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Opto-structural characterization of proton (3 MeV) irradiated polycarbonate and polystyrene

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Abstract

Polycarbonate (Makrofol-N) and polystyrene thin films were irradiated with protons (3 MeV) under vacuum at room temperature with the fluence ranging from 1×10^{14} to 1×10^{15} protons cm^{-2}. The change in optical properties, degradation of the functional groups and crystallinity of the proton-irradiated polymers were investigated with UV–vis, Fourier-transform infrared (FTIR) and X-ray diffraction (XRD) techniques, respectively. The UV–vis analysis revealed that the optical band gap of irradiated Makrofol-N is reduced by 30% as compared to 27.5% in polystyrene at highest fluence of 1×10^{15} protons cm^{-2}, owing to higher electronic energy loss of protons in Makrofol-N. The calculations of the number of carbon atoms per conjugation length, N and number of carbon atoms per clusters, M embedded in the network of polymers further revealed that Makrofol-N is more modified as compared to polystyrene on proton irradiation. FTIR results reveal the reduction in absorption intensity of the main characteristic bands of both the polymers after irradiation. The proton-irradiated Makrofol-N shows a strong decrease of almost all of its characteristic absorption bands at about 1×10^{14} protons cm^{-2}. Beyond a critical dose an increase of almost all its characteristic bands are noticed, however, no such effect had been observed in polystyrene at this particular fluence. Appearance of new –OH groups was observed at the higher fluences in the FTIR spectra of both proton-irradiated polymers. XRD measurements show the decrease of the main peak intensity and the crystallite size, confirming the increase of amorphization in polymers under irradiation.

Keywords: Makrofol-N; Polycarbonate; Polystyrene; Electronic energy loss; Carbon clusters; Crystallite size

1. Introduction

Ion irradiation can be used to change the physical properties of thin films in a controlled way or to modify the near-surface characteristics of a bulk polymer (Calcagno et al., 1992). There are several applications of ion-irradiated polymer such as microelectronics, biosensors production technologies, etc. (Leontyev et al., 1992).

Dramatic changes in the radiation-induced damage processes may occur if swift heavy ion irradiations are performed, instead of classical-condition irradiations such as electron beams or γ-rays. The reason is the very high value of the electronic stopping power of the ions, $(\mathrm{d}E/\mathrm{d}x)_e$, which induces an unusual density of electron–hole pairs close to the ion path. The mechanism of the interaction between protons and polymers is rather complicated. Many processes, such as the production of primary and secondary radicals, lead to the formation of double bonds and transformation of C–C bonds, and autooxidation occurs in the presence of oxygen. These reactions depend on the proton dose as well as on the environmental conditions during and after irradiations. Both cross-linking and degradation take place during irradiation and are closely related to the irradiation dose. Irradiation of 62 MeV protons on polypropylene and polytetrafluoro ethylene showed a decrease in their optical band gap, whereas no effect on the optical properties was observed in polyethylene terephthalate and polyimide (Mishra et al., 2000). The study of solubility changes for poly (methyl methacrylate) as a function of fluence of 1.5 MeV protons has been reported (Lee, 1999). The dose-dependent modification of polyallyl diglycol carbonate (PADC) by 62 MeV proton irradiation has been studied

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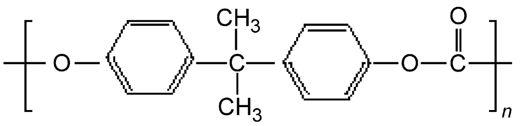
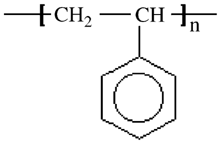
(Tripathy et al., 2001) and it was found that the crystallinity and the thermal stability of the polymer decreased as a function of dose, whereas there was no change in the optical band gap of the polymer.

In the present work, opto-structural characterization brought about by 3 MeV protons in the Makrofol-N polycarbonate and polystyrene is investigated. Makrofol-N is a bisphenol-A polycarbonate. It is light yellow in color, having high compact strength and wide applications. Polycarbonates are usually those polymers in which dihydric or polyhydric phenols are joined through carbonate linkages. The structure of the Makrofol-N polycarbonate is given as:



Polystyrene is one of the most stable organic polymers, which has made up a broad class of lightweight structural materials important in the automotive, aerospace and construction industries. The structure of the polymer-repeating unit can be represented as:



The presence of the phenyl (C_6H_5) groups is the key to the properties of these polymers. These large rings prevent the polymer chains from packing into close, crystalline arrangements. In addition, the phenyl rings restrict rotation of the chains around the carbon–carbon bonds, thus lending the polymer its noted rigidity.

2. Experimental procedure

Makrofol-N polycarbonate (100 μm) and polystyrene (125 μm) in the form of flat polished films manufactured by a castic process were procured from Good Fellow Ltd. (UK). Without any further treatment, the samples of the size ($1 \times 1\,\text{cm}^2$) were irradiated with proton (3 MeV) beam available from the Cyclotron facility, at Punjab University Chandigarh, India. A vacuum of the order of $\sim 4 \times 10^{-6}$ Torr was maintained during the irradiation. The beam current was kept low to suppress thermal decomposition and was monitored intermittently with a Faraday cup. The range of proton (3 MeV) was found to be more than the thickness of both the samples, as determined by SRIM 2003, i.e. 128.75 μm for Makrofol-N and 142.74 μm for the case of polystyrene (Zeigler, 2004). Three techniques have been employed to study the optical and structural degradation of proton-irradiated polycarbonate and polystyrene samples. The samples were analyzed with UV–vis spectroscopy in transmission mode using Hitachi Modal U-3000 spectrophotometer in the range 200–800 nm to observe the variation in optical band gap (E_g). The chemical changes were studied using Nexus 870 Fourier-transform infrared (FTIR) Spectrometer in the range 4000–500 cm^{-1}. The X-ray diffraction (XRD) patterns were recorded using the Cu K_α ($\lambda = 1.54\,\text{Å}$) radiation in θ–θ locked couple mode from the Brukar AXS D8 diffractometer with scan speed of $1^\circ\,\text{min}^{-1}$. The diffraction angle (2θ) has been varied from 5° to 45° with a step size of 0.02°. The measurements were done under ambient pressure conditions at room temperature. Each experiment was repeated at least twice and with both faces of the specimens alternatively exposed to the X-rays to check the reproducibility.

3. Results and discussion

3.1. UV–vis analysis

The UV–vis spectra of Makrofol-N and polystyrene irradiated with protons (3 MeV) with the fluence ranging from 1×10^{14} to 1×10^{15} protons cm^{-2}, respectively, are presented in Fig. 1(a and b). The spectra reveal a strong absorption at 260 nm for all irradiated samples. The intensity of this band increases with the increase of proton fluence. Generally, the large modification in the appearance of the polymer spectra corresponds to the strongest chemical changes. A shift in the absorption edge towards longer wavelength is observed for irradiated samples. This behavior is generally interpreted as caused by the formation of extended systems of conjugated bonds i.e. possible formation of carbon clusters. In the investigated range of wavelengths the absorption bands are associated to the π–π^* electronic transitions (Calcagno et al., 1992). These types of transitions occur in the unsaturated centers of the molecules i.e. in compounds containing double or triple bonds and also in aromatics. The excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelengths.

In the high absorption region (where absorption is associated with interband transitions), the absorption coefficient $\alpha(v)$ was given in quadratic form by Tauc (1974),

$$\alpha(v) = \frac{B_\alpha (hv - E_g)^n}{hv}, \tag{1}$$

where B_α is a constant, E_g is the optical band gap, $\alpha(v)$ is the absorption coefficient at a frequency of v and n is an index which can assume values of 0.5 for allowed direct transitions, 1.5 for direct forbidden transitions, 2 for allowed indirect transitions and 3 for forbidden indirect transitions. We are using $n = 2$, which is valid for the materials having α greater than $10^4\,\text{cm}^{-1}$ (Tauc, 1974). The value of E_g in any organic material obtained by plotting $(\alpha hv)^{1/2}$ versus hv and extrapolating the linear region of the plot $(\alpha hv)^{1/2}$ to zero, is used to define the so-called optical band gap, E_g, in polymers.

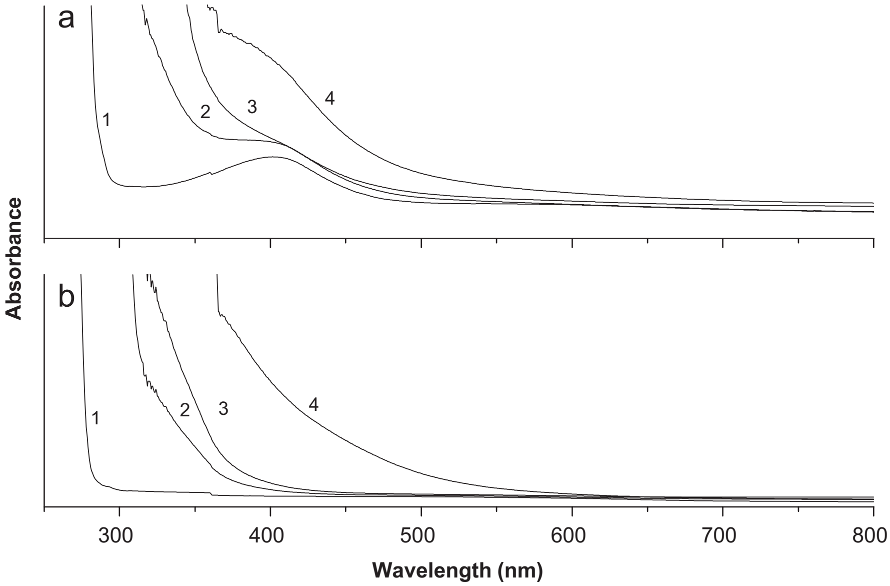


Fig. 1. UV–vis spectra of proton (3 MeV) irradiated: Makrofol-N at fluence (1) 0, (2) 1.0 $\times 10^{14}$, (3) 3.0×10^{14} and (4) 1.0×10^{15} protons cm^{-2}. Polystyrene at fluence (1) 0, (2) 1.0 $\times 10^{14}$, (3) 3.0×10^{14} and (4) 1.0 $\times 10^{15}$ protons cm^{-2}.

Table 1
The variation of band gap, transferred energy density, the number of carbon atoms per conjugation length (N) and the number of carbon atoms in the cluster (M) with the increase of proton fluence

Polymer	Fluence (protons cm^{-2})	Energy density (eV Å^{-3})	Band gap (eV)	N	M
Makrofol-N	0	0	4.31	~4	~63
	1.0×10^{14}	1.22×10^{-2}	3.24	~5	~112
	3.0×10^{14}	3.66×10^{-2}	3.06	~6	~126
	1.0×10^{15}	1.22×10^{-1}	3.02	~6	~129
Polystyrene	0	0	4.36	~4	~62
	1.0×10^{14}	1.37×10^{-2}	3.78	~5	~82
	3.0×10^{14}	4.11×10^{-2}	3.24	~5	~112
	1.0×10^{15}	1.37×10^{-15}	3.15	~6	~119

The values of E_g for virgin as well as irradiated samples are presented in Table 1. It is found that there is a decreasing trend of energy gap with the increase of proton fluence. It is observed that in Makrofol-N, proton has induced more change in optical band gap, i.e., 30% as compared to 27.5% in polystyrene, at the highest fluence of 1×10^{15} proton cm^{-2}. This can be attributed to the reason that at proton beam has more electronic energy loss in Makrofol-N i.e. 1.371 eV Å^{-1} as compared to 1.226 eV Å^{-1} in polystyrene.

For a linear structure, the number of carbon atoms per conjugation length, N, is given by (Wang et al., 1997),

$$N = \frac{2\beta\pi}{E_g}, \tag{2}$$

where $\pi = 3.14$ and 2β give the band structure energy of a pair of adjacent π sites. The value of β is taken to be 2.9 eV as it is associated with π–π* optical transitions in –C=C– structure. A shift of the absorption edge can be attributed to an increase of the conjugation length. The variation of number of carbon atom per conjugation length with the transferred energy density, obtained by relation (fluence × stopping power) can be seen in Fig 2. In both polymers, the number of carbon atom per conjugation length has increased up to 6 at the highest fluence of 1×10^{15} protons cm^{-2}. The increase of unsaturated conjugation length in both polymers results in the darkening of their colors, i.e., Makrofol turns yellow to dark brown and polystyrene turns transparent to brown at the fluence of 1×10^{15} protons cm^{-2}. Radiation can induce the formation of unsaturated bonds in polymers and these contribute to coloration since, as a rule, conjugated double bonds are responsible for the color of most organic compounds (Pardo et al., 1998).

The number of carbon hexagon rings (R) in the cluster can be calculated from the Robertson's relation (Robertson and O'Reilly, 1987):

$$E_g \approx \frac{2|\beta|}{\sqrt{R}}, \tag{3}$$

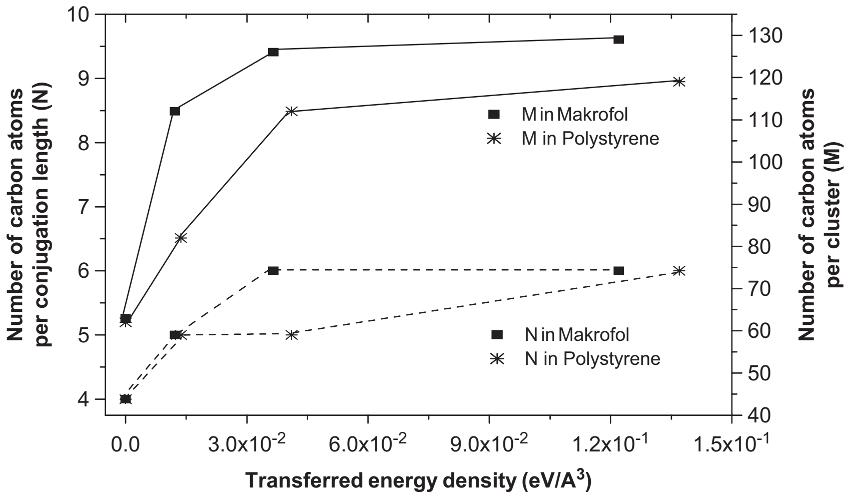


Fig. 2. The variation of number of carbon atoms per conjugation length (*N*) and number of carbon atoms per cluster (*M*) as a function of mean transferred energy density.

where 2β is the band structure energy of a pair of adjacent π sites and β is–2.9 eV for a six-membered carbon ring. Fink et al. (1995) showed that the Robertson equation underestimates the cluster size in irradiated polymers. Therefore, they assumed the structure of the clusters to be like a buckminsterfullerene, that is, a C_{60} ring instead of C_6, arriving at the following relation:

$$E \approx \frac{34.3}{\sqrt{M}}. \quad (4)$$

We have used this equation to obtain the number of carbon atoms per cluster (*M*) in the proton-irradiated Makrofol-N and polystyrene. The cluster size for the proton-irradiated Makrofol-N is found to lie between 63 and 129 atoms, while it lies between 62 and 119 atoms for polystyrene. The cluster size in the pristine polymer corresponds to the grain structure of the polymer due to the complexity of its monomeric units. The variation of cluster size with the transferred energy density can also be seen in Fig. 2. We find here that the cluster size increases with transferred energy density for both polymers on proton irradiation. However, the cluster size of Makrofol-N is found to be larger as compared to that of polystyrene.

It is also observed from Table 1 and Fig. 2 that the band gaps and parameters derived from them i.e. *N* and *M*, has reached a constant value with increasing fluence or energy density, which may be due to the overlapping of tracks at higher fluences.

3.2. FTIR analysis

The energy transferred to the molecules of the polymer under irradiation results in the breaking of chemical bonds and may also result in the recombination of molecular fragments to form new molecular bonds. These two different processes are found to be dependent on the irradiation dose. The FTIR spectra of the pristine and proton (3 MeV) irradiated Makrofol-N is depicted in Fig. 3. A strong decrease of all absorption bands is observed at the fluence 1×10^{14} protons cm^{-2}. Beyond a critical dose an increase in intensity of almost all its characteristic bands is noticed. This behavior of proton-irradiated Makrofol-N is attributed to the scissoring of bonds taking place at lower fluence and cross-linking at higher fluence. Our results are in well agreement with the previous results (Salah et al., 1998). On the other hand, the first phenomenon observed from the FTIR spectra of proton-irradiated polystyrene (Fig. 4) is the reduction in absorption intensity of all its characteristic bands, at the highest fluence of 1×10^{15} protons cm^{-2}. It is interesting to note that in proton-irradiated polystyrene no particular dose is found beyond which absorption intensity of all characteristic bands starts increasing (as in the case of proton-irradiated Makrofol-N).

The appearance of new band after irradiation is an important feature of heavy ion-irradiated polymers. It can be seen in Figs. 3 and 4 that a new peak appears at 3500 cm^{-1} in proton-irradiated Makrofol-N as well as in polystyrene, which is assigned to –OH group. The –OH group might have been formed due to the reaction of the polycarbonate and polystyrene with atmospheric oxygen/H_2O (moisture). The reaction might have taken place in the chamber during irradiation, as the vacuum of few micro-torr is not sufficient to remove all the oxygen/H_2O (moisture) contents. In addition to this post-irradiation factor is also a probable reason for the formation of such bonds. Similar results have been reported in case of other heavy ion-irradiated polymers (Singh et al., 2007). In polystyrene, $C{=}O$ group is also observed to form at around 1725 cm^{-1}, at the highest fluence of 1×10^{15} protons cm^{-2}.

It is also observed from Figs. 3 and 4 that the formation of –OH group is more in Makrofol-N as compared to polystyrene after irradiation. This shows that in

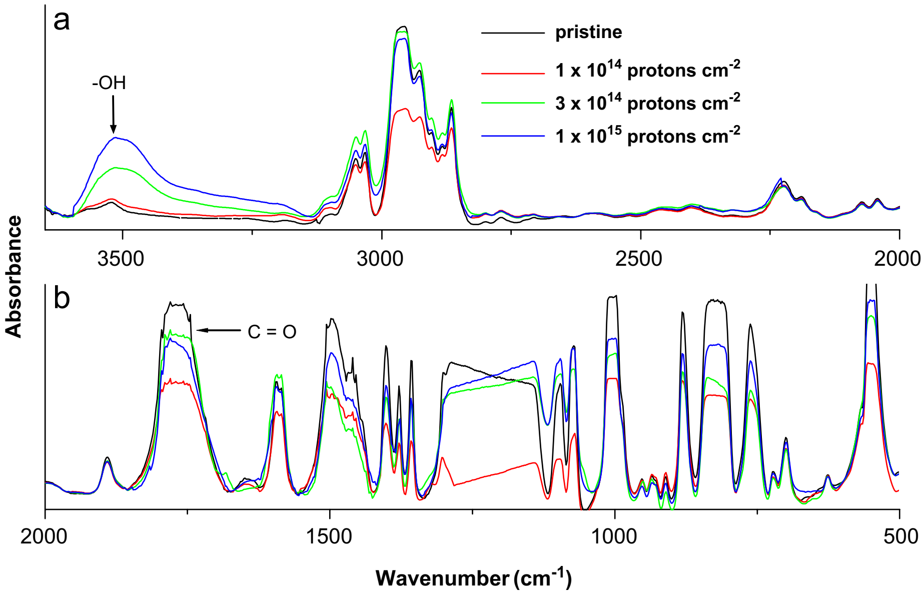


Fig. 3. FTIR spectra of Makrofol-N irradiated with 3 MeV protons. (a) ranges from 2000 to 3700 cm^{-1} and (b) ranges from 500 to 2000 cm^{-1}.

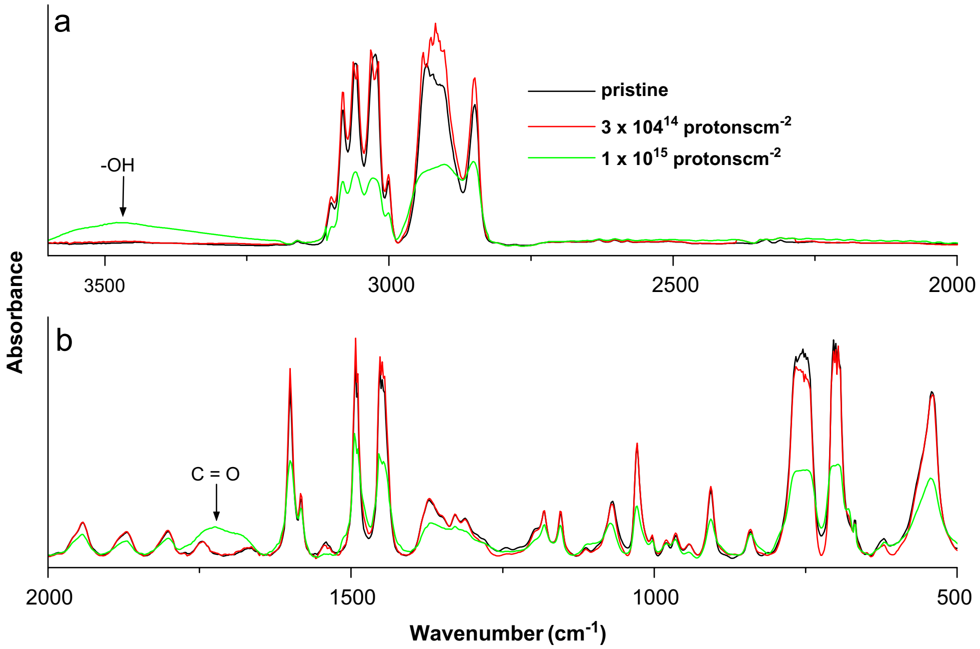


Fig. 4. FTIR spectra of polystyrene irradiated with 3 MeV protons. (a) ranges from 2000 to 3600 cm^{-1} and (b) ranges from 500 to 2000 cm^{-1}.

proton-irradiated Makrofol-N in addition to oxidation; chain scission may also taking place at carbonate site. The absence of the peak at around 3500 cm^{-1} in pristine Makrofol-N film shows the absence of the terminal hydroxyl group. The synthesis of this polycarbonate requires replacement of diphenyl carbonate with bisphenol-A, with the elimination of phenol as a side product. Thus, it is expected that the initial concentration of hydroxyl group will monotonously decrease with the increase in the chain length of the polycarbonate. In addition to the appearance of a peak around 3500 cm^{-1} there is a decrease due to irradiation of the intensity of the band around 1775 cm^{-1} which represent $C{=}O$ stretch, with the proton fluence. This indicates that chain scission may takes place at carbonate site with probable elimination of carbon dioxide/carbon monoxide and formation of hydroxyl group.

3.3. *XRD analysis*

The XRD curves of pristine and proton (3 MeV) irradiated Makrofol-N and polystyrene, respectively, with varying fluence is shown in Fig. 5(a and b). It is observed (Fig. 5a) that in pristine Makrofol-N there is a diffraction

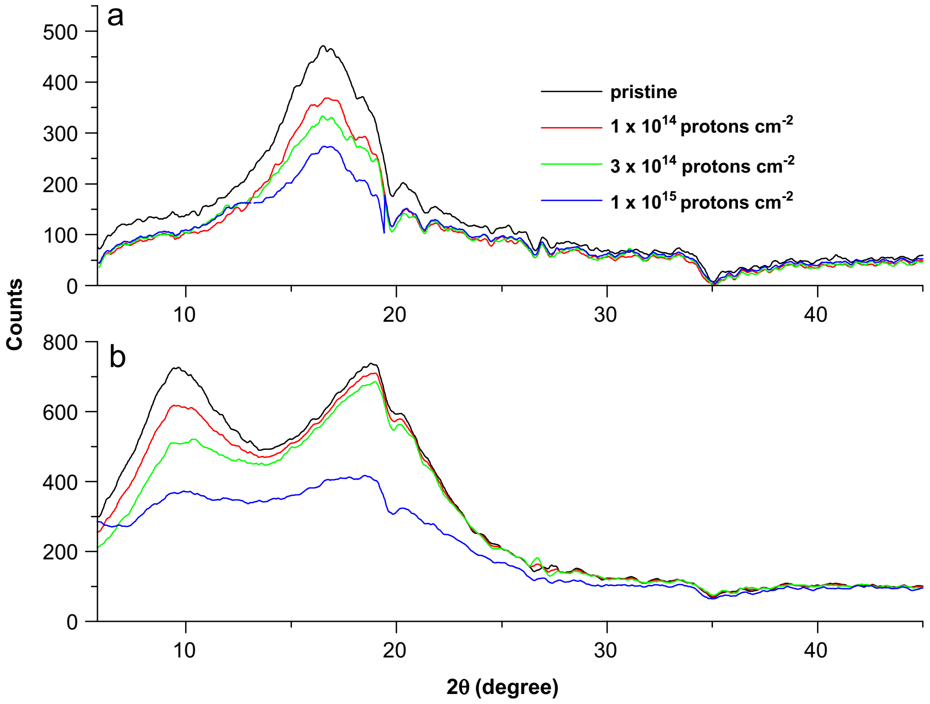


Fig. 5. X-ray diffraction spectra of proton (3 MeV) irradiated (a) Makrofol-N and (b) polystyrene.

peak at $2\theta = 16.54^\circ$ ($d \approx 5.35$ Å, $d = \lambda/2\sin\theta$ is the lattice spacing or crystalline interplaner distance), whereas in polystyrene, there are two strong diffraction peaks, first at $2\theta = 9.61^\circ$ ($d_2 \approx 9.20$ Å) and the second one at $2\theta = 18.78^\circ$ ($d_2 \approx 4.72$ Å). The XRD patterns and its relevant data in Table 2(a and b) indicate that there occurs a decrease in peak intensity I, and increase in the full-width at half-maximum (FWHM) β, with the increase of proton fluence. The increase in FWHM and decrease in peak intensity is generally associated with the decrease in crystallinity of the polymer. The larger are the crystals of a given component, the sharper are the peaks on the XRD pattern for each crystal plane. Thus the breadth of the peak can be related to the crystal size. The average crystallite size L, have been found out by Scherer formula (Singh and Singh, 2004):

$$L = \frac{k\lambda}{\beta\cos\theta}, \tag{5}$$

where β is the FWHM of the peak (in radian) and k is the shape factor whose value is equal to 0.9. Assuming $k = 0.9$ in the above equation, the crystallite sizes of virgin and irradiated polymers were calculated and the results are reported in Table 2. The crystallite size in Makrofol-N decreases by 29.5% on proton (3 MeV) irradiation. However, it is interesting to note that in proton-irradiated polystyrene the crystallite size decrease by 54% for the first peak and just 10% for the second peak.

It is also observed from Table 2(a and b) that in proton-irradiated Makrofol-N and polystyrene there is shifting of diffraction peaks towards smaller angle with the increase of proton fluence, which may be attributed to the increase of interplaner spacing. Chain scission and the introduction of –OH groups can be the possible reason for the increase of the average inter-molecular spacing, which ultimately results in the broadening of XRD peaks.

Table 2a
Relevant data XRD spectra (Fig. 5a) of pristine and proton (3 MeV) irradiated Makrofol-N at different fluences

Fluence (ions cm^{-2})	Peak 1				
	2θ (deg)	β (deg)	L (Å)	D (Å)	I
0	16.54	6.20	12.97	5.35	455
1×10^{14}	16.56	5.85	13.72	5.35	363
3×10^{14}	16.50	6.78	11.84	5.38	317
1×10^{15}	16.36	8.78	9.14	5.41	237

4. Conclusion

UV–vis, FTIR and XRD analysis reveal significant modifications in the optical and structural properties of Makrofol-N and polystyrene samples on irradiation with 3 MeV protons. The UV–vis analysis shows that the Makrofol-N is more affected by proton irradiation as compared to polystyrene. Optical band gap decreased by 30% in Makrofol-N as compared to 27.5% in polystyrene at highest fluence of 1×10^{15} protons cm^{-2}, owing to higher electronic energy loss of protons in Makrofol-N. The high value of energy deposition leads to heavy reorientation of the polymeric material, which further results in the

Table 2b
Relevant data XRD spectra (Fig. 5b) of pristine and proton (3 MeV) irradiated polystyrene at different fluences

Fluence (ions cm^{-2})	Peak 1						Peak 2			
	2θ (deg)	β (deg)	L (Å)	d (Å)	I	2θ (deg)	β (deg)	L (Å)	d (Å)	I
0	9.73	6.26	12.73	9.08	635	18.52	6.84	11.77	4.78	657
1×10^{14}	9.89	6.42	12.41	8.93	530	18.49	7.04	11.43	4.79	639
3×10^{14}	10.15	6.61	12.06	8.70	434	18.47	7.24	11.12	4.80	624
1×10^{15}	9.53	13.6	5.85	9.27	304	18.20	7.57	10.62	4.87	316

formation of carbon clusters. It has become clear from the calculations that the number of carbon atoms per conjugation length, N, and number of carbon atoms per clusters, M, embedded in the network of polymers that Makrofol-N is more modified as compared to polystyrene on proton irradiation.

The FTIR spectra of the pristine and proton (3 MeV) irradiated Makrofol-N revealed a strong decrease of almost all characteristics absorption bonds at about 1×10^{14} protons cm^{-2}. Beyond a critical dose an increase of all those characteristic bonds is noticed. However, in proton-irradiated polystyrene reduction in intensity of all characteristics absorption bonds at the highest proton fluence is observed, but like Makrofol-N no such critical dose has found up to the highest proton fluence beyond which the absorption intensity all characteristic bonds starts increasing. But the formation of new functional groups (–OH) has been observed in both polymers at the higher fluences.

From the analysis of XRD spectra, it has been observed that there is loss of crystallinity of both polymers on irradiation. The decrease in peak intensity and increase in the FWHM is observed. The crystallite size in Makrofol-N decreases by 29.5% on proton (3 MeV) irradiation. However, it is interesting to note that in proton-irradiated polystyrene the crystallite size decrease by 54% for the first peak and just 10% for the second peak.

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