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Dielectric constant/loss measurement in 75 MeV oxygen-ion irradiated poly (vinylidene fluoride) films

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The dielectric constant [ε' (ω)] and dielectric loss [ε'' (ω)] have been measured in 75 MeV Oxygen- ion irradiated (fluences; 5.6X10^{11} ions/cm^2 and 5.6X10^{12} ions/cm^2) 20 μm PVDF thin films in the temperature region 30°C -170 °C at different the frequency range from 1KHz-1MHz by taking unirradiated (pristine) 20 μm thin film as reference. The ε' (ω) of pristine film in low temperature region shows week dependence on the temperature and show strong dependence of temperature at higher temperature region. Trapped charge carriers make a large contribution to the dielectric parameters at lower frequencies. There is an overall decrease in ε' (ω) in ion irradiated samples. The decrease in ε' (ω) is more in samples irradiated with higher fluences. The secondary radiation induced crystallinity (SRIC) has been observed in low fluence (5.6X10^{11} ions/cm^2) irradiated samples. The increase in crystallinity, α_c-relaxation and free radical cross linking process govern the high temperature ε'(ω) and the dominance of radiation induced free radical cross linking has been held responsible for the sudden decline in ε' (ω) at very high temperature. Two relaxations; the α_{c-} and the α_{a-} relaxations, appearing from high temperature side to low temperature side in the dielectric loss versus temperature spectrum have been observed in present investigation.

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1. Introduction

Polycrystalline polymers such as Poly (Vinylidene Fluoride) (PVDF) are attractive for wide range of sensor and actuator applications. PVDF is one of rare polymer that exhibits diverse crystalline forms, having at least five phases known as α, β, γ, δ and ε or phases II, I, III, IV, V respectively [1-3]. Earlier reports have shown that molecules in α- phase are in a trans-gauche-trans-gauche (TGTG) conformation, while β- phase molecules are in all-trans planar zigzag conformation. The α- and β-phases have attracting more attention than the other phases because of having larger dipole moments formed the basis for number technological applications. The PVDF in its β-phase exhibits piezo- and pyroelectric properties due to the orientation of molecular dipoles. Because of the unique properties such as piezoelectric, pyroelectric, ferroelectric, and nonlinear optical of PVDF polymer promote its use in many technological applications in micro sensors and actuators, biomaterials and implantable medical devices, nonlinear optical components , ferroelectric memory and many more[4-9]. It is one of rare polymer which has strong candidature to be the smart material due to its excellent piezoelectric properties. The term smart materials generally relate to a material which changes it one or more properties in response to external stimuli in controlled manner. The properties of mart material can be tailored in an appropriate way to achieve the desire out comes for its different applications. The ion irradiation method is relatively new techniques for the material modifications/ tailoring the properties of the material.

The energetic heavy ion also termed as swift heavy ion (SHI), irradiation effect on PVDF have attracted attention during the last few years for its special applications as a biocompatible material with important applications in pharmaceutical and food industries[10]. The swift heavy ions having the velocity comparable with the Bohr electron velocity when traverse through the material medium losses its energy in displacing atoms of the material target by elastic collisions or in exciting the atoms by inelastic collisions. The elastic collision is the dominate process for low energy ions whereas the inelastic collision dominate process for high energetic ions (SHI). The energy thus deposited in later process (inelastic collision) causes the various modifications in the material. This provides an opportunity to tailor the properties of the material to achieve the desired structural, electrical, chemical and optical properties. The behavior of PVDF irradiated to different types of ions has been studied by several groups [11-16]. These studies reveal change in crystallinity of PVDF [12-16]. The decrease in crystallinity has been reported under electron and low-energy ion irradiation [12-14] whereas an increase in crystallinity has been reported under electron, X-ray and γ-ray irradiations [11, 14-16]. The crystallinity plays a crucial role in determining the piezoelectric, mechanical, optical, electrical and even thermal properties of polymers [12]. The conduction mechanism in ion irradiated polymer has not yet fully understood due to the complexity of the polymer structure. A few reports are available on the ion irradiation effect on various dielectric relaxation behaviors of polymers [17]. Dielectric relaxation behavior of PVDF has been investigated by several groups in pristine form

[18]. However, swift heavy ion induced effect on dielectric relaxation behavior of PVDF thin films are not yet explored.

The main objective of this paper to present the dielectric spectroscopy to elucidate the various dielectric relaxation processes in 75 MeV Oxygen-ion irradiated PVDF thin films, at different temperature and frequencies.

2. Experimental details

The poly-vinylidene fluoride used in the present study was procured form DuPont (USA) in film form of thicknesses 20 µm. The samples of size 1 sq. cm were mounted on a ladder for the irradiation in a vacuum chamber. The ladder was loaded in a chamber kept in a high vacuum of the order of 10−6 Torr. The films were then irradiated with 75 MeV Oxygen-ion beam at fluences; 5.6X10^{11} ions/cm^2, 5.6X 10^{12} ions/cm^2 (beam current of 0.5 PnA) using the PELLETRON facility at Inter University Accelerator Centre (IUAC), New Delhi. The ion beam fluence was measured by integrating the ion charge on the sample ladder with time. Ion energies were selected in such a manner that they can easily pass through the PVDF films. The depth profiles were estimated using SRIM calculations. The projected range of 75 MeV Oxygen- ion beams in the PVDF was calculated to be 105.35 µm using the SRIM-08 code (Ziegler 2008), which is five time larger than the thickness of PVDF samples.

The electric contacts were made by vacuum evaporation of high quality silver on the both surface of samples. The samples were fitted in a dielectric cell and specially prepared temperature controlled furnace. The furnace was shield against the stray pickups. The dielectric constant/ loss was measured from room temperature 30°C to 170°C with the help of HIOKI 3532-50 LCZ meter and Fluke PM 6306 programmable LCR meter in the frequency range 1KHz- 1MHZ.

Dielectric spectroscopy has been turned out to be indispensable tool for investigating molecular motions in polymer usually know as dielectric relaxation process during the application of the electric field. Dielectric relaxation processes not only affect the important physical and chemical properties but also electric, electromechanical, and piezoelectric properties of dielectric material such as PVDF.

The dielectric constant [ε' (ω)] and loss factor [ε" (ω)] of pristine and SHI irradiated PVDF thin films have been investigated in the temperature range 30°C -170 °C and in the frequency range 1KHz-1MHz. The dielectric parameters were evaluated by measuring equivalent capacitance C_p and tangent loss factor tanδ. The real part of the dielectric constant (ε') was calculated from

$$C_p = \varepsilon' \varepsilon_o A/d \quad (1)$$

where, ε_o is the dielectric constant (permittivity; 8.86 X 10^{-10} F/cm) for free-space,'d' (in cm) is the thickness and 'A' (in cm^2) is the cross-sectional area of PVDF thin films.

3. Results and discussion

3.1 Pristine and 75 MeV oxygen- ion irradiated PVDF

The variation of dielectric constant [ε'(ω)] with temperature for pristine and 75 MeV Oxygen- ion irradiated PVDF films at different fluences **(**fluences; 5.6X10^{11} ions/cm^2 and 5.6X10^{12} ions/cm^2**)** for 1KHz 10 KHz 100 KHz and 1MHz frequencies have been illustrate in Fig. 1 (a), (b), (c) and (d) respectively. The Fig. 2 (a), (b), (c) and (d) illustrate the variation of dielectric loss [ε"(ω)] for pristine and 75 MeV Oxygen- ion irradiated PVDF at different fluences **(**fluences; 5.6X10^{11} ions/cm^2 and 5.6X10^{12} ions/cm^2**)** for 1KHz 10 KHz 100 KHz and 1MHz frequencies.

In polymers, the thermal response of the dynamics of molecular motions and Brownian motion of main chain segment results in various relaxation processes. These relaxation process have direct relationship with the frequency and temperature dependence of dielectric parameters such as dielectric constant [ε'(ω)]) and dielectric loss [ε"(ω)] . In pristine PVDF, three type of relaxation process namely α, β, γ have been recognized respectively in the descending order of temperature [19]. The α-relaxation process is attributed to the rotation diffusional motion of the molecules from one quasi-stable state to another involving conformational rearrangement of main chain. The β-relaxation is associated with the orientation of the dipoles in the range of local environment where the rearrangement of the main chain is frozen.

It has been observed from ε'(ω) - T characteristics of pristine PVDF thin film [Fig. 1 (a), (b), (c) and (d)] that the behavior of variation of ε'(ω) with temperature is almost similar for all frequencies range. At low temperature ε'(ω) show little dependence on temperature for intermediate frequencies, but at higher temperature it show strong dependence on temperature for all frequencies and increases at higher rate for low frequencies (1KHz and10 KHz). This behavior of dielectric constant [ε'(ω)] is consistent with a Deby-type dielectric dispersion characterize by a relaxation frequency. The increase in ε'(ω) is due to the total polarization of PVDF. A rapid decrease in ε'(ω) after 140°C can be associated with change in the geometry of the sample (shrinkage) owing to release of the molecular orientation at start of dynamic melting temperature of the PVDF. The peak in ε'(ω) - T characteristics for 10 KHz frequency at 120°C may shows the presence of α_{c-} relaxation of phase II PVDF.

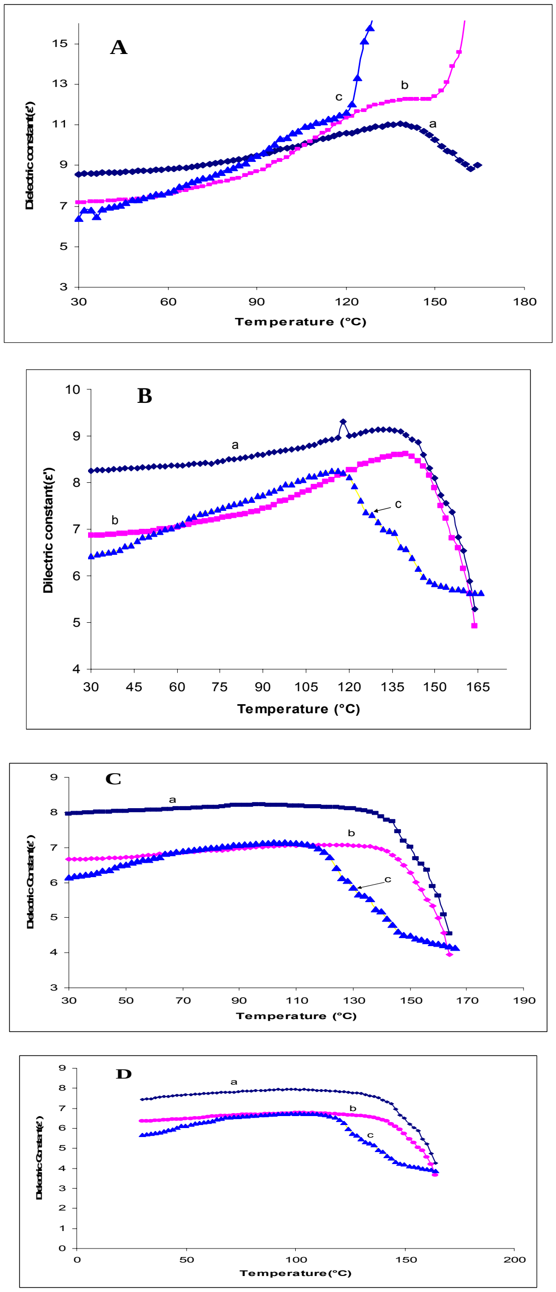

Fig. 1. (a) Variation in dielectric constant (ε') with temperature at 1 KHz frequency for pristine PVDF thin film (a) and 75 MeV Oxygen-ion irradiated PVDF thin films for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2; (b) Variation in dielectric constant (ε') with temperature at 10 KHz frequency for pristine PVDF thin film (a) and 75 MeV Oxygen-ion irradiated PVDF thin films for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2; (c) Variation in dielectric constant (ε') with temperature at 100 KHz frequency for pristine PVDF thin film (a) and 75 MeV Oxygen-ion irradiated PVDF thin films for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2 (d) Variation in dielectric constant (ε') with temperature at 1 MHz frequency for pristine PVDF thin film (a) and 75 MeV Oxygen-ion irradiated PVDF thin films for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2.

The $\varepsilon''(\omega)$ - T characteristics for pristine sample [Fig. 2 (a), (b), (c) and (d)] does no show any strong dielectric loss peaks but initial decrease in $\varepsilon''(\omega)$ with temperature at higher frequencies i.e 100KHz and 1 MHz [Fig. 2 (c) and (d)] could be the post-peak portion of the α_{a-} relaxation. It seems the loss maxima would occur at still lower temperature. The higher values of $\varepsilon''(\omega)$ at lower frequencies is attributed to trapped charge carriers at the crystalline amorphous interface [20] within the phase II PVDF polymer at higher temperature. Two loss valley were observed in $\varepsilon''(\omega)$ - T characteristics at 10 KHz frequency. One is around 70°C arising from the loss of molecular motion in the folds on the surface of crystallites and other at 120 °C which may be related to loss in the α_{c-} relaxation associated with the molecular motion of PVDF chain in the crystalline region of α-phase due to orientation of dipoles. This is in conformity with dielectric relaxation observed in the $\varepsilon'(\omega)$ - T characteristics of pristine PVDF.

The above discussion of dielectric constant and dielectric loss measurements [Fig. 1 (a), (b), (c) (d) and Fig. 2 (a), (b), (c),(d)] indicates some sign of presence of two relaxations designated as α_a and α_c-relaxation appearing from low temperature side to high temperature side of dielectric spectra. The α_c-relaxation observed in the present investigation has been attributed to the molecular motions in the crystalline regions of the polymer main chain whereas the α_a-relaxation is associated with the molecular motion in the folds on the surface of crystallites- amorphous interface.

The $\varepsilon'(\omega)$ - T characteristics [Fig. 1 (a), (b), (c) and (d)] of pristine and 75 MeV Oxygen- ion irradiated samples can be divide into the two segments 30-100°C and 100- 170°C .The main factors which can effect the $\varepsilon'(\omega)$ - T characteristics in irradiated samples are radiation induced cross linking, chain scission, production of free radical and the formation of unsaturated double bonds [21-22]. In addition, the swift heavy ion irradiation may also change crystalline morphology of polymer. Fascinatingly, all radiation effects have their own role to affect $\varepsilon'(\omega)$ in different way. For example free radical play dual role. On one hand, they try to enhance α_c – relaxation which result in an increase in $\varepsilon'(\omega)$ and on other hand they may undergo an irradiation induced free radical cross linking [23]. The free radical cross linking at higher temperature would not only ceases the orientation of molecular segment but also reduce the population of irradiation induced free radicals results a decrease in $\varepsilon'(\omega)$.

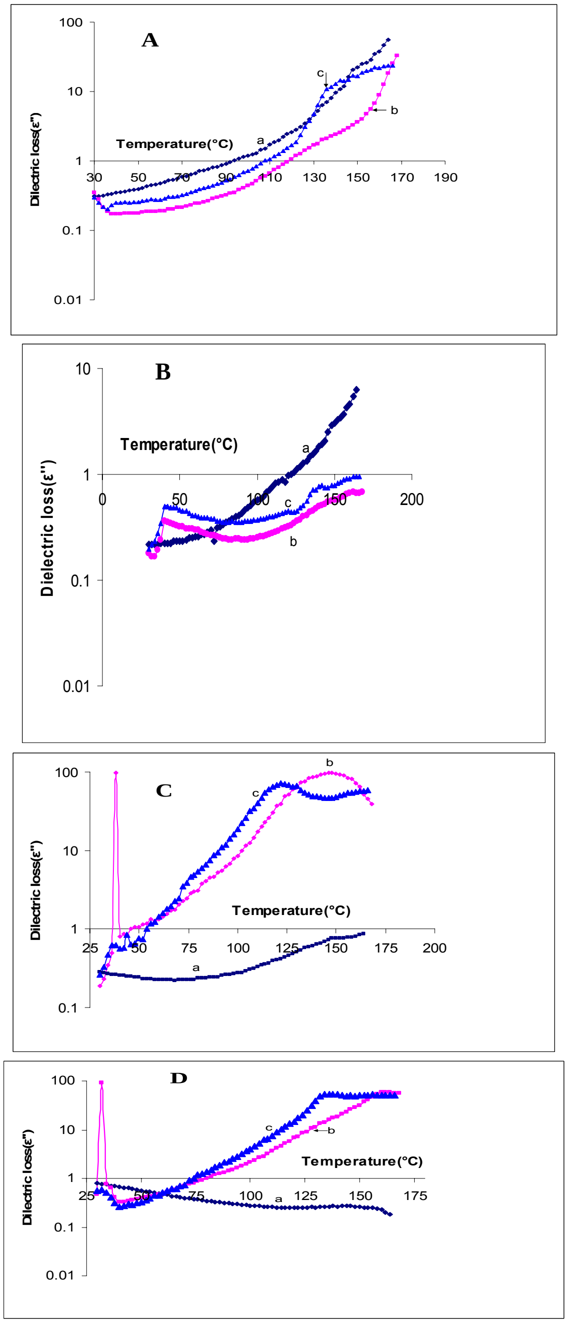

Fig. 2. (a). Variation in dielectric loss (ε'') with temperature at 1 KHz frequency for pristine PVDF (a) and 75 MeV Oxygen-ion irradiated PVDF thin films for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2; (b) Variation in dielectric loss (ε'') with temperature at 10 KHz frequency for pristine PVDF thin film (a) and 75 MeV Oxygen-ion irradiated PVDF thin film for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2; (c) Variation in dielectric loss (ε'') with temperature at 100 KHz frequency for pristine PVDF thin film (a) and 75 MeV Oxygen-ion irradiated PVDF thin films for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2; (d) Variation in dielectric loss (ε'') with temperature at 1 MHz frequency for pristine PVDF thin film (a) and 75 MeV Oxygen-ion irradiated PVDF thin films for fluences; (b) 5.6 X 10^{11} ions/cm^2 (c) 5.6 X 10^{12} ions/cm^2.

The $\varepsilon'(\omega)$ - T characteristics of pristine and ion irradiated samples is similar except the overall decrease in $\varepsilon'(\omega)$ for ion irradiated samples. In the temperature region 30-100°C, the $\varepsilon'(\omega)$ for pristine and ion irradiated samples show gradually increase with the increasing temperature before 40°C and the $\varepsilon'(\omega)$ for irradiated sample remain smaller than the pristine. After 40°C, the $\varepsilon'(\omega)$ for irradiated samples exceed the $\varepsilon'(\omega)$ of pristine at 1 KHz frequency [Fig. 1 (a)]. This temperature region mainly belongs to α_a relaxation process which may dependent on the crystal structure of PVDF. An enhancement in α_a relaxation process would be expected after ion irradiation own to the chain scission of various functional groups. The chain scissioning process accelerate the movement of functional groups which would increase the $\varepsilon'(\omega)$. On the contrary, in temperature region 30-40°C, a significant decrease in $\varepsilon'(\omega)$ after irradiation as compare to the pristine samples suggests that the effects of α_a - relaxation process on $\varepsilon'(\omega)$ is balanced by some other irradiation induced process in temperature range 30-40°C. This decrease in $\varepsilon'(\omega)$ for irradiated sample as compare to pristine sample may be associated with ion irradiation induced free radical cross linking process in the temperature range 30-40°C. It has been observed that the free radical cross linking will be proportional to the irradiance fluence and hence the decrease in $\varepsilon'(\omega)$ should be more with increase fluence [Fig. 1 (a), (b), (c) and (d)].

The crystallinity of PVDF is improve on low fluence oxygen-ion irradiation due to the emergence of new secondary radiation induced crystalline phase (SRIC) and destruction of SRIC at higher fluence irradiance has been observed in our XRD analysis earlier. The destruction of SRIC at higher fluence irradiance held responsible for the increase in $\varepsilon'(\omega)$ as compare to the $\varepsilon'(\omega)$ for lower fluence in temperature region 40-100°C.

An enhancement in interfacial polarization is expected in temperature region 100-170 °C , due to irradiation induced charge carriers trapping/detrapping at the defect sites results an increase in α_c - relaxation in irradiated samples cause of which $\varepsilon'(\omega)$ increases. The presence of α_c - relaxation process is also manifested in form of loss maxima at 142,148 and 158°C for 1 KHz frequency in $\varepsilon''(\omega)$ - T characteristics [Fig. 2 (a)]. In temperature region 100- 170°C the $\varepsilon'(\omega)$ first increases and then decreases. After this decrease the $\varepsilon'(\omega)$ increases suddenly with increase in temperature above 150°C. The decrease in $\varepsilon'(\omega)$ can be explain on the fact SRIC for low fluence irradiance and radiation induced free radical cross linking process for the high fluence irradiance counter balance the effect of α_c - relaxation process. The increase in $\varepsilon'(\omega)$ after the saturation region will be ignored for further analysis since it may be due to the electrode polarization or ionic conduction and may not truly represent the material property.

The $\varepsilon'(\omega)$ - T characteristics at higher frequencies [Fig. 1 (b), (c) and (d)] show a decrease in $\varepsilon'(\omega)$ in general for irradiated samples and particular for higher fluence irradiance at higher temperature side. This is quit interesting, since we expect increase in $\varepsilon'(\omega)$ due to mainly two reason, (i) high fluence irradiation destroys the SRIC

(ii) an enhancement in interfacial polarization due to the irradiation induced defect sites and production of free radicals results an increase in α_c – relaxation at higher temperature. This argument is further strengthen from the appearance of loss maxima in $\varepsilon''(\omega)$ - T characteristics [Fig. 2 (c) and (d)]. This shows that there are some other physical causes responsible in decreasing the $\varepsilon'(\omega)$. At least we can resolve this decrease in the $\varepsilon'(\omega)$ on the basis of dominance of the radiation induced free radical cross linking process for higher fluence irradiance and the formation of SRIC phase in low fluence irradiance which is further enhances with increasing temperature particularly in high temperature region. The decrease in $\varepsilon'(\omega)$ is more pounce in samples [see Fig. 1 (b), (c) and (d)] irradiated with higher fluence; 5.6 X 10^{12} ions/cm^2 since the free radical cross linking will more effective at higher fluence as discuss earlier. Further reduction in free radical density is also affected by the charge trapping in polymer matrix associated with the crystalline region. Thus it safe to conclude in present case the dominance of massive free radical cross linking process and increase in crystallinity over other irradiation induced processes at higher temperature results in decrease $\varepsilon'(\omega)$ in ion irradiated samples.

From the above discussions, it can be conclude that in the case of pristine and ion irradiated PVDF in entire temperature region, we observe the number of mechanism operating simultaneously, which either decrease or increase $\varepsilon'(\omega)$. An overall increase or decrease in $\varepsilon'(\omega)$ will be governed by the dominance of the respective mechanism.

4. Conclusions

Dielectric properties such as dielectric constant [$\varepsilon'(\omega)$] and dielectric loss [(ε'')] in pristine and 75 MeV Oxygen-ion irradiated (fluences; 5.6X10^{11} ions/cm^2 and 5.6X10^{12} ions/cm^2)PVDF thin films have been investigated. Charge carriers trapped at crystalline – amorphous interface make a large contribution to the dielectric parameter of pristine film at low frequencies

An overall decrease in $\varepsilon'(\omega)$ in Oxygen- ion irradiated sample as compare to the pristine sample has been describe by dominance of radiation induced free radicals cross linking process and increase in crystallinity with temperature. Two relaxations; the α_{c-} and the α_{a-} relaxations in the form of loss peaks in $\varepsilon''(\omega)$ - T characteristics have shown their presence in ion irradiated sample, appearing from high temperature side to low temperature side.

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