

# Modification of Optical Response of Polyvinyl Acetate Induced by 250keV D<sup>+</sup> Ion Bombardment

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## ABSTRACT

*The optical response of polyvinyl acetate (PVAc) polymer irradiated by 250 keV D<sup>+</sup> ion beam is studied by spectrophotometer technique in the UV-Visible range of 200-500 nm. It is observed that optical absorption varies with time of irradiation. The development of a new peak due to irradiation and its shifting towards the higher wavelength, with time of irradiation has been observed. Due to irradiation the change in the band shape and decrease in the band gap has also been observed.*

**KEY WORDS:** Polymer films, Deuteron beam irradiation UV-Visible absorption, Spectrophotometry.

## INTRODUCTION

Ion induced modification of polymeric materials can generate a very wide range of property changes. The problems are sufficiently complex that prediction of the effects are extremely difficult, although many general guidelines are beginning to emerge. To emphasise the predictive problems, the published examples include the conversions of crystalline material to an amorphous phase, as well as many physical and chemical changes may occur. Complex defects may develop, annealing may cause anti-site defects or clusters, and nearly every property of the original polymer can be modified. On the positive side, it is this flexibility which makes ion induced modification of polymers so attractive. On the negative side, the complexity makes prediction of detailed changes very difficult.

Polymers are a class of materials widely used in different fields of applications. In the field of optical telecommunication, polymers are discussed as a new class of materials for the fabrication of passive optical devices, the ion irradiation is a promising method to generate struc-

tures with a modified index of refraction, which is necessary for the guidance of light with different wavelengths in optical devices.<sup>1-4</sup> Polymers and organic materials are used as electrically insulating materials for various purposes as dielectric.<sup>5,6</sup> The recent interest of using polymers as electrically conducting materials for optical applications, light emitting diodes etc., is increasing. The use of thin films in these fields, specially in thin film transistors are very demanding from the point of view of fast developing technology.<sup>7,8</sup> Polymers are found very sensitive to energetic charged particle exposure and ionising radiation.<sup>9,10</sup> Different ions at various doses and at different energies, play an important role in polymer modification, the constituents of environment present during ion bombardment of polymeric target also play an important role in polymer modification.<sup>11-13</sup> The absorption of light energy by polymeric materials in the ultraviolet and visible regions involves promotion of electrons in  $\sigma$ ,  $\pi$  and  $n$ -orbitals from the ground state to higher energy states which are described by molecular orbitals.<sup>14</sup> The electronic transitions ( $\rightarrow$ ) that are involved in

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the ultraviolet and visible regions are of the following types  $\sigma \rightarrow \sigma^*$ ,  $n \rightarrow \sigma^*$ ,  $n \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ . The optical methods of studying defects have the advantage that if each defect has characteristic energy levels which lie within the forbidden energy gap, then they show separable optical absorption and luminescence bands. Many of the optical transitions which result from the presence of impurities have energies in the visible part of the spectrum, consequently the defects are referred to as color centers. Ion beam interaction with polymers generates damage which leads to the formation of new defects and new charge states. In order to obtain useful information from the ultraviolet or visible spectrum of the polymer the wavelength of maximum absorption ( $\lambda_{\max}$ ) and the intensity of absorption must be measured accurately.

## EXPERIMENTAL

The polyvinyl acetate polymer samples were prepared in our laboratory. Vinyl acetate monomer was polymerised with benzoyl peroxide catalyst and in semisolid condition it was put in polypropylene petri dish and was cured in an oven at 50°C for 6 hours. Then this polymer was cut to size. The sample of size  $1 \times 1 \text{ cm}^2$  and thickness  $250 \mu\text{m}$  was mounted on the target holder and placed inside the scattering chamber for irradiation. A magnetically analysed, monoenergetic deuteron beam of 250 keV in diffused condition was obtained from the AN 400 Van de Graaff accelerator for irradiation. The ions strike the polymer target in a Vac-Ion pumped scattering chamber, the high vacuum of the order of  $2.4 \times 10^{-8}$  Torr in the system prevents any carbon deposition on the sample due to residual vapor cracking during the ion bombardment. A typical experimental arrangement is shown in Fig. 1. The polymer samples were irradiated for different time intervals: 2 hours, 3 hours, and 4 hours respectively, in order to study the effect of dose variation. The exact ion dose measurement was carried out with a new technique in which a cylindrical

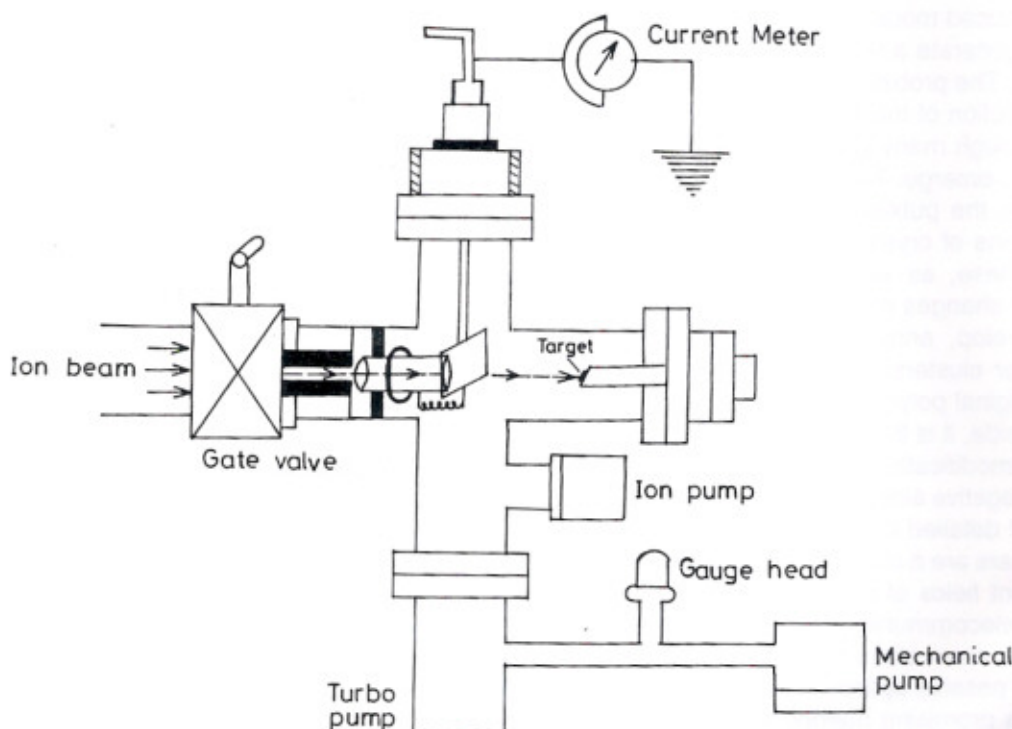


Fig. 1. Schematic layout for a typical experimental arrangement for  $D^+$  ion beam irradiation at the Van de Graaff accelerator



Faraday cup along with magnetic suppression of charge species was carried out with the help of a circular magnet and metallic shutter the arrangement is shown in Fig. 1. The ions current was recorded for two minutes duration with a beam flux of  $5 \mu\text{A}/\text{cm}^2$ . The beam current was kept at  $5 \mu\text{A}$  so as to avoid excessive heating of the target during the irradiation, the total doses were varied from  $2.4 \times 10^{17}$  to  $4.8 \times 10^{17}$  ions/ $\text{cm}^2$ . A set of three identical samples was irradiated under the same physical condition. The photospectrometry in the UV-VIS range of both irradiated and virgin samples was carried out on a spectrophotometer.

## RESULTS AND DISCUSSION

Figure 2(a) shows an absorption spectra of virgin polyvinyl acetate polymer. It shows maximum absorption between 200 to 280 nm, the flat region, which may be attributed to the band-gap of the monomer of this polymer. For the wavelength higher than 280 nm the absorption decreases slowly and comes to zero value around 425 nm, thus allowing transmission of the full wave between 425-500 nm.

Figure 2(b) shows the optical absorption spectra of two hours deuteron irradiation at a dose of  $2.4 \times 10^{17}$  ions/ $\text{cm}^2$ . It is observed that the flatness is lost and followed by the slowly moving slope towards the higher wavelength, with the maximum absorption at 200 nm. The absorption decreases slowly and comes to zero value around 330 nm, thus allowing transmission of the wave whose wave length is lying between

330-500 nm. Due to irradiation the range of transmission is increased by 95 nm towards the lower wave length side. The absorption decreases almost for all the wave lengths, this effect may be correlated with degradation and sputtering occurring in the polymer due to irradiation.

Figure 2(c) reports the UV-VIS absorption spectra of three hours deuteron irradiation at a dose of  $3.6 \times 10^{17}$  ions/ $\text{cm}^2$ . At this dose, the development of a new peak which appears around 212 nm has been observed, the absorption maxima is shifted towards the higher wavelength, in comparison with two hrs. irradiated sample, with 30% increase in absorption. The increase in absorption may be due to beam induced polymerisation and prompt color formation which alter the reflectivity of polymer samples. After 212 nm the absorption decreases slowly for higher wavelengths and comes to zero value around 310 nm. Thus the range of transmission is further increased by 20 nm towards the lower wavelength side.

Figure 2(d) shows the optical absorption spectra of four hrs. deuteron irradiated sample. The absorption maxima is further shifted towards the higher wavelength and appears at 225 nm, the main peak is further shifted by 13 nm with 30% of again increase in absorption. A comparison of fig. 2(a) to 2(d) shows that the spectral pattern between 300-450 nm is almost identical with slightly increased absorption in the case of irradiated one. This effect may be correlated with the recovery of some of its original property due to recombination.

Figure 3 shows the changes in the absorption behavior with respect to time of irradiation, with peaks at 200, 212, and 225 nm. It is clear that the absorption decreases initially up to 2 hr of irradiation for all three wavelengths. The initial fall and the final rise in the absorption may be correlated with scissioning (degradation) and crosslinking (polymerisation) and prompt color formation occurring in the polymer due to irradiation.

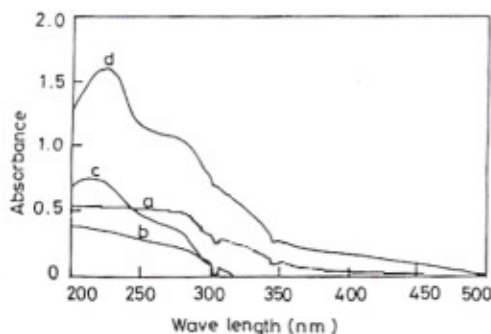


Fig. 2. Optical absorption spectra of a polyvinyl acetate (a) virgin polymer, (b)  $2.4 \times 10^{17}$  D<sup>+</sup> ions/ $\text{cm}^2$  irradiated, (c)  $3.6 \times 10^{17}$  D<sup>+</sup> ions/ $\text{cm}^2$  irradiated, (d)  $4.8 \times 10^{17}$  D<sup>+</sup> (ions)/ $\text{cm}^2$  irradiated.

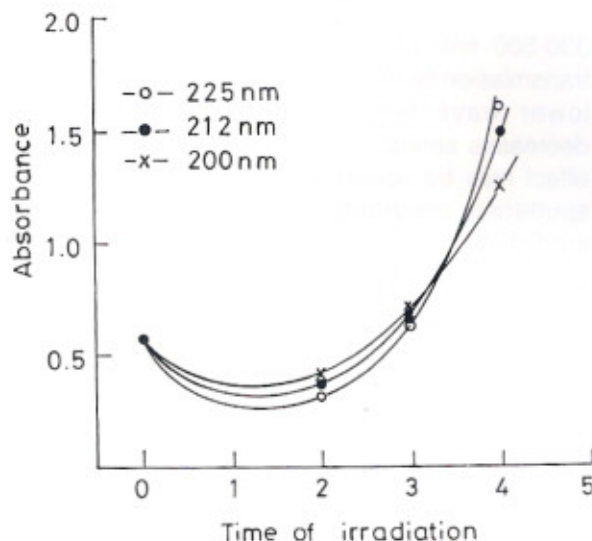


Fig. 3. Variation of optical absorption behavior of vinyl acetate with dose, at three characteristic wavelengths (200, 212, and 225 nm).

### CONCLUSIONS

The initial decrease in the absorption along all the wavelengths can be correlated with scissioning of polymer chains. The development of a new peak at 212 nm due to irradiation is may be due to some new arrangement of the electronic structure is taking place. The shifting of peak by 13 nm after 4 hr of irradiation is may be due to the conjugation of some chromophoric groups in the polymer. The color formation is due to trapped free radicals or charged species.

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As the dose increases, the absorption edge shifts towards the higher wavelength and, therefore, the band gap of the irradiated samples are decreased.

### REFERENCES

1. M.D. Ruck, J. Schulz, N. Deusch, *Nucl. Instrum. Meth. B* **131** (1997) 149.
2. J.R. Kulish, H. Rancke, A. Singh, R.A. Lessard, E.J. Knystautas, *J. Appl. Phys.* **63** (1998) 2517.
3. C. Darraud, B. Bennamane, C. Gagnadre, J.L. Decossas, J.C. Vareille, J. Stejny, *Polymer* **35** (1994) 2447.
4. B. Bennamane, C. Gagnadre, J.L. Decossas, J.C. Vareille, *Nucl. Instrum. Meth. B* **62** (1991) 48.
5. A. Das, S. Bera, S. Dhara, A. Patnaik, *Nucl. Instrum. Meth. B* **134** (1998) 377.
6. S. Osaki, *J. Polym. Sci. Polym. Lett.*, **28** (1990) 147.
7. A.J. Lovinger, L.J. Rothberg, *J. Mater. Res.* **11** (1996) 1581.
8. R.F. Service, *Science* **273** (1996) 878.
9. C. Darraud, B. Bennamane, J.L. Decossas, J.C. Vareille, *Nucl. Instrum. Meth. B* **131** (1997) 198.
10. J. Davenas, G. Boiteux, and X.L. XU, *Nucl. Instrum. Meth. B* **32** (1988) 136.
11. R.N. Chakraborty, A.K. Srivastava, B.K. Singh, R. Pathak, U.K. Chaturvedi and A.K. Nigam, *Nucl. Instrum. Meth. B* **62** (1991) 239.
12. U.K. Chaturvedi, A. Patnaik, R. Pathak, R.N. Chakraborty and A.K. Nigam, *Mater. Res. Soc. Symp. Proc.* **100** (1988) 749.
13. M. Dole, C.D. Keeling and D.G. Rose, *J. Am. Chem. Soc.* **76** (1954) 4304.
14. J.R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, 1994, p 7.