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Optical and electrical properties of some electron and proton irradiated polymers

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Abstract

Ion beam treatment studies have been carried out to investigate the potential for improvements in conductivity properties of the polymers Polytetrafluroethylene (PTFE), Polyimide (PI), Polyethyleneterepthalate (PET) and Polypropylene (PP), after 2 MeV electron and 62 MeV proton irradiation. The shift in optical absorption edges as observed by UV–VIS spectra of the irradiated polymers has been correlated to the optical band-gap using Tauc's expression. A decrease in the optical band-gap has been observed in irradiated PP and PTFE, but no considerable change was found for the optical band-gaps of PET and PI. Further AC conductivity measurements confirmed an increase in conductivity in electron irradiated PP. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

From the start of their commercial use at the turn of the century, and their intellectual recognition in the 1930s, polymeric materials have been the subject of immense commercial and scientific interest. The application of radiation in polymer technology is of great importance with a view to achieve some desired improvements in polymer properties.

The optical absorption method provides information regarding the optically induced transitions and the variation in energy band-gap after irradiation. The polymer irradiation leads to a shift in the optical absorption edges, which indicates a lowering of the energy gap. The decrease in energy band-gap which implies an increase in conductivity of the irradiated polymers might be due to the

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formation of clusters with rings, or due to the formation of conjugated double bonds or quinonic structures [1].

Electron spin resonance measurements reveal that in irradiated polymers, there exists a high density of unpaired spins, localised deeply in the band-gap which shows up when degassing of light volatile components is completed. Therefore, one might speculate that the clusters are conjugated π-bonded carbonaceous inclusions [2]. Emission of low mass carbon cluster ions such as C_2^+ or C_3^+ is a common event in electronic sputtering of most organic compounds [3]. The carbon cluster formation depends on the original chemical configuration of the targets. For e.g. polytetrafluoroethylene (PTFE), PS and PE targets, the yield of C_n^+ $(1 < n < 30)$ is very low, but it is relatively high for PVDF and PVDC [4,5]. The detection of C_{60} and C_{70} fullerenes in the bulk of carbon containing materials after a high dose irradiation with very fast heavy ions (i.e., for very high deposited energy densities) has also been reported [6]. The formation of fullerenes is a remarkable example of the fast chemistry occurring in the wake of a fast ion.

Earlier, some of us [7] studied the damage of polyvinylalcohol (PVA) by 16 MeV electrons and found that for the same transferred energy density, energetic electrons were slightly less efficient in the polymer damage than the energetic ions. Though the cluster growth rate with transferred energy density was found to be nearly the same for ion irradiated and electron irradiated polymers, the threshold energy density for cluster formation by electron irradiation was found to be higher by about one order of magnitude in comparison to light and medium heavy ions, and about two orders of magnitude higher in comparison to heavy ions.

Infra-red and UV–VIS spectra reveal that ion implantation in polymers results in the breakage of molecular chains, creation of double bonds and oxidation which is connected to the formation of carbonyl groups. The increase in the electrical conductivity is essentially caused by the increase of concentration of conjugated double bonds [8] which promote the motion of charge carriers along the polymeric chains. Charge carrier transition from one molecule to the other takes place via electron hopping or even tunneling processes.

In the present work, we have studied the effect of 2 MeV electron and 62 MeV proton impact onto Polypropylene (PP), Polyethylene terephthalate (PET), Polyimide (PI) and PTFE by means of UV–VIS spectroscopy and AC conductivity measurements. As the electron and proton irradiation doses used by us are in a comparable order of magnitude (differing by no more than 20%), a rough comparison of the two radiative effects appears to be possible. Taking into account the about 20 times lower deposited energy density of the 2 MeV electron beam in comparison to the 62 MeV proton beam, this signified a correspondingly higher electron fluence during the irradiations.

2. Experimental aspects

2.1. Preparation of the targets

Pieces of each PTFE (composition: C_2F_4, density: 2.2 g cm^{-3}), PI (composition: $C_{22}H_{18}O_5N_2$, density: 1.42 g cm^{-3}), PP (composition: C_3H_6, density: 0.9 g cm^{-3}) and PET (composition: $C_{10}H_8O_4$, density: 1.41 g cm^{-3}) of sizes (2 × 2) cm^2 were cut from commercially available sheets. The thicknesses of the polymer foils were measured by a Heidenhain device within an accuracy of ±0.1 μm. They were found to be 200, 8, 10 and 13 μm for PTFE, PP, PI and PET, respectively. They were washed thoroughly with soap solution and then with deionised water. The cleaned samples were then dried inside a vacuum desiccator. A polymer stack was prepared of the above mentioned polymers, and covered at both ends by methylene blue-doped (PVA) foils. This target assembly was then taken for electron irradiation.

Similarly, (1 cm × 1 cm) large foils of PTFE (200 μm), PI (50 μm), PP (8 μm) and PET (13 μm) were cut, cleaned and dried. Target stacks these foils were prepared and covered at both ends by PVA foils. This target assembly was then taken for proton irradiation.

The PVA foils were used for dose control and to check the uniformity of the impinging beam [11,12].

2.2. Irradiation

The irradiation of the first target stack was done by a 2 MeV electron beam from the electron generator of the Ion Beam Laboratory "ISL" at the Hahn-Meitner Institute (HMI), Berlin. The electron beam was allowed to pass through a collimator and to fall on the target stack placed perpendicularly, at a distance of 2 m from the collimator. The dose of the 2 MeV electron beam was 10 Mrad. The beam size was bigger than (2 cm × 2 cm), hence it covered the whole target area homogeneously.

The second target stack was irradiated by 62 MeV protons from the heavy ion accelerator of the ISL (HMI Berlin), up to 8 Mrad dose. The collimated proton beam was allowed to fall perpendicularly onto the target stack. As the beam size was (0.3 cm × 1 cm) in this case, the target stack was adjusted in such a way that the proton beam passed through the centre of the stack perpendicularly, which was indicated by decolorisation of the methylene blue dopant of the PVA foils at that particular area.

Whereas the electron irradiation took place at ambient air conditions, the proton irradiation took place at high vacuum (around 10^{-7} torr). In both cases, the target temperature during the irradiation hardly exceeded some 30°C during the irradiations as was found out by a thermocouple connected to the samples. The irradiated target stacks were stored for about 24 hours in an exsiccator to allow induced radioactivity to fall below the safe limits of handling. The samples were then separated, marked and preserved in plastic boxes within an exsiccator.

2.3. UV–VIS spectrometry

Prior to spectral analysis, all the samples were washed with luke-warm water in order to have a clear surface. For the study reported here, only one foil of each stack (the first one) was used; the other ones will be subject to different examinations, to be reported at another occasion.

UV–VIS spectroscopy of the first foil of the irradiated sample stacks each were done by a Beckman DU-650 spectrophotometer. All the spectra were taken with the pristine one as reference. The scanning speed of the apparatus was 1200 nm min^{-1} and the scanning wavelength region was 200–800 nm. The wavelength range of the absorption edges was found to be within 200–345 nm for PTFE, 400–550 nm for PI, 300–330 nm for PET and 200–255 nm for PP. The shift in absorption edges from UV to the visible region under irradiation was correlated with the optical band gap E_g according to Tauc's expression [9],

$$\omega^2 \varepsilon_2(\lambda) = (\hbar\omega - E_g)^2, \quad (1)$$

where $\varepsilon_2(\lambda)$ is the optical absorbance and λ is the wavelength. The intersection of the extrapolated spectrum with the abscissa of the plot $\varepsilon_2^{1/2}/\lambda$ versus $1/\lambda$ yields the gap wavelength λ_g from which the energy gap is derived as

$$E_g = hc/\lambda_g. \quad (2)$$

Thus, this optical absorption method was used for investigating the optically induced transitions and for providing information about the band structure and energy gap in crystalline and non-crystalline materials [10].

The error in the measurement of the thickness of the foils is of the order of ±0.1 μm. For determining the wavelength gap, the best linear fit of the points on the curve $\varepsilon_2^{1/2}/\lambda$ versus λ^{-1} was always performed. Taking into account the accuracy of that fit, the extrapolation towards the band-gap wavelength λ_g is possible within an error not exceeding a few % in case of PP and PET, and within around ±10% in case of PI and PTFE. This corresponds to a maximum possible error in the energy band-gap determinations of ±0.1 eV.

2.4. AC Conductivity measurement

As a second part of the experiment, we had performed AC conductivity measurements of electron irradiated PP along with the virgin sample by a low frequency (LF) impedance analyser.

The 2 MeV electron irradiated polypropylene samples of size (1 × 1) cm^2 were cut and cleaned. Silver paste was then applied to contact the polymers. As the silver particles of the silver paste have diameters of typically 1 μm, they stick to the sample surface only, so that there is no fear that the silver might influence the conductivity by interaction with the polymer.

The AC conductivity set-up comprised of a stainless steel chamber, a Hewlett Packard LF Impedance analyser, and a Lake Shore 340 Temperature controller.

The steel chamber consisted of a sample holder, connected to a heater coil, and two platinum resistance thermometers. Two platinum resistance thermometers were connected, one near the heater coil and the other near the sample to see the temperature difference.

For our measurements with the LF Impedance Analyser, we chose a frequency range from 50 kHz to 5 MHz. These frequencies are said to be stable within ca. $\pm 5 \times 10^{-5}$ at operating temperatures between 0°C and 55°C. In our case, the ambient temperature was 40°C, and the relative humidity was less than or equal to 95%.

The Lake Shore 340 temperature controller is needed to maintain a constant temperature of both the heater and the sample. Both the impedance analyser and the temperature controller are connected to the stainless steel chamber.

3. Results and discussion

Vinyl polymers having hydrogen atom substituents $(\text{–H}_2\text{C–CH}_2\text{–})_n$ or $(\text{–H}_2\text{C–CRH–})_n$ – e.g., polypropylene – undergo dominant homolytic rupture of the C–H bonds to form hydrogen-free radicals which crosslink with each other. With increasing dose, the degree of crosslinking increases [13]. The formation of free radicals decreases the energy band-gap from 5.2 eV in case of the virgin polymer to 4.9 and 5.0 eV for electron and proton irradiated polypropylene, respectively, as shown in Table 1. The UV–VIS spectra for irradiated PP along with the pristine one are shown in Fig. 1. Whereas the electron irradiation leads to an increase in absorbance for all wavelengths, the proton irradiation is seen to increase the absorbance only for the lowest wavelengths.

PTFE, a polymer with high temperature resistivity [14], undergoes radiative degradation which involves initial excitation and bond rupture, followed by free radical formation in presence of oxygen. The UV–VIS spectra of irradiated PTFE along with the unirradiated one are shown in Fig. 2. One sees that electron irradiation leads to a

Table 1
The values obtained by Tauc's plot clearly showing the variation in E_g (eV) after irradiation[a]

Polymer	E_g (eV)		
	Pristine	Electron exposed	Proton exposed
PP	5.2	4.9	5.0
PET	3.8	3.9	3.9
PTFE	1.5	0.7	1.13
PI, 10 μm	2.30	2.27	Not measured
PI, 50 μm	2.23	Not measured	2.21

[a] The accuracy of the E_g determinations is better than ±0.1 eV.

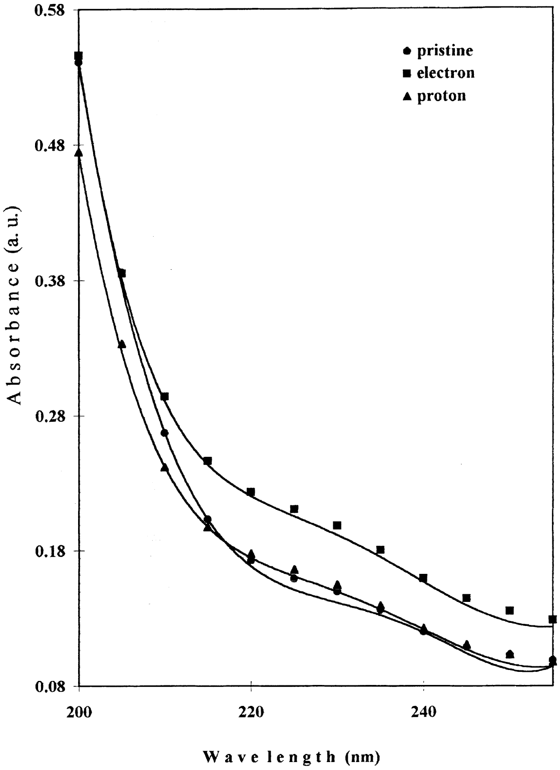

Fig. 1. UV–VIS spectrum of irradiated along with virgin PP. Electron irradiation: 2 MeV, 10 Mrad, proton irradiation: 62 MeV, 10 Mrad. Absorbance in arbitrary units.

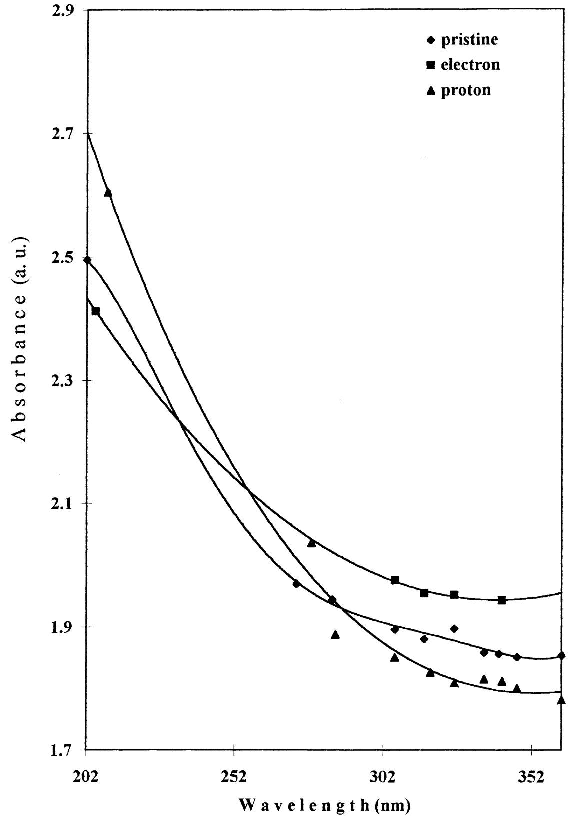

Fig. 2. UV–VIS spectrum of irradiated along with virgin PTFE. Electron irradiation: 2 MeV, 10 Mrad, proton irradiation: 62 MeV, 10 Mrad. Absorbance in arbitrary units.

decrease in absorbance at low, and to an increase in absorbance at higher wavelengths, whereas proton irradiation behaves just oppositely. These differences exceed well the measuring accuracy, and hence cannot be discarded as an artefact. At present we do not yet have any explanation for this finding. The band-gap for virgin PTFE was found to be 1.5 eV, which reduced to 0.7 eV after electron irradiation and to 1.13 eV after proton irradiation.

It was observed that in PET, even at the highest applied dose, the aromatic rings are not destroyed, but undergo a modification from di-substituted to mono-substituted benzene groups [14]. The presence of aromatic groups in repeating units of a polymer accounts for radiation stability. Consequently, no considerable change in energy gap is observed by us in irradiated PET, see Table 1.

The optical band-gap of pristine PI does not change upon prolonged exposure to sunlight [1,16,17]. The same holds for its exposure to energetic electrons, as was observed after 10 min of 16 MeV electron irradiation at 14 mA at irradiation temperatures of up to 140°C [1]. The presence of imide and aromatic rings in the structure of polyimides is the reason for the improved heat resistance and stability to ionising radiations [15]. In fact, in the present study, we reconfirmed that the E_g of PI foils did not change within the experimental errors after both electron and proton irradiations, see Table 1.

Comparing the irradiation effects of both electrons and protons with each other in Table 1 and Figs. 1 and 2, and correcting for the 20% difference in irradiation doses of our electron and proton irradiations (10 and 8 Mrad, respectively), we find that in all cases the electron irradiation is slightly more efficient in damaging the polymers than is the

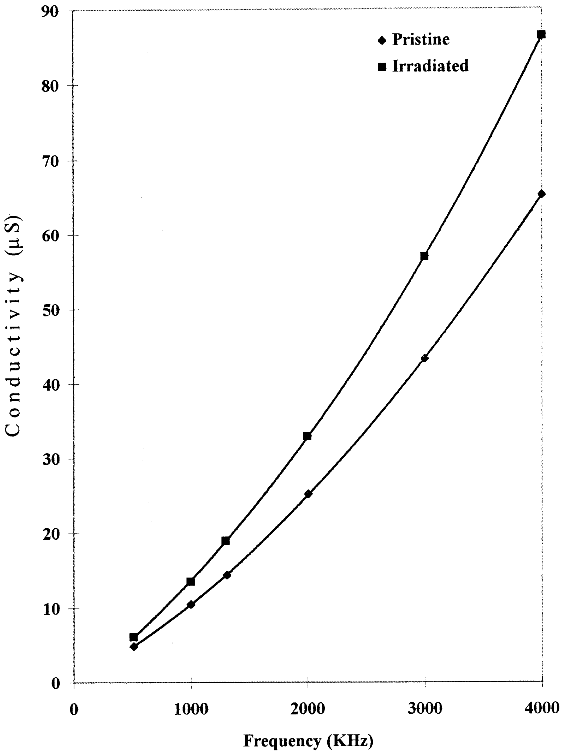

Fig. 3. AC conductivity plot for pristine and electron irradiated (2 MeV, 10 Mrad) PP.

proton irradiation. Interestingly, this contrasts to our earlier findings of PVA irradiation [7], for a yet unknown reason.

The AC conductivity measurements were performed for 2 MeV electron irradiated PP as well as for unirradiated PP. An increase in conductivity of the irradiated polymer showed up, which is attributed to the formation of conjugated double bonds [8], the later ones promoting the delocalization of charge carriers, and hence their motion in an applied external electric field. Fig. 3 shows that an increase in the frequency leads to an increase in conductivity, due to a gradual approach towards the resonance frequency of the charge carriers along the polymeric chains.

4. Conclusion

2 MeV electron and 62 MeV proton irradiation have led to a decrease in energy band-gap in PTFE and PP, whereas no considerable change in band-gap was observed in PET and PI for the given irradiation doses of 8 to 10 Mrad. However, for higher doses, a decrease in the energy band-gap is also expected for PET and PI. This is the subject of our presently ongoing study which will be reported later elsewhere. The increase in conductivity of electron irradiated PP has been confirmed by AC conductivity measurements.

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