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Radiation Physics and Chemistry 59 (2000) 31–37

Radiation Physics and Chemistry

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# Study of electrical and optical frequency response of neutron irradiated polyvinyl acetate thick films

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Received 6 February 1999; accepted 20 December 1999

This paper is dedicated to late Prof. A.K. Nigam, Department of Physics, Banaras Hindu University, Varanasi

**Abstract**

Electrical and optical frequency response of polyvinyl acetate (PVAc) polymer has been studied by making capacitors, using PVAc film irradiated with neutron, and unirradiated, as their dielectric. It has been observed that the neutron irradiation induces crystallinity in the virgin sample of PVAc. The UV absorption studies of this polymer show an increase in its absorption after neutron irradiation which is in agreement with the increase in dielectric constant in the capacity measurements. It also reflects the possibility of 16% increase in the crystallinity of the sample which is supported by X-ray diffraction analysis of both the virgin and the irradiated polymer. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The study of electrical loss characteristics and optical absorption behaviour of various polymers irradiated with different forms of radiation, e.g., protons, neutrons, electrons and gamma rays, is of great practical importance. It is well known that irradiation causes delinkage of polymeric chains due to scissioning, giving rise to both uncharged sites and charged vacancies (Laghari and Hammound, 1990).These irradiated polymeric materials when subjected to impedance analysis reveal variations in their electronic properties which are very sensitive to irradiation (Macdonald, 1987). The polymers that possess polar characteristics having residual electric dipoles will display this effect more predominantly.

Polyvinyl acetate (PVAc) happens to be one of the polymers which possesses large dipole moment and high relaxation time (Erlikh and Shcherbak, 1955; Tager, 1972). It has been reported that PVAc possesses high values of $\tan\delta_{max}$ of segmental loss and $\tau$, the relaxation time (Tager, 1972; Fisher, 1957). The reason assigned to this was in the structure of its formula, i.e. its side chains are connected to ester oxygen. Further, the virgin PVAc has regions separated by wider potential barriers due to its long molecular chain. Some investigators have observed and reported that the neutron irradiation of polymers increases their dielectric constant due to creation of V-centres or charge centres (Bhateja, 1983; Bhateja et al., 1983; Shrinet et al., 1984). A random inducement of crystallinity is expected to occur as a result of scissioning. With this in mind, an effort was made to irradiate various polymers available with us, e.g., polyvinylidenefluoride (PVDF), polyvinylidenechloride (PVDC), polymethylmethacrylate (PMMA), polyvinylacetate (PVAc), poly-

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PII: S0969-806X(00)00182-1

ethyleneterephthalate (PET) and polyimide (Kapton). Among them, PVAc showed a very interesting behaviour in impedance analysis as well as in UV absorption measurements as compared to that in the other polymers. This prompted us to make a detailed and careful study of PVAc samples irradiated with different 14.4 MeV neutron fluences. This aspect has not been studied so far on this polymer and is of great academic and practical interest.

The concept of increase in crystallinity due to fast neutron irradiation can be clearly understood from the following. When the semicrystalline polymers are exposed to radiation, the crystalline region lamellas may be broken into two or more portions, whereas the long molecular chains of amorphous regions may be broken at different places, leaving a free smaller chain which immediately comes to a stable position by collecting its whole length into regularly arranged lamella form, of course, of smaller size. This concept can be visualised from Fig. 1.

## 2. Experimental details

The PVAc samples were prepared in our laboratory. Vinyl acetate monomer was polymerised with benzoyl peroxide catalyst and, in semisolid condition, it was put in a polypropylene Petri dish and was cured in an oven at 50°C for 6 h. Then this sample was cut to size. The sample of size $1 \times 1$ cm$^2$ and thickness 0.25 mm, was mounted in front of the Faraday cup of our AN 400 Van de Graaff accelerator, to be irradiated with 14.4 MeV neutrons produced by bombarding the tritium target with 250 keV deuteron beam. The neutron flux produced was $2 \times 10^7$ neutrons/cm$^2$/s. The samples were irradiated in air at the atmospheric pressure in the temperature range of 18–20°C, for different time intervals such as 30 min, 1, 2, 3, and 4 h. The photospectrometry in the UV range, of both irradiated and virgin samples, was carried out on a Cary 2390 UV–Vis–IR spectrophotometer (Varian, Switzerland). A Frequency Response Analyser (Model No. 1250, Solartron Instruments England) was employed for frequency response analysis of the capacitors made of the irradiated and virgin PVAc samples. This instrument is capable of making the frequency response analysis of the capacitors even at very low frequencies. Its range is from $10^{-4}$ to $10^6$ Hz. On both sides of the samples, thin films of Ag were deposited to prepare capacitors with polymeric material as the dielectric. The frequency response data so recorded has been analysed and plotted with the help of a PC computer.

## 3. Results and discussions

All our experiments can be divided into three types of measurement — capacitance measurements of the capacitors prepared from PVAc, UV spectroscopy and XRD spectra of the virgin and irradiated samples.

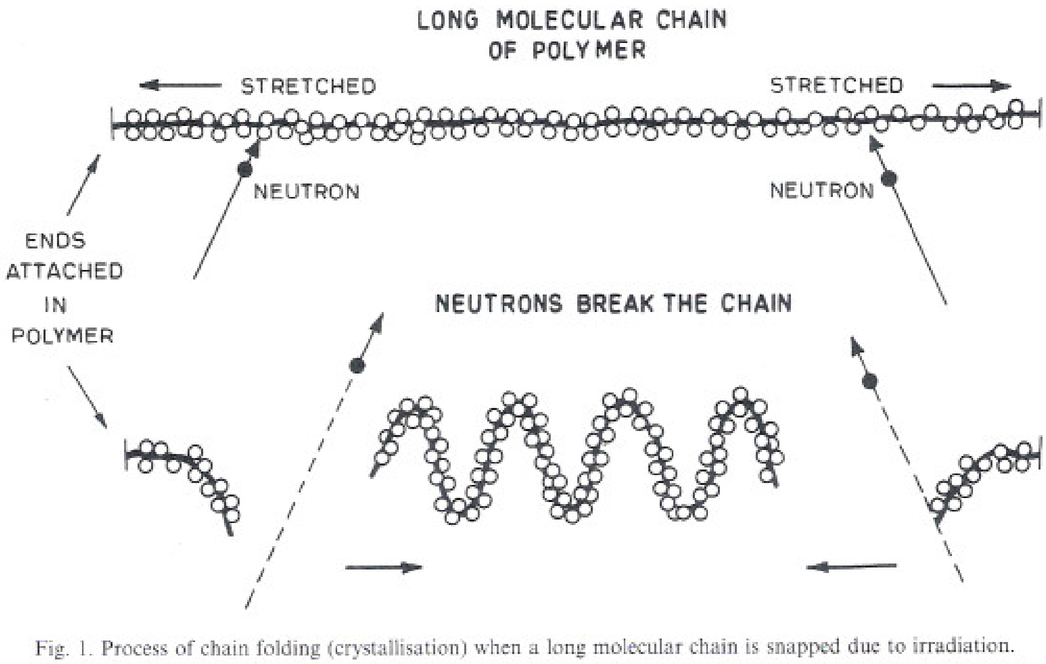


Fig. 1. Process of chain folding (crystallisation) when a long molecular chain is snapped due to irradiation.

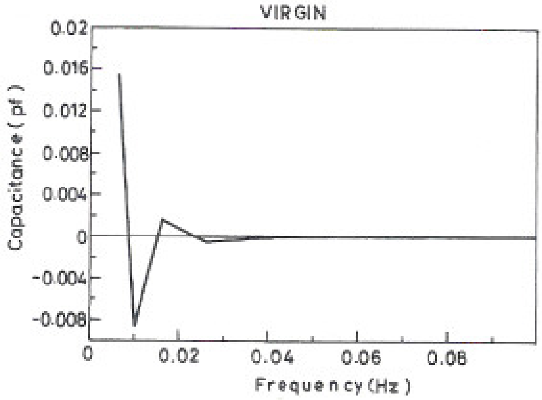


Fig. 2. Frequency response of the capacitor formed with a virgin sample of thick polyvinyl acetate (PVAc) film.

### 3.1. Capacitance measurements

Fig. 2 shows the frequency response of the capacitor formed with a virgin sample of 0.25 mm thick PVAc film. The variation at a frequency of 0.01 Hz shows a dip towards negative capacitance and then oscillates dampingly to stabilize at a positive value corresponding to the normal polymeric behaviour. The negative and oscillatory capacitance can be attributed to the polar characteristics of PVAc virgin sample. The existing residual electric dipoles in the sample under the influence of the alternating voltage signal at a frequency of 0.01 Hz are induced to oscillate at the applied voltage frequency. As the frequency is increased, the dipoles are not able to cope up with the applied alternating voltage frequency above a certain value, as shown in Fig. 2. Thereafter, they become stationary.

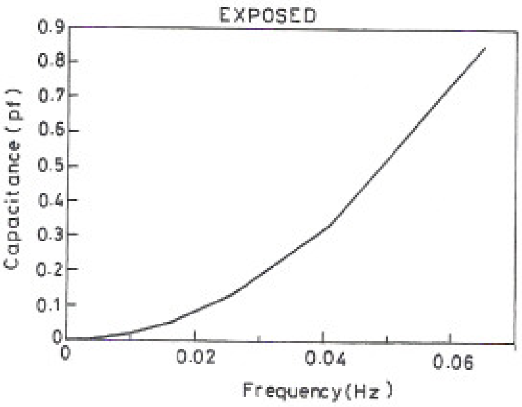


Fig. 3. Frequency response of the capacitor formed with an identically thick PVAc film exposed to 14.4 MeV neutrons for 4 h.

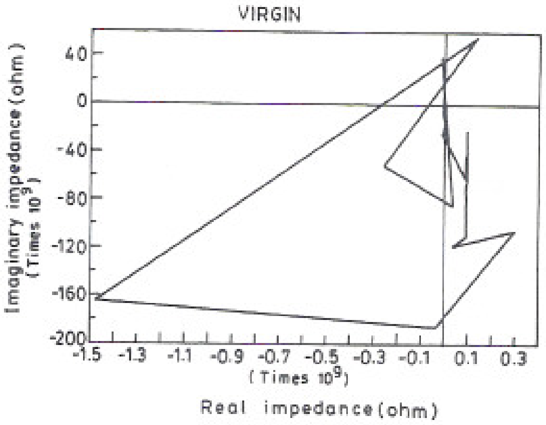


Fig. 4. Imaginary impedance vs. real impedance of the virgin PVAc sample in the sense of Cole–Cole representation.

When the above sample was exposed to neutrons for 4 h, the frequency response of the capacitor with the identically thick neutron-irradiated sample is shown in Fig. 3. One can see an exponential rise in capacitance with respect to the frequency. This variation in capacitance, i.e. that of the dielectric constant, is due to the inducement of V-centres in PVAc sample by neutron irradiation. V-centres or charge centres oscillate, giving rise to circulatory currents under the influence of applied voltage stress of nearly 2 mV across the electrodes between which the polymer was kept for the measurement of the frequency response of the capacitor. The positive charges being heavy, only vibrate slowly, whereas the free electrons generate circulatory currents. These circulatory currents develop inductive behaviour in the polymer dielectric, resulting in the increase of the capacitance as observed in Fig. 3.

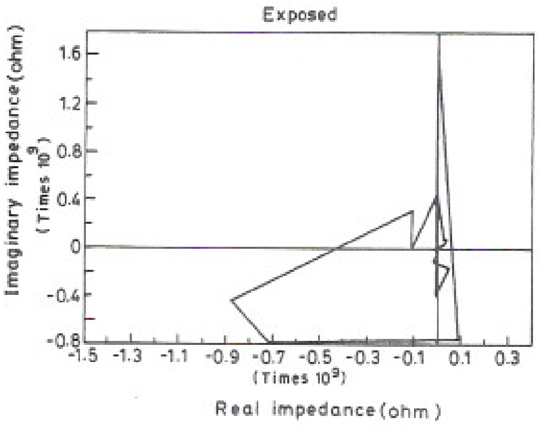


Fig. 5. The Cole–Cole representation of the 4 h neutron irradiated PVAc sample.

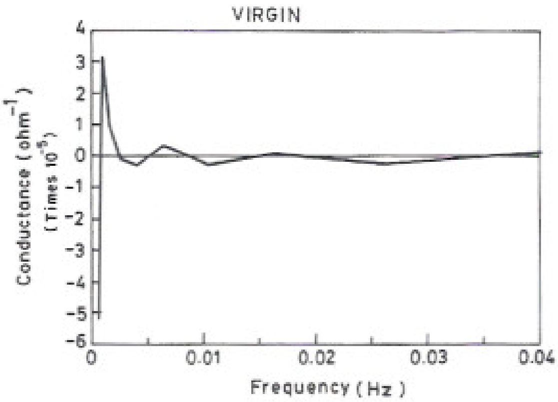


Fig. 6. Frequency response of the conductance of the virgin PVAc sample.

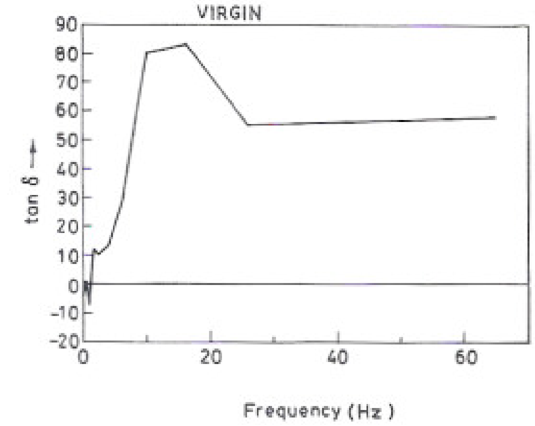


Fig. 8. Variation of tan $\delta$ of the virgin PVAc sample with frequency.

On plotting the imaginary impedance against the real impedance of the material in the sense of Cole–Cole representation (Cole and Cole, 1941; Macdonald, 1987), we find an interesting variation in Fig. 4, which indicates that the material used is highly dielectric. The same Cole representation of the 14.4 MeV neutron irradiated sample is shown in Fig. 5. The comparison of these two Cole plots shows that the magnitude of the Cole–Cole plot of the irradiated sample reduces by two order of magnitude, compared to that of the virgin sample. Reduction in the imaginary impedance leads to an increase in the dielectric constant of the material as a result of irradiation. The comparison also shows the change in the polarisability behaviour of the material.

Figs. 6 and 7 show the conductance–frequency response of the virgin and 4 h neutron irradiated samples. In both the cases, at extremely low frequencies, the conductance of the sample shows oscillatory behaviour due to the impressed oscillations of dipoles as discussed earlier. The variation in the conductance behaviour in the two cases also shows that there is a change in the conductance process after neutron irradiation.

Fig. 8 shows tan $\delta$ of the virgin sample plotted against the frequency which suggests that the relaxation frequency of the material is around 1.5 Hz, as the value of tan $\delta$ at about 1.5 Hz is 0. At this frequency, the signal can be communicated with minimum energy loss. Fig. 9 shows that after 4 h of neutron-irradiation, the relaxation frequency of the material has shifted to a higher value of about 15 Hz. The tan $\delta$ values are negative from 0 to 15 Hz which corresponds to inductive behaviour of the material as discussed earlier.

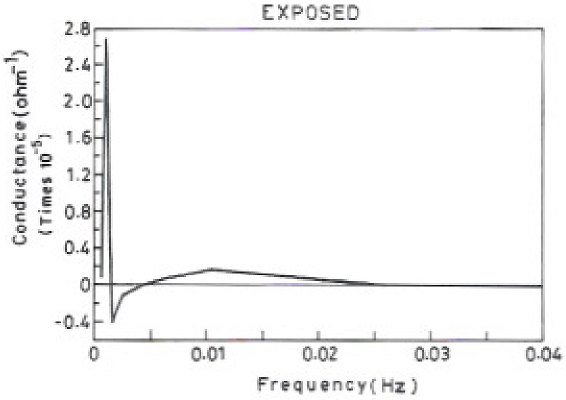


Fig. 7. Frequency response of the conductance of the 4 h neutron irradiated PVAc sample.

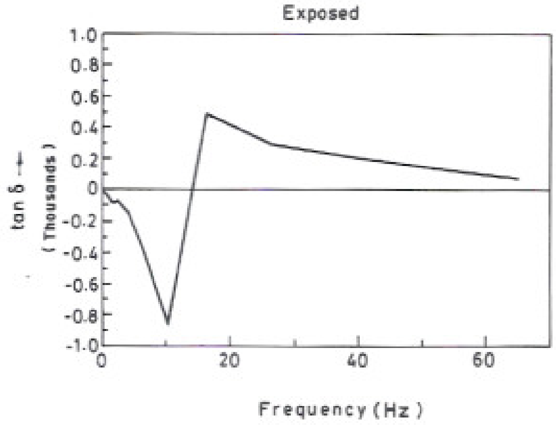


Fig. 9. Variation of tan $\delta$ of the 4 h neutron irradiated PVAc sample.

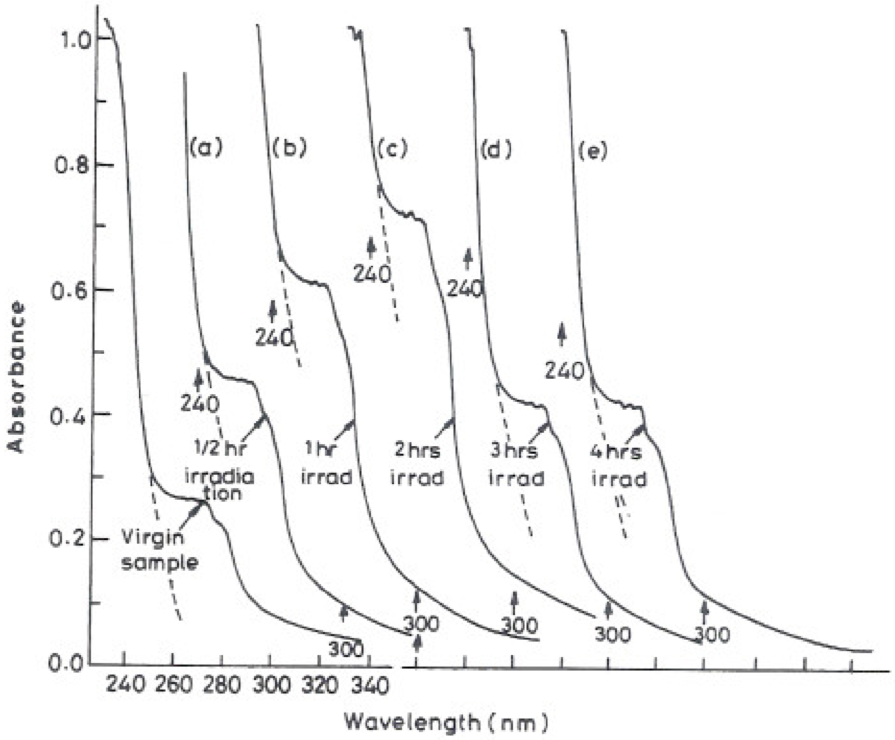


Fig. 10. Comparison of the UV-absorptive behaviour of the PVAc thick samples irradiated with different doses, with that of the virgin sample. The fluences of neutrons are (a) $3.6 \times 10^{10}$, (b) $7.2 \times 10^{10}$, (c) $14.4 \times 10^{10}$, (d) $21.6 \times 10^{10}$, and (e) $28.8 \times 10^{10}$ n/cm$^2$.

### 3.2. Spectrophotometry in the UV-range

The first curve in Fig. 10 shows the absorption behaviour of the thick virgin PVAc sample in the UV-range. The curves (a–e) of Fig. 10 display the variation of the UV absorption in PVAc sample due to neutron-irradiation dose. The UV absorption reduces initially from 90% to 46%, in the wavelength range 230–260 nm, followed by a flat region between 260 and 277 nm. Thereafter, the curve falls sharply for larger UV wavelengths.

A very interesting variation of the magnitude of the constant absorption region of the UV spectrum of identical samples irradiated for different time intervals is shown in Fig. 11, which has been derived from Fig. 10. The constant absorption region of the unirradiated sample is due to superposition of absorption and scattering of UV rays together. The initial rise of the curve suggests an increase in the crystallinity of the PVAc polymer with the time of irradiation. The newly generated crystalline regions (lamellas) may act as the scattering centres for the UV-rays and, consequently, increase the extinction of UV-rays by the scattering process.

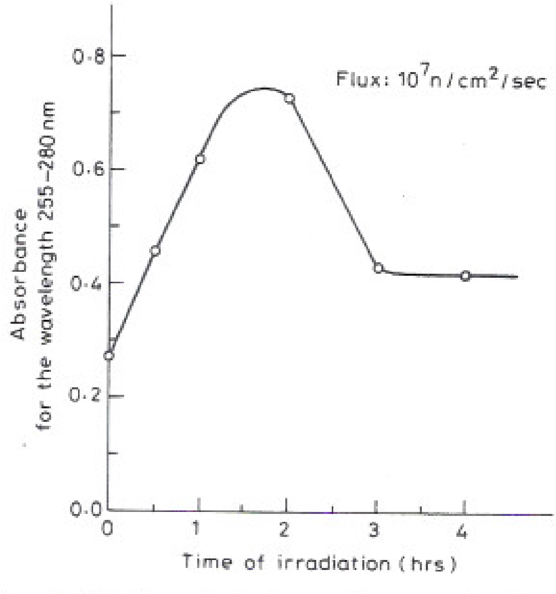


Fig. 11. Variation of absorbance with neutron-irradiation time, i.e. dose for the wavelength lying between 225 and 280 nm.

One can see, in Fig. 11, that the absorption falls after 2 h of neutron irradiation. This may be attributed to scissioning in the polymer due to irradiation, resulting in a permanent network of semi-crystalline polymer, i.e. the crystallinity of the polymer increases and stabilises at a higher level than that of the virgin sample. One can roughly estimate from Fig. 11 that there is nearly a 16% increase in the absorption. In Fig. 11, the absorbance (log $I_0/I$) is plotted on the linear scale from 0 to 1, i.e. from 0 to 90% absorption. The absorbance of the virgin sample is 0.26 or 46% and of the sample after 3 h of irradiation is 0.42, i.e. 62%. So the UV absorbance of the PVAc increases initially with neutron dose and then reduces and settles down at 0.42 (62%) or so. There is an increase in absorbance by 16% due to increase in the scattering losses from the increased number of smaller lamellas or smaller crystallites. In other words, the 16% increase in crystallinity causes increased absorption of UV-rays only through the scattering processes.

### 3.3. XRD spectra studies

To confirm the possibility of an increase of crystallinity in the PVAc sample as a result of neutron irradiation, the X-ray diffraction (XRD) spectra of these samples, i.e virgin and 4 h neutron-irradiated samples, were taken. The XRD spectrum of the virgin sample (Fig. 12(a)) shows that the sample is a semi-crystalline polymer. There are two peaks at angles $2\theta = 14°$ and 16.8°, respectively, superimposed on a wide diffused peak distribution of diffracted X-rays. Fig. 12(b) of the irradiated sample shows that there is a development of two new peaks at lower angles, 11° and 12.5°, in addition to the two original peaks at 14° and 16.8° with a considerable reduction in their intensities after 4 h of neutron irradiation of the PVAc sample. This indicates that bigger crystallites or lamellas are broken into smaller ones or destroyed. Even long molecular chains in the amorphous region, after being broken at two places, as explained earlier, create new smaller crystallites or lamellas. Development of new peaks indicates that there is a recrystallisation of the sample. Comparison of full width at half maxima (FWHM) of the original crystalline peaks of the virgin sample with that of the irradiated one, suggests that bigger lamellas (crystallites) are breaking into smaller ones.

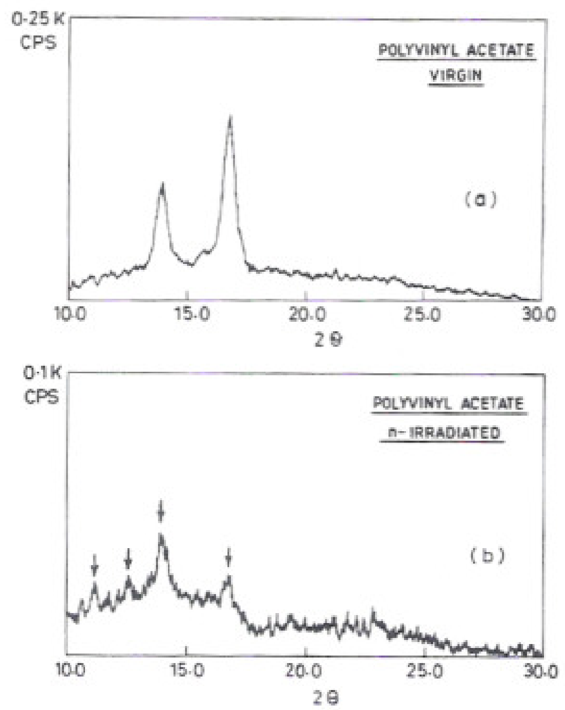


Fig. 12. X-ray diffraction spectrum of (a) virgin and (b) 4 h neutron-irradiated PVAc samples.

## 4. Conclusion

The 14.4 MeV neutron irradiation of PVAc film induces crystallinity as well as V-centres in the samples. As a result, there is a change in polarisability of the sample resulting in the increase of its dielectric constant. This fact is confirmed by the plots of the imaginary vs. real impedances of the virgin and irradiated samples, showing a change in polarisabilities. The UV spectrum of the sample confirms the increase in the crystallinity of the sample, which is also confirmed by the XRD spectra.

## Acknowledgements

The authors are grateful to Prof. S. Chandra for providing the Solartron equipment for capacitance measurements of the sample capacitors. The help in the measurement of UV-spectra of the sample using Cary 2390 UV–Vis–IR Spectrophotometer rendered by Mr. Bipin Srivastava, Department of Chemistry of Banaras Hindu University, Varanasi is gratefully acknowledged.

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