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Chemical, Electrical and Morphological Properties of Kapton Polymer Irradiated by Gamma Radiation

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Abstract: ***Kapton polymer has proven their potential in the field of electronics, space and nuclear technology, also found to have very good electrical properties, mechanical strength and high melting points (260°C to 350°C) due to the presence of aromatic ring in the polymer back bone. In this paper, we have studied the Chemical, Electrical and Morphological properties of virgin and high dose (500 - 2000 kGy) γ - irradiated samples of Kaptonpolymer. This polymer samples were analysed by using Fourier transforms infrared (FTIR) spectrophotometer, Model 1720 with 0.5 wave number resolution in the range (4300 - 500 cm^{-1}). The FTIR spectrum shows no major change except a small increase in the intensities of some identified band due gamma irradiation. This indicates that Kapton is radiation resistant. The dielectric study was carried out by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range (10 Hz - 30 MHz) at ambient temperature. The increase in A C conductivity with radiation dose is attributed to scissioning and crosslinking on the surface of the polymer. The surface morphology of Kapton polymer was characterized by scanning electron microscope (SEM) using (JEOL, Model No.3300) operating at 30 kV accelerating voltage. The scissioning is responsible for the evolution of gases from the surface and the respective erosion***

Keywords: Gamma irradiation; Kapton; FTIR; Frequency Impedance Analyzer; SEM

1. Introduction

The importance of polymers such as Kapton with improved surface and bulk properties has increased during the last few decades because of their low weight, low cost easy processability and easy fabrication of thick and thin films. Kapton is known to be a high performance aromatic polymer and primarily used for insulation all over the world now with very high heat - durability and heat - stability. Kapton is a polyimide film that can remain stable in a wide range of temperature from - 273ºC to +400ºC. It has some very good properties such as mechanical performance, electric insulation, radiation resistance, corrosion resistance (other than alkali), etc. Kapton polymer has been commercially used from many years and is now commonly applied in the electronics industry as an insulating barrier, gas separation membrane applications, etc. [1 - 3]. Particularly the radiation resistance, and fire resistance, have made this polymer a favourite choice for applications like wire insulation, electrical components seal assemblies, in nuclear power plants, military aircraft and space shuttles [4, 5]. It is worthy to have the knowledge about the properties of the material that change when it is exposed continuously for a long time by the radiations like gamma rays, etc. Hence, the qualitative as well as quantitative studies of the radiation damage of "radiation resistant" polymers like Kapton at such a high level dose, is gaining more and more importance in engineering and technology [6, 7]. The chemical structure of Kapton polymer is shown in Fig.6.1.

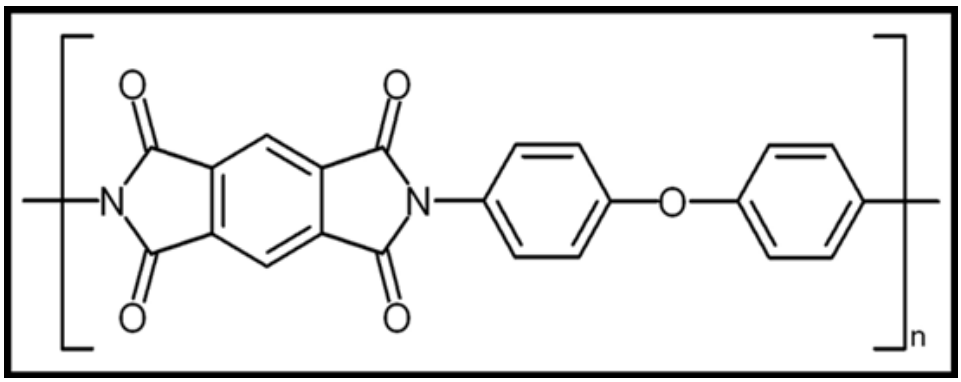

Figure 6.1: Chemical structure of Kapton polymer

Early investigations revealed that an aromatic polymer like polyimide possesses a desirable range of characteristics, such as radiation resistance, low dielectric constant, selective permeability to gases, film toughness under rigorous conditions of air aging, and retention of high mechanical strength over a wide range of temperature [8]. These adaptable properties have stimulated interest in expanding the applications of Kapton polymer in the manufacturing of modern electrical appliances, transportation, national defence, nanotechnology, device technology and materials science [9 - 11].

Kapton can also be utilized for various aerospace applications because of low density. However, the low density of the polymer pertains to light weight material that can reduce the mass of the spacecraft for more efficient fuel

expenditure. Kapton is also used as a control coating for exterior spacecraft surfaces due to its good thermal stability and chemical resistance [12]. This material layered on the outer surface of a spacecraft because of its resistance to harsh environmental conditions and fluctuated temperature [13]. Due to the importance of Kapton in aerospace applications, many experiments have been conducted over the last few decades to investigate the effect of exposure of this polymer after irradiation.

In this regard, out of a wide range of low as well as high energy radiations that can be used to modify/improve the properties of polymers. Gamma irradiation is one among them which induces several physico - chemical changes in the polymers such as crosslinking, scissioning, formation of free radicals, radiochemical alterations, unsaturation or formation of double bonds, evolution of gases, formation of carbonaceous clusters, change in intrinsic free volume, creation of defects (free radicals or impurities), amorphization, phase transitions, etc. Kapton is known to be particularly resistant to ionizing irradiation, induced degradation when irradiated with heavier atom possessing kinetic energy in MeV.

Polymers were extensively studied and known to be stable for Gamma rays and electron beams up to 100 MGy of radiation [14, 15]. Radiation assisted diffusion, grafting, blending, are a few well known applications of radiation processing of polymers [16 - 18]. The energy deposited in polymers due to ion bombardment leads to chemical changes and breakage of chemical bonds of polymer thereby releasing gases, which are independent of the nature of ionizing radiations. The electrostatic charge deposited during ion bombardment may play an additional important role in polymers [19].

The FTIR studies provide precise information about the orientation of specific functional groups within the polymer film. The frequency region of the FTIR spectroscopy covers the absorption due to the fundamental vibrations of all common functional groups of organic compounds.

The electrical properties of Kapton polymer have attracted much of attention in the last few years due to gamma irradiation. Various studies related to the modifications of polymers were expected to play a major role to attract the attention of researcher to prove that this polymer is conductive [20 - 24]. The significant increase in the electrical conductivity of this polymer with increasing irradiation dose was also reported [25]. The XRD studies show that the crystalline peaks superimposed upon the broad amorphous peaks, confirming the partial crystalline structure of Kapton polymer. However, in this polymer the approximate percentage of the crystalline phase and amorphous phase has been 25% and 75%, respectively. The increase in glass transition temperature Tg from 392C^{o} to 418C^{o} in radiation induced Kapton polyimide as reported earlier has been attributed to be due to cross - linking [26]. The surface roughening and formation of blisters and pores appear due to gamma irradiation were observed using SEM analysis [27 - 29]. Although, a lot of work has been done to investigate the effect of ion irradiation on the polymeric materials but the dependence of effect parameters related to ionizing radiation has not been completely understood. Therefore, in the present work, we decided to undertake the comparative study of Kapton polymer with higher gamma dose levels.

2. Experimental Details

Kapton polymer sheets of thickness 250μm (both polymers) were brought from M. S. Good Fellow U. K. (United Kingdom) and were used without any further treatment. The polymers samples of size (2x1) cm2 were cut from the commercially available sheet. One sample was kept as virgin and the other four samples were subjected to irradiation of different doses. The samples were irradiated using 1.25 MeV gamma radiation source of Co60 in the radiation chamber (which is in the form of cylindrical chamber of 14 cm length and 10 cm diameter) with dose rate 4 kGy/h and source strength of 2 K Curie. The samples were irradiated in the dose range of 500 kGy to2000 kGy at UGC – DAE Consortium for Scientific Research, Kolkata Centre.

The irradiated samples were characterized by using FTIR spectroscopy, High Frequency Impedance Analyzer (HFIA) and SEM, to observe the possible modifications that could take place in the Kapton polymer by irradiation.

2.1 Chemical Study (FTIR Spectroscopy)

Chemical modifications were evaluated using Perkin Elmer, Fourier transform infrared (FTIR) spectrophotometer, Model 1720 with 0.5 wave number resolution in the range (4300 - 500 cm - 1). FTIR spectroscopy was carried out to monitor scissioning of various bonds and formation of new functional groups, especially with regard to oxidation.

2.2 Electrical Response (High Frequency Impedance Analyzer)

The dielectric study was carried out by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range (10 Hz - 30 MHz) at ambient temperature. The impedance analyzer was equipped with a small furnace for high temperature measurements. The data generated from the instrument were collected through an interface between instrument and the computer using data acquisition and control software PSM 1735.
The dielectric permittivity evaluated using the standard relation

$$\epsilon r = C\, d/\epsilon 0 A. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.1)$$

where C is capacitance, d the thickness of the sample, $\epsilon 0$ = 8.854×10–12 F/m and A the effective area of the sample. The A. C. conductivity was calculated by using the equation.

$$\sigma ac = 2\pi f (\epsilon r) \tan\delta. \quad \ldots\ldots\ldots\ldots\ldots\ldots (6.2)$$

2.3 Surface Morphology (SEM)

The surface morphology of Kapton polymer was characterized by scanning electron microscope (SEM) using (JEOL, Model No.3300) operating at 30 kV accelerating voltage. Surface of each sample was coated with a thin layer of gold (3.5 nm) by using the vacuum evaporation technique

to minimize sample charging effects due to the electrons beam.

3. Results and Discussion

In the present study the results obtained from the different techniques/measurements of the virgin and gamma irradiated samples of Kapton polymer have been discussed separately as under:

3.1 Chemical Studies

The FTIR spectra of pristine and gamma irradiated Kapton polymerin the range 500 to 5000cm $^{-1}$are shown in Fig.6.6. The FTIR spectra shows that the overall structure of the polymer remains same except some minor changesare observed. This indicates that the inter - chain separation is not effected by gamma irradiation. The position of peaks almost remains unshifted, but only the values of absorbance and transmittance of the functional groups are found to change. That kind of changes may be due to a decrease in the concentration of the already existing bonds. The peak at 3120 cm^{-1} corresponds to aromatic C–H stretching and at 3630 cm^{-1}corresponds to hydroxyl groups (OH), respectively. The absorption band at 3486 cm^{-1}represents N–H bond stretching vibration. The carbonyl groups (C=O, stretching) are found at 1888.31 - 2023.33 cm^{-1}.

The FTIR spectra of virgin and irradiated Kapton polymer samplesshow relatively large absorbance at 1888.31cm $^{-1}$, 2023.33cm $^{-1}$, 3120cm $^{-1}$and 3610.5cm $^{-1}$ and they were selected for analysis in this work. A small change in the intensity of these bands/functional groups is attributed to the evolution of adsorbed gases just below the surface of the polymer [30]. It is inferred that the reduction in specific height is due to deterioration of these groups in the form of H_2, CO, or CO_2 gas. The release of these gases results in the blister formation on the surface of thermally stable Kapton polymersamples after irradiation. The minor changes in the peaks of the irradiated spectra may be due to the breakage of one or two bonds in the ladder structure, but this will not change the overall structure of the polymer [31, 32]. It isalso observed from the FTIR spectra that the overall bond structure of unirradiated sample remainsintact, however these bonds gradually scissioned after irradiation. All these, make the Kapton polymer a radiation resistant.

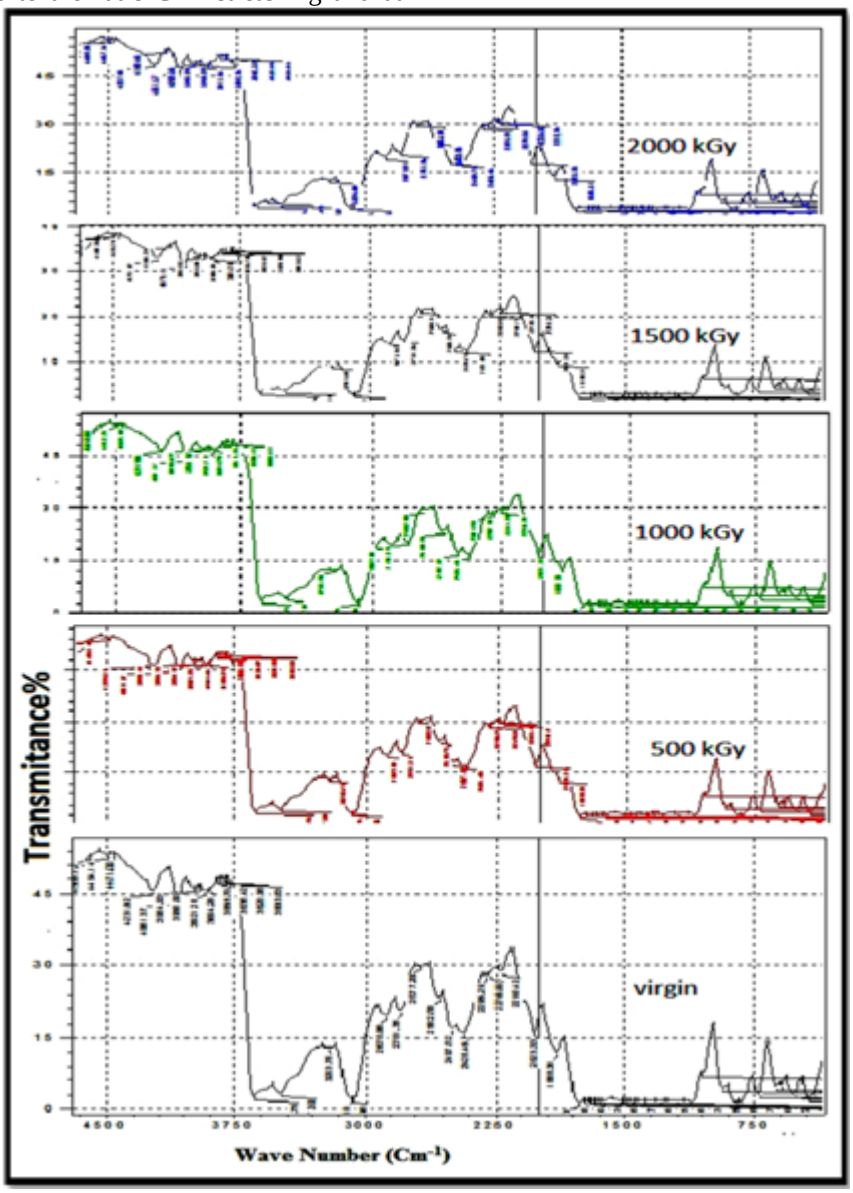

Figure 6.6: FTIR spectra of virgin and gamma irradiated Kapton polymer samples

3.2 Electrical Studies

The A C conductivity, dielectric loss and dielectric constant measurements were performed for the virgin and gamma irradiated Kapton polymer samples by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range, 10 Hz to 30 MHz. The data obtained from the instrument were plotted as a function of frequency as shown in Figs.6.7 - 6.9.

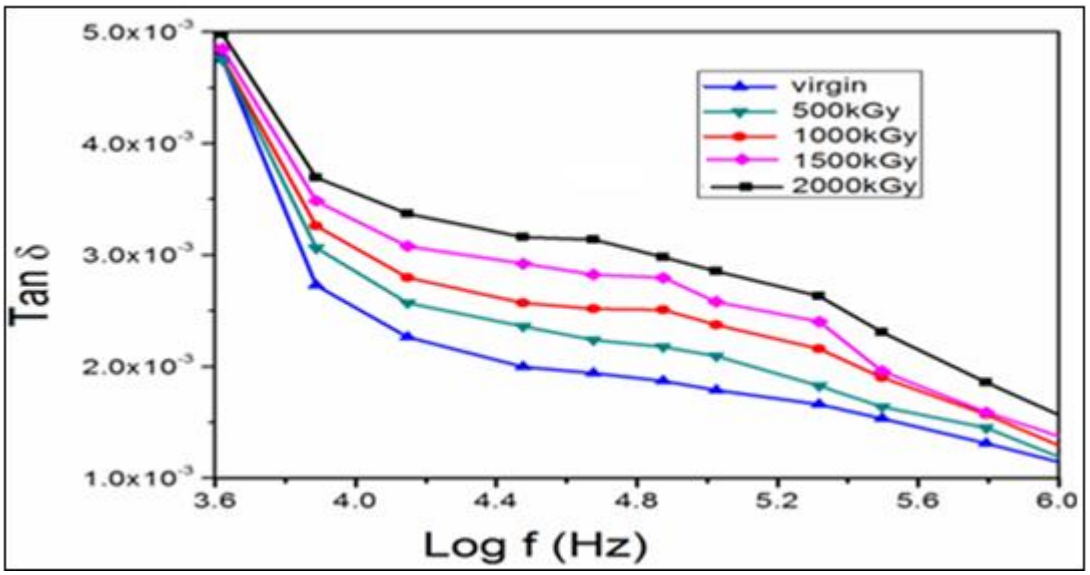

Figure 6.7: Variation of tan δ with log of frequency for virgin and irradiated Kapton polymer samples

The variation in dielectric loss for virgin and irradiated polymer samples is shown in Fig.6.7. It is observed that tan δ loss decreases with the increasing frequency [33]. The increase in losses at low (Log 3.8) frequency could be associated with the polarization due to bound/trapped space charges. With the increase of frequency, polarization decreases and becomes vanishingly small at relatively higher (Log 5.8) frequency. The increase in dielectric loss with increasing dose (from 500 kGy to 2000 kGy) is attributed to chain scissioning in polymer samples, resulting in an increase of free radicals, unsaturation, etc.

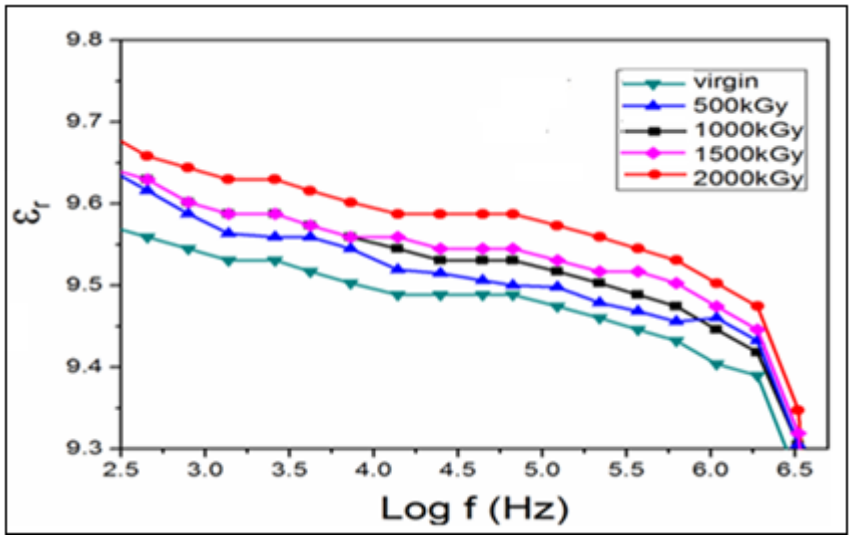

Figure 6.8: Plot of dielectric constant for virgin and irradiated Kaptonpolymer samples

Fig.6.8 shows the plot of dielectric constant Vs log of frequency for the virgin and irradiated Kapton polymer samples. This indicates that the dielectric constant (ϵr) remains almost uniform at low (Log 2.5 - Log 6.0) frequencies and decreases after this value of frequency [34]. From the constant portion of the plot, it is expected that the space charge distribution remains unaltered at low frequency range and thus the dielectric constant remain uniform. However, at relatively higher frequency, a redistribution of the bound/trapped space charges takes place, causing a decrease in the dielectric constant. Similar type of decreasing behaviour of dielectric constant at higher frequency side was also reported, and can also be explained by Jonscher's Power Law [34]. Moreover, for pyroelectric materials, it is very important to reduce the dielectric constant and dielectric loss.

The A C conductivity plot of the virgin and irradiated samples shown in Fig.6.9 indicates that σac decreases towards the lower frequency side. This may be due to the

creation of some defects in the energy gap as a result of gamma irradiation. These defects (sometimes called traps or clusters) create barriers against the motion of charge carriers already existing in non - irradiated polymeric materials [35].

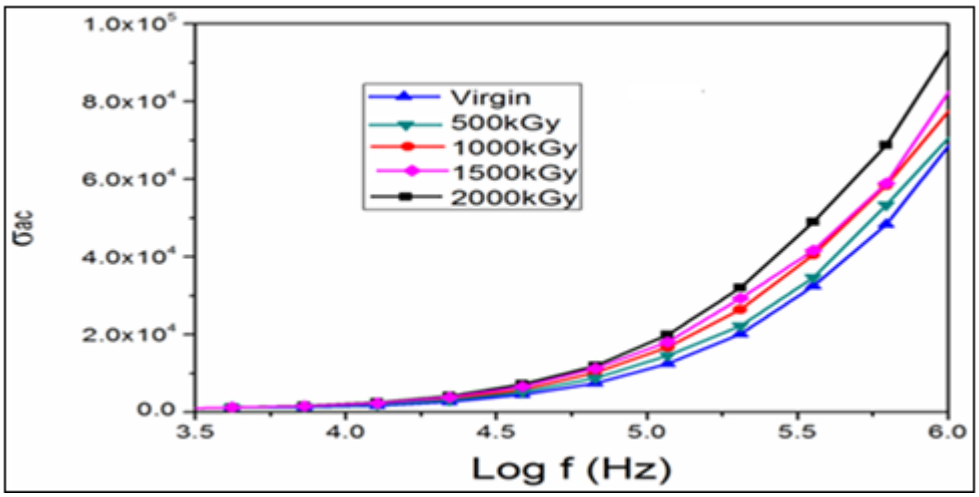

Figure 6.9: AC Conductivity plot for virgin and irradiated Kapton polymer samples

The applied A. C. field beyond the frequency Log 5.2 creates the net polarization in all the Kapton polymer samples, which is out of phase with the field. This results an increase of A C conductivity at higher (Log 5.2 - 6.0) frequencies. A sharp increase in the A C conductivity was observed in virgin and irradiated samples with increasing gamma dose at higher frequencies. This may be due to scissioning of polymer chains and migration of long lived radicals from (normally trapped in) crystalline region to an amorphous region, resulting in an increase of free radicals, unsaturation, etc.

3.3 Surface Morphology

The optical micrographs of the virgin and gamma irradiated Kapton polymer samples at dose levels 500 kGy, 1000 kGy, 1500 kGy and 2000 kGy, are shown in Fig.6.10. The effects of 1.25 MeV gamma irradiation on Kapton polymer samples, clearly show sequential development of blisters on the surface of the samples. Blistering is just because of plastic deformation of the irradiated surface layer under the cumulative influence of a large number of gas atoms that evolve near the top surface of the samples. The blister formation, involves three important stages: (i) bubble nucleation, (ii) bubble growth and (iii) plastic yielding.

Fig.6.10 (a) shows SEM micrograph of the virgin Kapton polymer sample. It is observed from this micrograph that the overall surface of the pure Kapton is smooth. Fig.6.10 (b) of gamma irradiated Kapton at a dose level 500 kGy shows a number of small size blisters on the surface of the sample. It is found that the size of blisters increases with increasing irradiation dose, which is an important observation made by us during its examination. As the radiation dose increases, the growing bubbles at certain stage of their growth suddenly combine to form a disc shaped cavity parallel to the surface. When the gas pressure inside the cavity becomes large, the overlapping material layer is plastically deformed to produce a dome shaped structure under the thrust of the gas pressure. The increase in the surface area of blisters and surface roughness due to gamma irradiation, may be attributed irradiation induced scissoring and crosslinking on the surface of Kapton polymer as shown in 6.10 (d - f). Some of the scissioned polymer chains may further crosslink. This may change the free part of the surface, due to which the surface appears imperfect after irradiation. Another reason behind surface roughening may be due to thermal effects induced by irradiation [36, 37].

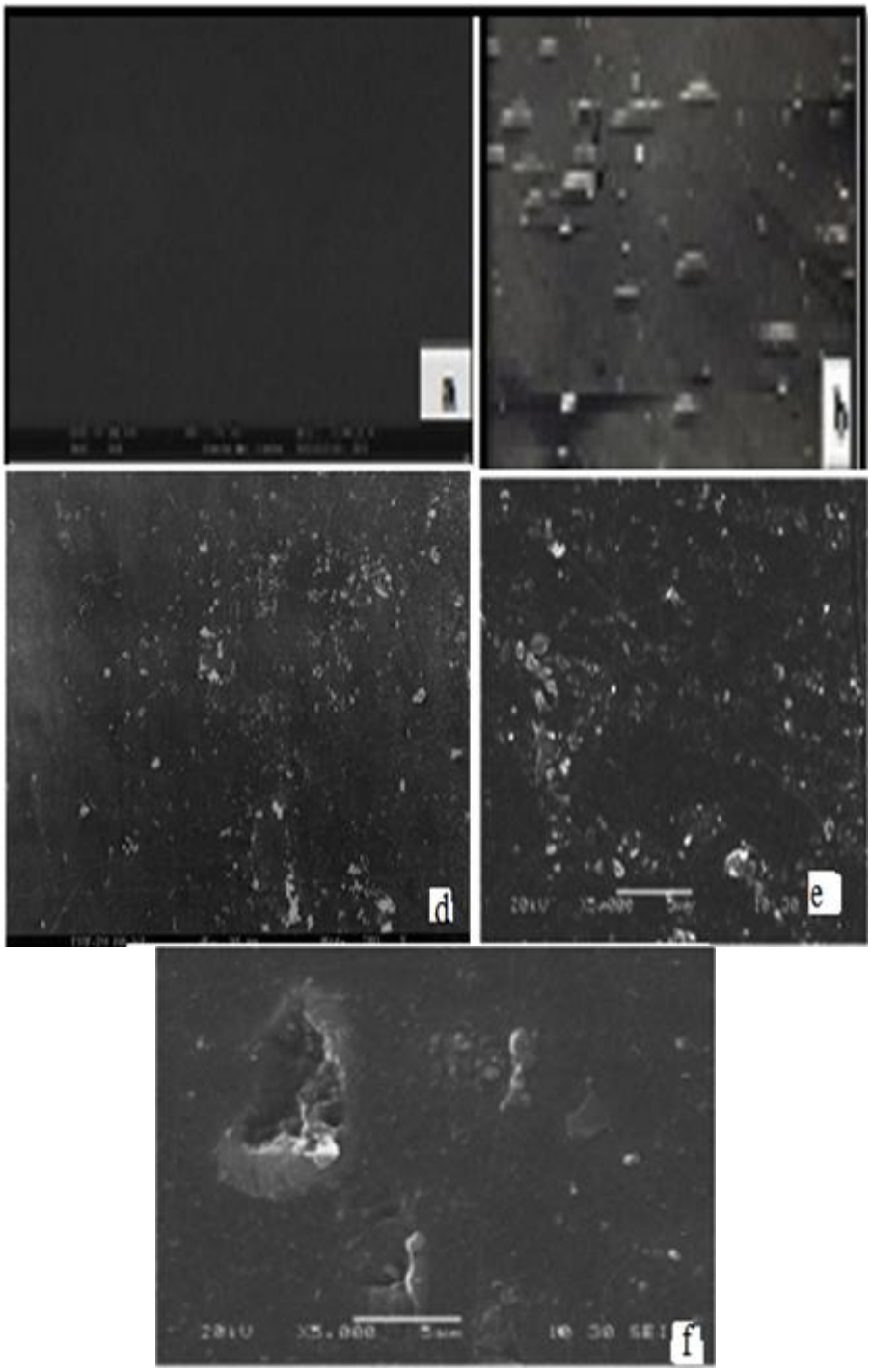

Figure 6.10: SEM images of virgin and gamma irradiated Kapton polymer samples

4. Conclusions

The FTIR spectrum shows no major change except a small increase in the intensities of some identified band due gamma irradiation. This indicates that Kapton is radiation resistant.

The decrease in dielectric loss means the polarization decreases and becomes small at higher frequencies. However, the dielectric constant remains uniform.

The increase in A C conductivity with radiation dose is attributed to scissioning and crosslinking on the surface of the polymer.

The scissioning is responsible for the evolution of gases from the surface and the respective erosion.

The increase in the surface area of blisters and surface roughness after increasing radiation dose is observed as a result of rupture of chemical bonds and formation of low molecules gases.

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