical and electrical behavior of PVA_xPS_(1-x) films have been studied by UV-Vis spectroscopy and DC electrical measurements. The absorbance peak range in UV region slightly shifted to higher wavelength side with the increase of PS concentration from $x = 0.0$ to 1.0 in PVA_(1-x)PS_x matrices. Also the absorbance peak position in UV region for PVA_(1-x)PS_x polymer films is modified with respect to γ -ray irradiation. The variation of σ_{dc} with irradiation dose markedly depends on the concentration of PS in PVA matrix. It may be presumed that the activity of gamma rays results in excitations of its molecules and creation of free electrons and ions that migrate through the polymer network till they are trapped somewhere, leaving deficient regions. These electronic and ionic configurations cause the changes in the electric conductivity of PVA_xPS_(1-x) polymers.

I. INTRODUCTION

Modification of polymers by irradiation, with ionizing radiation in particular, is an expanding field of research and application because of its technological implications. In addition, γ -irradiation has been proved to be a significant tool [1] for such modifications. It is well known that γ -irradiation can amend the electrical, optical, thermal properties etc. of the polymeric materials by changing their morphology through various processes of chain accessioning and cross linking [2-4]. The polymer irradiation leads to shift in optical absorption edges, which shows a lowering of the energy-gap. The effects of ultraviolet (UV) radiation and thermal annealing on the optical and mechanical properties of polyvinyl alcohol (PVA) were studied by El-Kader et al. [5]. Initially electrically insulating PVA/AniHCl blend has been remarkably transformed into the electrically conducting PVA/PANI nanocomposites where the conductivity increases by 5 orders of magnitude after exposure to 50 kGy. 10, 50, 100, 150 and 250 kGy dose irradiated poly (vinyl) alcohol/gelatin copolymer (PVA/Gel) with different entrapped carotene (Carot) films were studied by Lofty et al [6]. They clearly demonstrated that the electrical conductivity of PVA/Gel/Carot films was increased from two to three orders of magnitude due to carotene doping, and decreased one order of magnitude due to gamma irradiation. The obtained results can be attributed to the existence of the conjugated double bonds in the aliphatic side chain of the carotene molecule.

It is evident from the literature that no studies were reported on the effects of gamma irradiation on the properties of PVA_(1-x)PS_x. Prepared films were irradiated at different doses viz., 1.0 and 1.5 kGy at a dose rate 1.19 Gy per second at room temperature. γ -ray irradiated and unirradiated films were subjected to UV-Vis spectral analysis and DC analysis and the results are discussed herein.

II. EXPERIMENTAL DETAILS

Polyvinyl alcohol (PVA) and polystyrene (PS) monomers (98% with molecular weight less than 3500) were obtained from Sigma Aldrich. The dimethyl sulphoxide (DMSO) and double distilled water (DDW) were used as a solvent. The preparation of PVA_(1-x)PS_x films were already reported elsewhere [7]. The prepared polymer film sheets were cut into small films and subjected to ⁶⁰Co γ -radiation of two different dosages viz. 1.0 and 1.5 kGy at a dose rate 1.19 Gy per second at room temperature. γ -ray irradiated and unirradiated films were cut into circular pieces with 6.5 mm radius and both surfaces of the film were coated with a good graphite layer. The DC electrical conductivity measurements were carried out to an accuracy of $\pm 1\%$ for all the nine prepared thin film samples at different temperatures ranging from 30 – 90 °C.

The resistances of the thin film samples were measured using a four-probe setup. The voltage drops (V) across the samples were measured at constant current (I). The thickness (d) of the thin film samples were measured using a thin film thickness measuring unit model US MProbe visible spectroscopic reflectometer. The DC conductivity (σ_{dc}) of the sample was calculated using the relation

$$\sigma_{dc} = Id/(VS), \quad (1)$$

Where I is the constant current, d is the thickness of the thin film, V is the measured voltage drop across the sample, S is the surface area covered by the electrode on the thin film sample.

III. RESULTS AND DISCUSSIONS

The absorption spectra of the PVA_(1-x)PS_x (x = 0.0, 0.25, 0.50, 0.75 and 1.0) polymer films were recorded before and after γ -irradiation to different absorbed doses (1.0 kGy and 1.5 kGy) and the recorded spectra are shown in figure 1-2 . The absorbance spectra of the unirradiated and irradiated films show a single peak in the UV region. The unirradiated PVA has an absorption peak in the range of ultraviolet around 254 nm. The absorbance peak range in UV region slightly shifted to higher wavelength side with the increase of PS concentration from x = 0.0 to 1.0 in PVA_(1-x)PS_x matrices. Also the absorbance peak position in UV region for PVA_(1-x)PS_x polymer films is modified with respect to γ -ray irradiation. This may be due to high density and toughness of the film formed by irradiation such as cross linking and grafting [8].

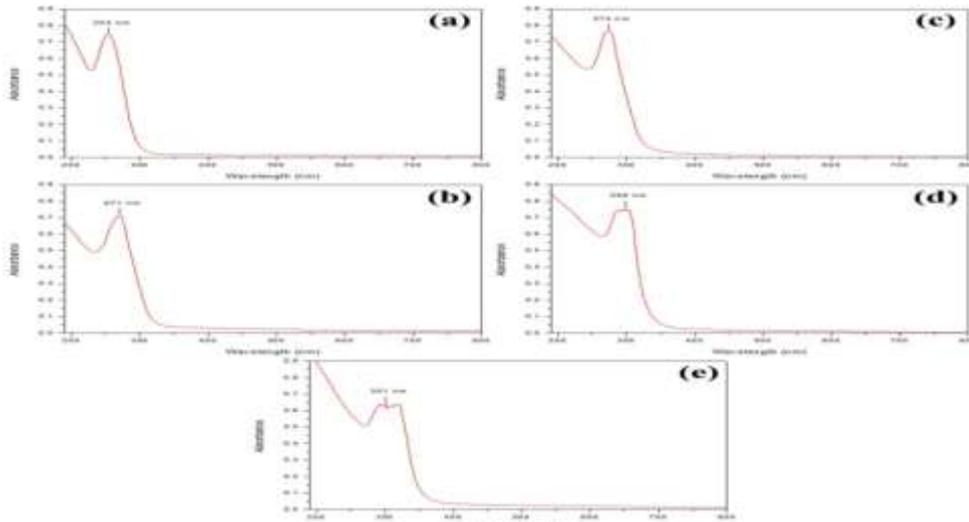


Figure 1: UV-Vis absorption spectra of (a) PVA (b) PVA_{0.75}PS_{0.25} (c) PVA_{0.5}PS_{0.5} (d) PVA_{0.25}PS_{0.75} (e) PS unirradiated polymer film

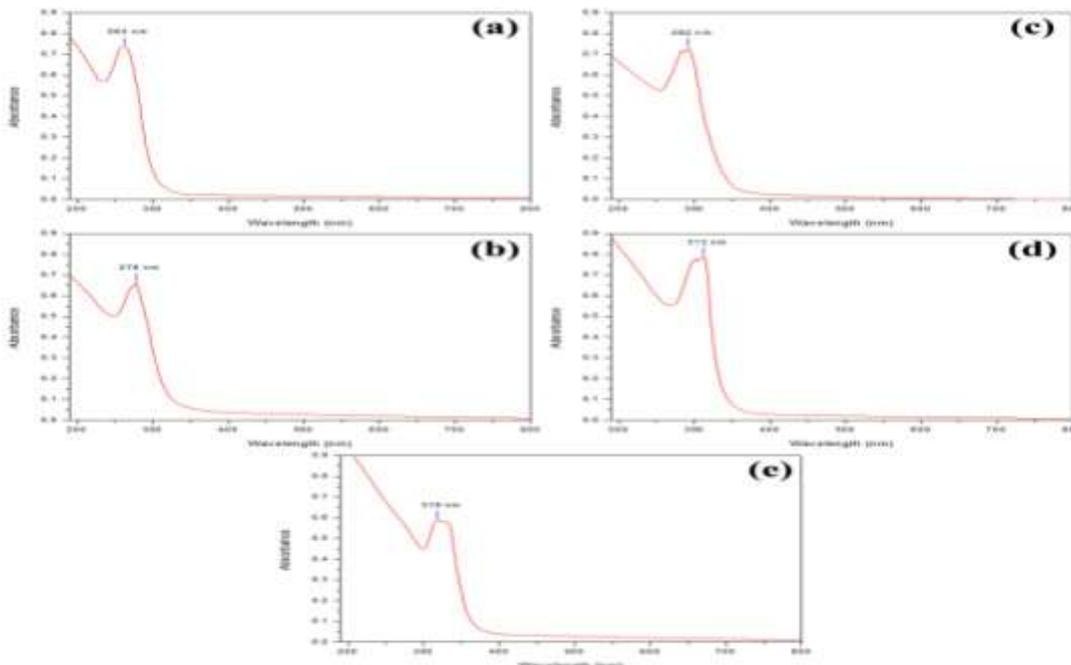


Figure 2: UV-Vis. Absorption spectrum of (a) PVA (b) PVA_{0.75}PS_{0.25} (c) PVA_{0.5}PS_{0.5} (d) PVA_{0.25}PS_{0.75} (e) PS polymer films irradiated with γ -ray 1.0 kGy.

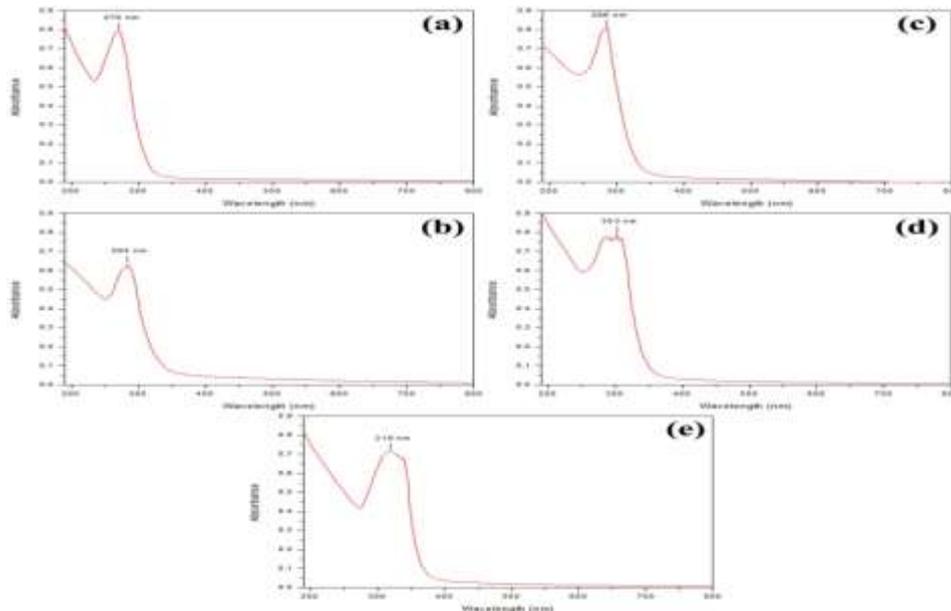


Figure 3 : UV-Vis. Absorption spectrum of (a) PVA (b) PVA_{0.75}PS_{0.25} (c) PVA_{0.5}PS_{0.5} (d) PVA_{0.25}PS_{0.75} (e) PS polymer films irradiated with γ -ray 1.5 kGy.

The plots of energy vs $(\alpha h\nu)^2$ for PVA_(1-x)PS_x polymer films under unirradiated and irradiated with different dosage is shown in Figures 3.37 – 3.41.. It is observed from the plots that the values of E_g have decreased by increasing the concentration of PS from $x = 0.0$ to 1.0 as well as increasing γ -ray irradiation for the concentration $x = 0.0, 0.25, 0.75$. The high energy γ radiation interacts with the PVA_(1-x)PS_x polymer matrices in three different ways i.e. photoelectric effect, Compton scattering and pair-production. Also the interaction depends upon the γ -ray irradiation dosage photons. It is well known that in the Compton Effect the momentum of the incident photon is shared between inelastically scattered photon and the ejected electron, and not transferred to atom or nuclei, so, γ ray photon remains have sufficient energy to knock out an atom from its position after irradiation on the polymer films. Hence, micro strain, dislocation density and distortion parameters decrease with an increase in γ -ray irradiation dose from 0.0 Gy to 1.5 kGy. PVA_(1-x)PS_x ($x = 0.0, 0.25, 0.50, 0.75$ and 1.0) polymer film is irradiated by γ -ray may be caused to formation new bonds due to the crosslink chain after irradiation [9]. In our present optical study reveals that the prepared PVA_(1-x)PS_x polymer films are useful for gamma ray dosimeter.

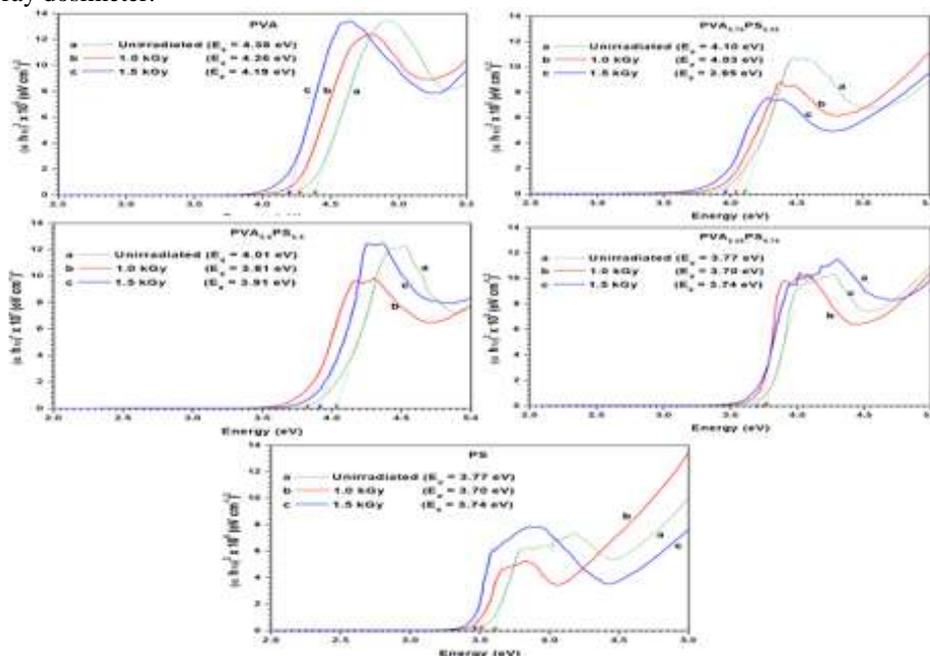


Figure 4: Plots of energy vs $(\alpha h\nu)^2$ for PVA_(1-x)PS_x polymer film with different dosage of γ -ray irradiation

The temperature dependence of dc conductivity (σ_{dc}) was studied over the temperature range 27–138 °C of unirradiated and γ -irradiated PVA_xPS_(1-x) thin films with different dosages is provided in Figure 5. With increasing temperature, the dc conductivity of unirradiated and γ -irradiated PVA_xPS_(1-x) thin films is found to increase.

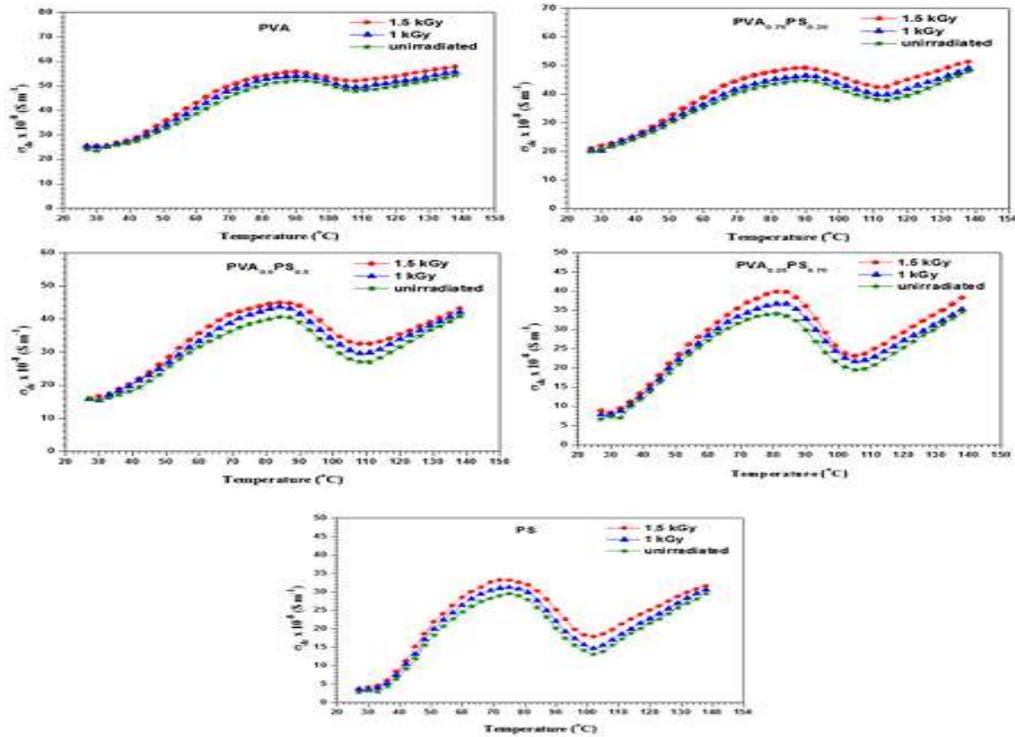


Figure 5: The variation of DC Conductivity with temperature at different γ -ray irradiation dosage for PVA_(1-x)PS_x polymer film

The variation of σ_{dc} with temperature is assigned to four regions round 27 – 70 °C (region I), 70 – 90 °C (region II), 90 – 110 °C (region III) and 110 – 138 °C (region IV). All data are satisfactorily linear fitted with their respective region using the well known Arrhenius equation [10] as shown in Figure

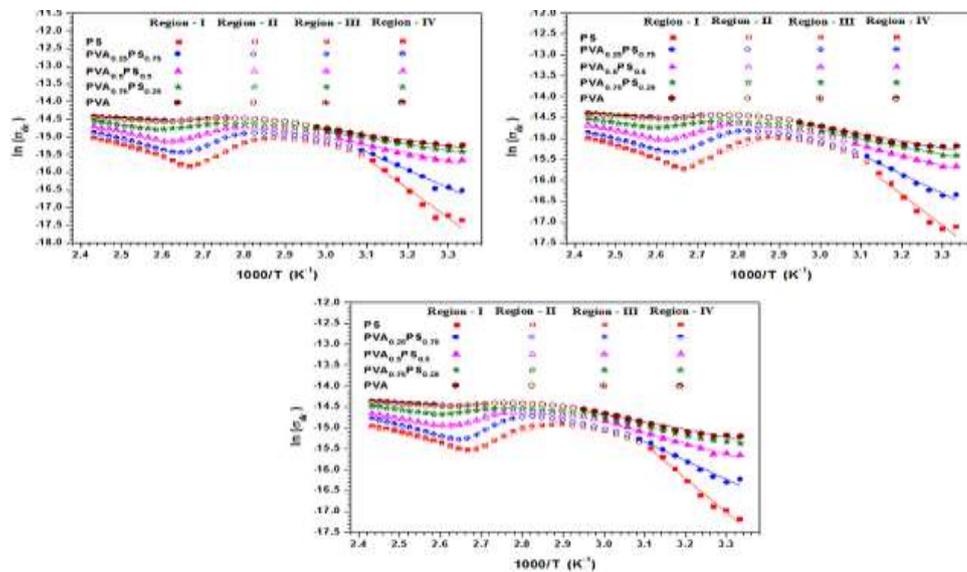


Figure 6.: Plots of $\ln\sigma_{dc}$ vs $1000/T$ for different compositions of PS in PVA_xPS_(1-x) films for

i) unirradiated condition ii) 1kGy and 1.5 kGy γ -radiation.

The σ_{dc} decrease with increasing temperature (region I) that any of this material bears a negative thermal coefficient of resistance, the interpretation of this is that the polymer chains and cross linkage [11] act as traps the charge carriers which transited by hopping process. At a certain temperature later (region II) traps are saturated hence the σ_{dc} almost maintained as constant. As the temperature further increases, we observed significant degradation in σ_{dc} . This was because that some of the trap charges collide with the nearby traps, hence they deteriorated the conductivity. By increasing the temperature beyond 110 °C, segments of the polymer being to move, releasing the trapped charges. The release of trapped charges is intimately linked with molecular motion. The gain of current with temperature is assigned to two main parameters, charge carriers and mobility. The increase of temperature will increase the number of charge carriers exponentially, thus σ_{dc} increase sharply. Similar behavior was observed for γ -ray irradiated films, however, as we increase the irradiation dosage the range of temperature regions are slightly shifted towards the lower temperature side. This may be due to the γ -ray irradiation breaks the crosslinking bonds of the polymer films, thus the crystallinity of the films is improved which increases the σ_{dc} . The increase in conductivity at high temperature may be accounted for by the liberation of electrons or ions through the amorphous region of PVA_xPS_(1-x) [12]. Thus γ -ray irradiation makes the PVA_(1-x)PS_x polymer films more conducting in nature .

IV. CONCLUSION

Solution casted PVA_xPS_(1-x) thin films were analyzed for their optical and DC conductivity measurements under unirradiated and γ - irradiated conditions. The results revealed that γ -ray irradiation produce a typical change in their optical and electrical behaviour. Micro strain, dislocation density and distortion parameters decrease with an increase in γ -ray irradiation dose from 0.0 Gy to 1.5 kGy, which favours the applications of these films in gamma ray dosimeter. Also γ -ray irradiation makes the PVA_(1-x)PS_x polymer films more conducting in nature

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