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Electron-beam induced modifications of optical and dielectric properties of polypropylene films

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ABSTRACT

Polypropylene (PP) films were irradiated with 8 MeV electron beam radiation at varied doses in the range 0-20 kGy in order to investigate the modifications in its optical and dielectric properties. The variations in the optical band gap and activation energy were determined from the UV-Vis absorption spectra of the pristine and the irradiated PP films at different doses of electron radiation. The results showed that optical band gap and activation energy decreased with the increase in electron irradiation. The results further revealed that the dielectric constant, the dielectric loss and the ac conductivity enhanced with increase in the dose of electron radiation.

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KEYWORDS

Polypropylene;
Electron-beam irradiation;
UV-Vis spectroscopy;
Dielectric constant;
Optical band gap;
Activation energy.

INTRODUCTION

Recently there has been a special interest in the study of modifications of polymer properties by radiations due to its increasing use in radiation environments *viz.*, nuclear power plants, spacecrafts, high energy particle accelerators etc.^[1-3]. The study of radiation effects in polymers is an interesting subject not only from the stand point of understanding radiation induced polymer reactions, but also for the development of polymers having a superior physical properties suitable for different scientific and technological applications. The main effect of interaction of ionizing radiations with polymers is to produce excitation and ionization of the atoms and molecules in the polymers, which cause subsequent rupture of the chemical bonds resulting in polymer chain fragments and free radicals. These transformations are

responsible for most of the physical and/or chemical changes observed in the polymers^[3-6]. The optical and the electrical properties of polymers are the ones which are highly sensitive to the radiations and Many experiments aimed to improve the optical and the electrical conductivity of polymers by radiations have been reported and discussed^[7-13].

The study of optical absorption is a useful method for optically investigating the induced transition which provides information about the band structure and optical energy gap of the material. Further UV-Vis spectroscopy is sensitive to the optically active cluster region *i.e.*, visible cluster size. Few Researchers investigated the formation of these carbonaceous clusters in an irradiated polymer films from the absorption edge of UV-Vis spectra^[14-16]. Clusters are small nano-sized particles containing fewer than 10^4 atoms or molecules.

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Such clusters are known to be formed along latent tracks of energetic ions in the polymers. The clusters are supposed to be carriers of electrical conductivity in irradiated polymers and influence the optical properties of such materials^[14].

Among the synthetic polymers, polypropylene (PP) has occupied a prominent position because of its low cost and many desirable physical properties such as low density, high stiffness, good chemical resistance and electrical properties. The PP, besides its commercial applications, is widely used in medical, electrical, optical, electronic and thermal application^[17-20]. Polypropylene belongs to the family of polyolefin. It is a vinyl polymer having hydrogen atom substituent, $(-H_2C-CH_2-)_n$ or $(-H_2C-CRH-)_n$ and undergoes dominant homolytic rupture of C-H bonds to form hydrogen free radicals, which cross-link with each other. It has been found that both the cross-linking and degradation reactions proceed at almost same rate in PP leading to the deterioration of its physical properties. There have been a several studies on irradiation effects on physico-chemical properties of polypropylene^[21-24]. However, not much information is available on the effects of high-energy electron-beam irradiation (8MeV) over the dose range 0-20 kGy on the structural, optical and dielectric properties of PP. In the present work hence efforts have been made to understand the effects of high energy electron-beam irradiation on the structural, optical and dielectric properties of the PP films employing FTIR, UV-Vis and LCR impedance techniques over the electron dose range of 0-20 kGy using a 8 MeV electron beam from a Microtron accelerator.

EXPERIMENTAL

The polypropylene (PP) samples in the form of granules was compression molded into films of thickness 50 μ m using polymer press equipment (Techno search, India, PF-15). The compression molding was carried out by placing the polymer granules between the stainless steel dies at a temperature of 165 $^{\circ}$ C under a pressure of 10 MPa for 10 min and was then cooled under pressure by circulating water through the mold platens.

The electron-beam irradiation of the PP films was carried out in air using 8 MeV monochromatic electron

beam from the Microtron accelerator at the Microtron Centre, Mangalore University, Mangalore, India. The beam current was maintained at 20 mA with a pulse repetition rate at 5 Hz and a pulse width of 1.5 μ sec during the irradiation. The electron beam was made to fall on the polymer samples in a target holder placed at a distance of 30 cm. The beam spot on the target at this distance was about 6.0 cm. The polypropylene films were irradiated separately over the electron doses of 5, 15, 20 KGy.

For structural analysis, the FTIR spectra of pristine as well as irradiated polypropylene films were recorded using a FTIR spectrometer (Perkin-Elmer) over the wave number range of 4000 - 400 cm^{-1} with a resolution of 4.0 cm^{-1} .

For the analysis of optical properties, the polypropylene films were cut into 0.5 \times 0.5 cm^2 dimension and placed on a matt-black sample holder. The absorption spectra were recorded using UV-Vis spectrophotometer (Secomam-Anthelie) having resolution of 1.0 nm over the wavelength range of 200-800 nm using air as reference.

The PP films were cut into dimension 1.0 \times 1.0 cm^2 and a thin coating of air drying type silver paste was provided on both sides of the films to achieve good electrical contact for dielectric measurements. As the silver particles of the paste have diameter of typically 1 μ m, they stick to the sample surface only and hence do not influence the conductivity by interacting with the polymer. The samples were held between two nominally spring loaded copper plates and were subjected to dielectric measurements using the LCR Hitester (HIOKI-3532-50) over the frequency range of 100 Hz-1 MHz at the ambient temperature of 28 $^{\circ}$ C. The values of the dielectric constant (ϵ'), dielectric loss (ϵ'') and ac conductivity (σ_{ac}) were estimated from the measured values of the capacitance (C_p) and loss tangent ($\tan\delta$) at the different frequencies using the following relations^[25].

$$\epsilon' = C_p / C_0; \epsilon'' = \epsilon' \times D; \sigma_{ac} = 2\pi f C_p D t / A \text{ (ohm}^{-1}\text{cm}^{-1}\text{)} \quad (1)$$

where, C_0 is the geometrical capacitance of vacuum of the same dimensions as that of the sample; $D = \tan \delta$ where δ being the phase angle; t , the thickness and A is the cross-sectional area of the PP films.

RESULTS AND DISCUSSIONS

Structural analysis

Figure 1 shows the FTIR transmission spectra in the wave number range 4000–400 cm^{-1} for pristine as well as electron-beam irradiated polypropylene films over doses 5, 15 and 20 kGy. From the FTIR spectra of both the pristine and the irradiated samples, one can see the strong bands in the wave number region 2840–3000 cm^{-1} corresponding to C–H stretching vibration of methylene ($-\text{CH}_2$) group. The bands corresponding to bending of $-\text{CH}_2$ group appears at $\sim 1463 \text{ cm}^{-1}$ and bands corresponding to symmetrical bending of $-\text{CH}_3$ group can be seen at $\sim 1375 \text{ cm}^{-1}$. The Bands at 1165 cm^{-1} , 997 cm^{-1} and 977 cm^{-1} indicates that the polymer is isotactic and therefore methyl group is located on one side of the plane of the carbon atom chain. Since the electron irradiation of the polymer films were carried out in atmosphere the effects of oxygen is important. The increase in the intensity of band near 3440 cm^{-1} and 1720 cm^{-1} respectively showed the formation of oxidation hydroxyl (OH) and carbonyl (C=O) groups. Thus electron irradiation of PP results in structural modification which leads in the increment of chromophore groups in the irradiated samples.

Optical properties

Figure 2 shows the UV-Vis absorption spectra for both the pristine as well as the electron-beam irradiated PP films plotted in the wavelength range of 190–600 nm. From the spectra one can observe shift in absorption edge towards the longer wavelength region for the irradiated films. This behavior is generally interpreted as caused by the formation of chromophore groups or extended system of conjugated bonds, i.e. possible formation of carbon clusters as a consequence polymer chain scission, cross-linking, formation of radicals and unsaturated bonds in the irradiated samples. In the studied range of wavelength, the absorption bands are associated to the $\pi \rightarrow \pi^*$ electron transition.

In the high absorption region the absorption coefficient (α) as a function of photon energy ($h\nu$) can be expressed as^[26].

$$h\nu = B (h\nu - E_g)^r \quad (2)$$

where ($h\nu$) is the incident photon energy, E_g the optical band gap energy and B is a constant ($=4\pi\sigma_0 / nc\Delta E_g$). where c, speed

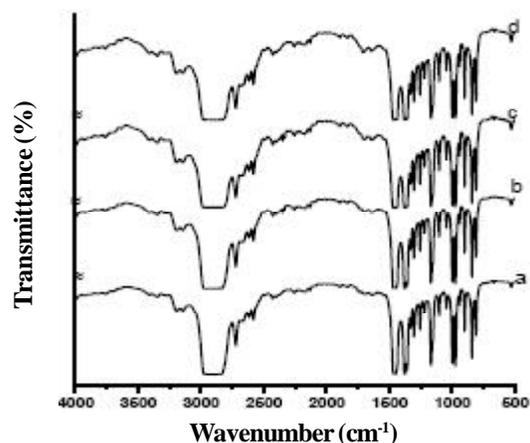


Figure 1: FTIR spectra for the pristine as well as the irradiated PP films at different doses of electron radiation (a) Pristine (b) 5 kGy (c) 15 kGy (d) 20 kGy

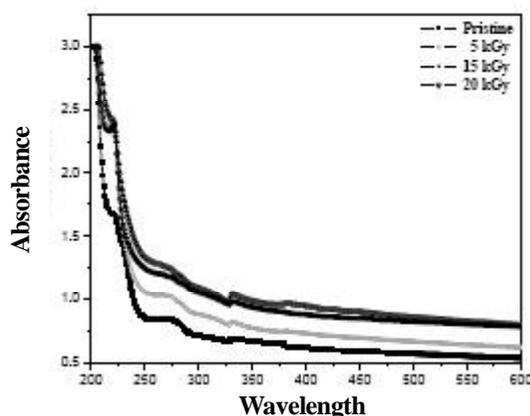


Figure 2: UV-Vis absorption spectrum for the as well as the irradiated PP films at different doses of electron radiation

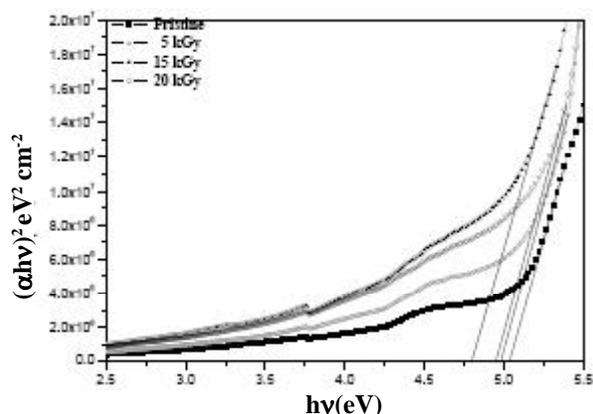


Figure 3: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the pristine as well as the irradiated PP films at different doses of electron radiation

of light, σ_0 , extrapolated dc conductivity at $T = \infty$, ΔE , measure of the extent of band tailing, n, refractive index and r is an

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exponent which can take values $\frac{1}{2}$, $\frac{3}{2}$, 2 and 3 depending on the nature of the electronic transition responsible for the optical absorption.

The best value of r can be determined from the slope of the linear part of $(\alpha h\nu)^{1/r}$ versus $h\nu$. We obtained a good straight line fit to our spectral data for $r = \frac{1}{2}$, which indicates that the transition is allowed direct. We estimated the values of the band gap energy from the extrapolation of the straight line part of the plot of $(\alpha h\nu)^2$ versus $h\nu$ to the zero photon energy as shown in figure 3. The absorption spectra showed an extending tail for lower photon energies below the band edge, which can be described by Urbach's formula given by^[27].

$$\alpha = A \exp(h\nu/E_u) \quad (3)$$

where E_u is the activation energy which is a measure of energy width of the tail of localized states in the band gap. Figure 4 shows a plot of $(\ln \alpha)$ versus $h\nu$ at different electron radiation doses for the PP films. The activation energy E_u was estimated from the reciprocal of the slope of the linear portion of the behavior of $(\ln \alpha)$ with $h\nu$. The estimated values of the optical band gap energy (E_g) and the activation energy (E_u) are given in TABLE 1. We observe that both the optical band gap and the activation energy decrease slightly with increase in the electron radiation dose. A similar decrease in the value of E_g of gamma irradiated polyvinylchloride (PVC), polypropylene (PP) films have been reported by others^[21,28,29]. Abdel-Fattah et al.^[29] reported that the irradiation of the unpalsticized PVC films by 25 MeV proton beams over a fluence range from $0-1 \times 10^{15}$ ions/cm² decreases its optical band gap from 4.35 to 2.04 eV. Sinha et al.^[21,28] showed that gamma irradiation of PVC and PP films over the dose range of 0 - 10^6 Gy decreases their optical band gap energy from 2.68 to 1.43eV and 4.59 to 2.07 eV respectively. The small decrease in the optical band gap of PP films with increasing dose of electron radiation could be attributed to the formation of extended systems of conjugated bonds, e.g. carbon clusters.

Although the number of carbon hexagon rings (M) in the cluster can be estimated from the Robertson relation given by^[30].

$$E_g = 2|\beta| M^{-0.5} \quad (4)$$

where 2β is the band structure energy of a pair of adjacent π sites and $\beta = -2.9$ eV for six-membered carbon ring, C_6 . But Fink

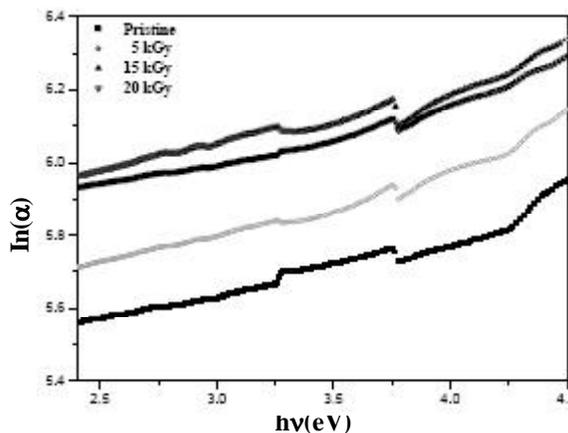


Figure 4: Plot of $(\ln \alpha)$ versus $h\nu$ for the pristine as well as the irradiated PP films at different doses of electron radiation

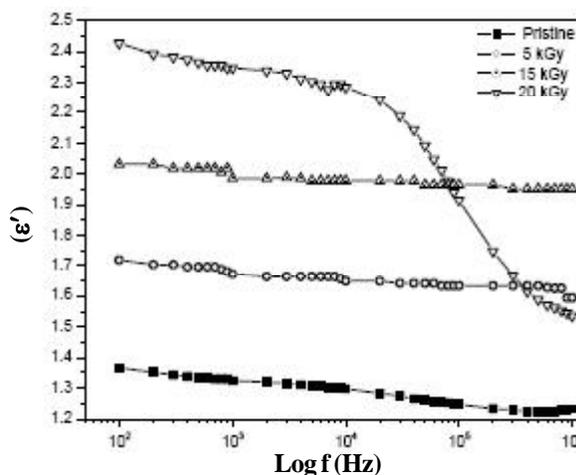


Figure 5: Plot of dielectric constant (ϵ') versus $\log f$ for PP films irradiated at different doses of electron radiation

et al.^[16] have shown that the Robertson equation underestimates the cluster size and hence they assumed the structure of the clusters to be like that of Buckminsterfullerene, C_{60} , instead of C_6 , and arrived at the following relation given by

$$E_g \approx 34.3/\sqrt{N} \quad (5)$$

where N is the number of carbon atoms per cluster.

We obtained using this relation the number of carbon atoms per cluster in the irradiated PP films and are given in TABLE 1.

Dielectric properties

The variation of the dielectric constant (ϵ') with $\log f$ for the pristine and the electron-beam irradiated PP films is given in figure 5. It can be observed that the ϵ' measured at 1 kHz increases from 1.3 for the pristine to 2.4 for the irradiated PP films at

TABLE 1: The estimated values of the optical band gap energy (E_g) and number of carbon atom per cluster size (N) for the pristine as well as the electron-beam irradiated PP films at different doses

Dose (kGy)	E_g (eV)	E_u (eV)	N
0	5.03	0.08	~46
5	4.97	0.07	~47
15	4.94	0.06	~48
20	4.79	0.06	~51

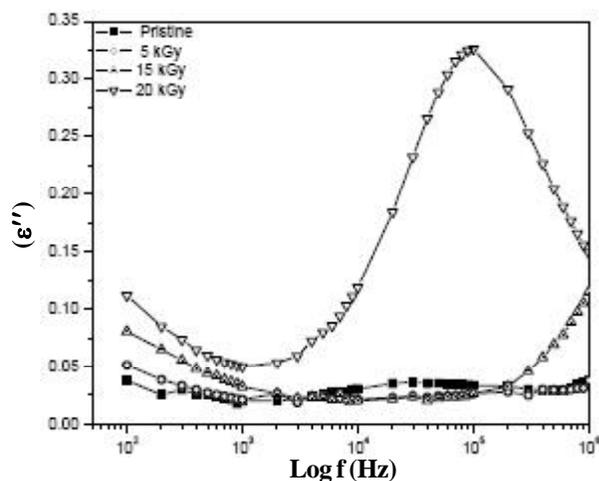


Figure 6: Plot of dielectric loss (ϵ'') versus $\log f$ for PP films irradiated at different doses of electron radiation

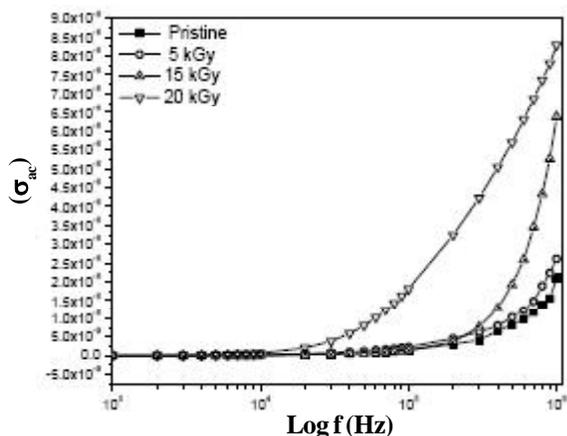


Figure 7: Plot of ac conductivity (σ_{ac}) versus $\log f$ for PP films irradiated at different doses of electron radiation

20 kGy. Figure 6 shows the change in the dielectric loss (ϵ'') as a function of $\log f$ for PP films irradiated with different electron doses in the range 0–20 kGy. It is observed that the ϵ'' for the PP films also increases with increase in the electron irradiation. The observed increase in the dielectric properties of the PP films with increase in electron doses could be attributed to scissoring of the polymer molecular chains, which

leads to the formation of defect sites in the band gap of the polymer. These defects could result in traps of charge carriers that increase the ability of the polymer to store charges and hence cause an increase in the dielectric constant as well as the dielectric loss of the samples. The experimental results further showed that the ϵ' for the electron-beam irradiated PP films decreases slightly at the higher frequencies. This is, perhaps, as the frequency increases the charge carriers migrate through the dielectric getting trapped against a defect site, which induces an opposite charge in its vicinity and thus the polarization of the trapped and the bound charges cannot take place and hence the dielectric constant decreases at these frequencies. However, at the lower frequencies, the mobility of the free charge carriers is constant and thus the dielectric constant remains unchanged at these frequencies.

Figure 7 depicts the dependence of the ac conductivity (σ_{ac}) on $\log f$ at the ambient temperature for both the pristine and the electron-beam irradiated PP films. It is observed that σ_{ac} of the PP films increases with increase in the electron radiation dose; and in fact, a sharp increase in the conductivity is observed above 10^4 Hz for all the irradiated films. The increase in the conductivity of the PP could be understood in terms of the free electron model wherein the release of hydrogen from polymer chain upon irradiation might result in an increase in the free radicals, unsaturated bonds, which obviously lead to an increase in the free-electron density in the polymer that contributes to an enhancement in the conductivity of the films. Further in the high frequency region a net polarization might occur which is out of phase with the field. This result in ac conductivity, it appears at frequencies greater than that at which the traps are filled or emptied.

CONCLUSION

We conclude from the present studies that the electron-beam irradiation modified the structural, optical, dielectric properties of PP films. The UV-Vis spectroscopic studies showed decrease in the optical band gap and the activation energy of PP films with the increase in the doses of electron radiation. The results on dielectric properties showed an increase in the dielectric constant, dielectric loss and ac conductivity of the PP films

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upon irradiation, which could be attributed to formation of new defects and an enhanced free electron density in the irradiated samples as a consequence of molecular chain scission, formation of free radicals and unsaturated bonds.

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