Pre-photoexcitation effects in 75 MeV oxygen ion irradiated kapton-H polyimide

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The pre-photoexcitation effect measured in the form of dark polarization ($I_d$) under visible radiation in 75 MeV oxygen ion irradiated (Fluence: $1.8\times10^{11}$, $3.1\times10^{12}$ and $1.8\times10^{13}$ ions/cm$^2$) kapton-H polyimide has been investigated. The dependence of $I_d$ on exposure (ranging from 0 to 10000 W/m$^2$) and the time interval $\Delta t$ (ranging from 0 to 7 min) between the end of illumination and the outset of the polarizing electric field have been studied at operating temperatures of 80°C and 200°C under a biasing field of 240 kV/cm. The variation of $I_d$ with exposure shows a transitory saturation followed by a gradual descent. The band-band transition and the conversion of trapping sites into recombination centers have been held responsible for such behaviour. The ion irradiated samples, in general, show a decrease in $I_d$ as compared to pristine samples. The effect of fluence on $I_d$ is mainly associated with the enhancement of charge trapping density and the charge carrier mobility.

Keywords: Ion irradiation, Kapton-H, Pre-photoexcitation effects, Polymers

1 Introduction

The effect of ionizing radiations on chemical, mechanical and electrical properties of polymers has been extensively studied by several groups.$^{1-7}$ However, limited work has been reported on the photo-physics of ion irradiated polymers. The photo-physics of polymers, particularly $\pi$-conjugated polymers is an area of research which has drawn considerable attention during the last few years.$^{8-11}$ The $\pi$-conjugated polymers are known to display a strong fluorescence from the singlet excited state and long lived transients associated to the triplet states formed by intersystem crossing.$^8$ Photogeneration and recombination of charge carriers are the processes which are involved in many applications of $\pi$-conjugated polymers.$^{10-13}$ In view of the remarkable photo-physical properties of $\pi$-conjugated polymers, it is imperative to have an apt understanding regarding the effect of energetic ion irradiation on the photophysical behaviour of these polymers. In the present paper, the pre-photoexcitation effect in 75 MeV oxygen ion irradiated kapton-H polyimide, a high performance $\pi$-conjugated polymer, has been reported.

The pre-photoexcitation or preliminary excitation usually provides an additional reservoir of charge carriers, resulting in an enhancement in the total induced polarization in the polymer when subjected to an electric field. Owing to the excitation effect, the optical radiations not merely generate the photopolarization but raise the original dark polarization as well. The relative contributions of the dark and photo components to the total polarization can alter the photoelectret state. The analysis of components can give significant information on photoinduced charge carrier generation, their trapping and recombination processes.

2 Experimental Details

The experiments reported here were performed on kapton-H polyimide (chemical name poly 4,4’ oxydiphenylene pyromellitimide) supplied by Dupont USA. The samples were irradiated with 75 MeV oxygen ions at different fluences ($1.8\times10^{11}$, $3.1\times10^{12}$ and $1.8\times10^{13}$ ions/cm$^2$) using the PELLETRON facility of Nuclear Science Center, New Delhi. The pristine and ion irradiated samples, referred as KP and KI, respectively (thickness: 25 µm, area: 1×1 cm$^2$), were metallized on one surface by vacuum evaporation of aluminium (served as back electrode) and a 3 mm thick transparent conducting (NESA) glass, served as front electrode. The sandwiched samples were vertically suspended in the furnace. This assembly was kept in a specially prepared temperature controlled furnace, shielded against the stray pickups, provided with a window for illumination and maintained at the desired constant...
temperature \((T_p)\) as shown in Fig. 1. The pre-photoexcitation of specimen for a certain duration \(t_{ex}\) (ranging from 0 to 15 min) was accomplished with a 100 W incandescent lamp having spectral range of 350-750 nm. The sample position is normal to the light source. After a certain time interval \(\Delta t\) (varying from 0 to 7 min) from the removal of illumination, it was polarized in darkness for 0-30 min by a constant electric field \(E_p\). The dark depolarization current versus time was monitored with the help of an electrometer (610 C Keithley). The experiments were repeated at different temperatures (ranging from 30° to 240°C). The magnitude of dark current \(I_d\) after 1 min discharge (when the initial rapid stage of decay is over) have been cited as a measure of dark polarization \(P_d\) owing to a direct correspondence between the two. The general procedure adopted for studying the excitation effect has been shown in Fig. 2.

3 Results

Fig. 3 (a and b) shows the dependence of \(I_d\) on exposure for KP and KI samples at 80° and 200°C, respectively. The variation of \(I_d\) with exposure can be divided in two regions the low exposure region, where a rise in \(I_d\) and the high exposure region is observed, where a transitory saturation followed by a gradual descent in \(I_d\) is observed, with exposure. The effect of irradiance at low \(T_p\) is to reduce \(I_d\) with increasing fluence. However, at high \(T_p\) and in the high exposure region a significant increase in \(I_d\) is seen for samples irradiated with high fluence [Fig. 3(b)].

Fig. 4 (a and b) shows the variation of \(I_d\) with fluence of irradiance for the ion irradiated KI samples for different exposure at poling temperature 80° and 200°C, respectively. The nature of variation of \(I_d\) with fluence is significantly affected by the poling temperature. Particularly in case of high fluence irradiated samples this dependence is more pronounced. At low temperature [Fig. 4 (a)] with increasing fluence after an initial rise a significant decrease in \(I_d\) is observed, whereas at high temperature [Fig. 4(b)] after an initial decrease we observe a significant increase in \(I_d\) is observed at high fluence.

Fig. 5 (a and b) shows the variation of \(I_d\) with poling time \((t_p)\) for KP and KI samples at 80° and 200°C, respectively. For KI samples, the \(I_d\) increases initially with \(t_p\) followed by saturation, whereas KP samples

![Fig. 1—Experimental set-up for the excitation effect measurements](image)

![Fig. 2—General scheme of the experimental procedure adopted for the study of the pre-photoexcitation effect](image)

![Fig. 3 (a and b)—Variation of \(I_d\) with exposure for pristine and 75 MeV oxygen ion irradiated samples at different fluences, \(t_{ex}=10\) Min (a) \(T_p=80°C\), (b) \(T_p=200°C\)](image)
show a transitory saturation followed by a descent with increasing $t_p$.

Figs 6 (a & b) shows the dependence of $I_d$ on $\Delta t$ for KP and KI samples, respectively. For KP and low fluence KI samples, a reduction in the dark polarization ($I_d$) is observed with increasing $\Delta t$. However, in high fluence irradiated samples $I_d$ increases initially with $\Delta t$ followed by a saturation.

4 Discussion

The pre-photoexcitation of conjugated polymers is associated with the band-band or band-trap transitions of electrons. After the completion of photoexcitation, the application of electric field (in darkness) results in a non-uniform distribution of electrons in the trapping levels which constitutes the dark polarization. This not only results in an increase of the electron density in the conduction band, but also the filling of trapping levels. In the absence of an electric field, the process of filling the trapping levels proceeds randomly, but uniformly in the sample. Sariciftcin et al. have discussed the formation of two polarons which do not interact with each other in conjugated polymers under primary photoexcitation. Under the uniform illumination of the sample, an equilibrium is established between the capture and the thermal release of electrons from their respective trapping levels.
levels. Earlier Pillai et al. have shown that in the case of photoconductors where the light (optical) Fermi level could sweep through the trap levels towards the transport band edges, significant changes in the density of trapping centers can result due to the conversion of trapping sites into recombination centers. Since the trapping probability is proportional to the product of trap density and the density of free carriers, charge carrier trapping becomes more effective at higher illumination levels. This explains to some extent, the initial rise in \( I_d \) with exposure in the low exposure region. Significant changes in the density of trapping centers may occur due to the conversion of trapping sites into recombination centers. Thus, \( I_d \) can saturate or even decrease with the intensity of incident radiation (high exposure region (Fig. 3a & b). At a certain temperature, a distinction between the trapping and the recombination centers can be obtained by introducing a parameter \( K \) defined as:

\[
K = \frac{\text{probability of recombination with charge carriers of opposite nature}}{\text{probability of thermal transition in to one of the allowed bands}}
\]

Using the expression for the probability of an electron transition, one obtains for a captured electron at a trap depth \( E_t \):

\[
K_n = \frac{\beta_n \cdot p}{\beta_n \cdot n_e \exp\left(-\frac{E_t}{kT}\right)} \quad \text{...(1)}
\]

Similarly for a captured hole at same level:

\[
K_p = \frac{\beta_p \cdot n}{\beta_p \cdot p_v \exp\left(-\frac{(E_g - E_t)}{kT}\right)} \quad \text{...(2)}
\]

where \( p_v \) is the effective density of states in the valence band for holes, \( n_e \) the effective density of states in the conduction band for electrons, \( \beta_n \) and \( \beta_p \) are recombination coefficients for electrons and holes, respectively, \( E_g \) the band gap of the kapton-H, \( n \) the equilibrium electron density in the conduction band and \( p \) is the equilibrium hole density in the valence band.

The traps corresponding to \( K_n \) (or \( K_p \)) < 1 act as trapping sites for electrons (or holes) while those with \( K_n \) (or \( K_p \)) > 1 as recombination centers.

Furthermore, the hypothetical demarcation levels (between trapping and recombination levels) viz. \( E_d^n \) for electrons and \( E_d^p \) for holes are characterized by \( K_n \) (or \( K_p \)) = 1.

The temperature and illumination dependence of \( K \) is quite obvious from Eqs (1) and (2). At a certain temperature, an increase in the light exposure increases the free carrier densities, causing a shift in the demarcation levels towards the respective energy bands. However, this shift in the demarcation levels takes place in the opposite direction if the temperature is increased with exposure fixed. Therefore, it is very likely that a substantial change in temperature and/or exposure may convert the nature of several trapping centers i.e. converting trapping sites into recombination centers or vice versa. In KI samples, the possibility of such a change in the nature of trapping sites will be more significant due to the fact that energetic ion irradiation causes several morphological changes in the polymer.

The transitory saturation in \( I_d \) followed by decay [Fig. 3 (a and b)] despite the ongoing exposure is not surprising. As stated earlier, owing to a continuous illumination of the sample, the corresponding demarcation levels gradually shift towards their respective allowed energy bands, thereby transforming some trapping sites into recombination centers. Thus, we have two processes operating simultaneously, but in opposite mode. On the one hand, there is an increase in the production of charge carriers available for trapping and on the other hand, the number of trapping levels, to accommodate them is suppressed. Thus, at a certain moment the dominance of a particular process would determine the nature of the experimentally observed excitation effect. The observed reduction in the dark polarization for prolonged exposures can be associated to the overall dominance of recombination process over the trapping. The establishment of a transient dynamic equilibrium between these two processes would result in an intermediate saturation stage. Though the general nature of \( I_d \) versus exposure curves in KI samples [Fig. 3(a and b)] is almost similar to those of KP samples the suppression of the entire \( I_d \) versus exposure curve for irradiated samples shows the dominance of recombination process over charge trapping mechanism in KI samples. This is further confirmed from the fact that a significant decrease in \( I_d \) occurs at higher fluences particularly at low \( T_p \).
[Fig. 4(a)]. However, at high operating temperature $T_p=200^\circ$C, Fig. 4(b)] a sudden increase in $I_d$ for high fluence KI sample is observed. This looks unusual but is not uncommon. Several groups$^{21,22}$ have reported a similar type of fluence dependent effects in the change of polymer behaviour. The ion irradiation of polymers not only leads to the destruction of short range order (chemical arrangement), but also to the destruction of its long range order (crystallinity). Particularly the change in crystallinity has been observed to vary in different ways. Papaléo et al.$^{23}$ have reported an overall decrease in crystallinity in PET after irradiation which decreases continuously with fluence first slowly and after a certain fluence quite rapidly. An increase in crystallinity with increasing fluence up to certain fluence and thereafter, a sudden decrease has been reported$^{22}$ in PVDF. In the present study also, secondary radiation induced crystallinity (SRIC) appears to govern $I_d$ to some extent.

The dependence of $I_d$ on poling time [Fig. 5(a)] confirms the recombination and trapping mechanism of charge carriers in KP and KI samples. Saturation in $I_d$ occurs when equilibrium is established between the trapping and the recombination processes. Interestingly the response time (the time at which the maximum value of $I_d$ occurs) decreases for irradiated samples as compared to pristine samples. This shows the overall dominance of shallow energy trap centers in irradiated samples which are more responsive to illumination as compared to deep energy trap centers. The fluence related induced effects are very complex in nature and we cannot make any comment with full authenticity on this aspect. However, two major consequences of irradiation of polymers viz. (i) increase in charge mobility owing to enhanced crosslinking$^{24}$ and (ii) increase in charge trapping density may determine the nature of variation of $I_d$ in KI samples. In addition, an enhancement in the conjugation of double bonds due to irradiation in polymers affecting its conductivity has been reported by Fink$^{25}$. An increase in mobility and conductivity (due to conjugation of double bonds) will result in a decrease in $I_d$ whereas increase in charge trapping density will result in an increase in $I_d$. The overall change in $I_d$ will be determined by the dominance of a particular consequence.

During the interval ($\Delta t$) between the end of pre-photoexcitation and the application of field, the system is left in a non-equilibrium state, the relaxation of which under a field free condition is expected to occur in two phases (i) the excess of photo-induced positive and negative charges undergoes a decay process via recombination with highest recombination cross-section centers and thereafter (ii) the decay in $I_d$ occurs via thermal release of carriers from traps into transport bands and eventual recombination with recombination centers.$^{19,26}$ Thus, during $\Delta t$ the stored charge is always subjected to a spontaneous decay, resulting in a gradual decrease in the number of electrons available at the trapping states. However, in high fluence irradiated samples ($1.8 \times 10^{13}$ ions/cm$^2$) we find an initial build up in $I_d$ [Fig. 6(b)]. Though, we cannot offer any definite mechanism for this behaviour, it can be associated with phosphorescence like processes occurring in high fluence irradiated samples. Wisocki et al.$^{27}$ have also discussed the ion induced phosphorescence light emission in polyethylene.

The time variation of $I_d$ for pristine and ion irradiated samples is shown in Fig. 7. The nature of decay of $I_d$ reveals the presence of shallow and deep energy trap centers in kapton-H polyimide responsible for initial fast and eventual slow decay, respectively. The effect of fluence on the half decay time, $t_h$ (the time in which the value of $I_d$ reduces to half of its initial value) a measure of decay rate is presented in Table 1. There is an overall increase in $t_h$ in irradiated samples as compared to pristine samples which is

![Image](https://example.com/figure7.png)

**Fig. 7—Dark decay characteristics for pristine and 75 MeV oxygen ion irradiated samples at different fluences, $T_p=80^\circ$C, exposure=460J/m$^2$, $t_p=10$ min**

<table>
<thead>
<tr>
<th>Fluence (ions/cm$^2$)</th>
<th>$t_h$ (Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>40</td>
</tr>
<tr>
<td>$1.8 \times 10^{11}$</td>
<td>50</td>
</tr>
<tr>
<td>$1.8 \times 10^{12}$</td>
<td>55</td>
</tr>
<tr>
<td>$1.8 \times 10^{13}$</td>
<td>60</td>
</tr>
</tbody>
</table>
quite obvious. High energy ion irradiation causes
demerization of carbonyl groups and formation of free
radicals, resulting in an increase in charge trapping
density affecting the decay rate.

5 Conclusions

The pre-photoexcitation effect measured in the
form of dark polarization has been investigated in
energetic ion irradiated kapton-H polyimide. The
pre-photoexcitation effect is mainly accomplished
with a band-band transition and conversion of
trapping sites into recombination centers. The new
deep and shallow trap centers formed due to
irradiation accounts for an enhancement in $I_d$
due to increased charge trap density. However, the radiation
induced cross-linking effect results in an increase in
charge mobility and is responsible for decreasing $I_d$.
After irradiation, demerization of carbonyl groups and
formation of free radicals result in an increase in
charge trapping density which affects the decay rate.

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