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The effect of gamma irradiation on chemical, morphology and optical properties of polystyrene nanosphere at various exposure time

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Abstract. Irradiation of polymers causes structural, chemical and the optical properties changes. Polystyrene nanosphere was drop coated to substrates and the gamma irradiation was carried out in a Cesium-137 (Cs-137) source chamber at different time (1-5 hours) with constant dose of 30 kGy. Fourier transformation infrared spectroscopy (FTIR) and Raman spectroscopy were employed to characterize the chemical properties of irradiated polystyrene while Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to study the surface morphological changes of the samples. The optical energy band gaps of the thin films were investigated and studied using transmittance and absorbance measurements. The results obtained revealed that as irradiation time increases the optical properties changes and polystyrene gradually undergoes crystal to carbonaceous from its amorphous state. The average particles diameter and roughness of the samples decreases with increasing irradiation time.

1. Introduction

Polymers are often exposed in radiation environments such as gamma rays [1][2] laser [3][4][5], X-rays [6] electrons beam [7][8], photonic and ions [9] which may affect the chemical and physical properties of these materials where atomic or molecular excitation and ionization occurred resulting in the changes of chemical bonds, intermolecular cross-linking, formation of free radicals and unsaturated bonds, etc. These processes cause defects and re-arrangement of polymer matrices, which are responsible for most of the changes observed in the physico-chemical properties of polymers [7]. Polymers have been extensively studied as promising materials for integrated optical device due to the broad spectrum of possible applications in data transmission and processing systems [10].

Polymers have become a very attractive for photonic device due to their easily processed; offer high flexibility, tailor made properties and have a relatively low cost, especially polystyrene, PMMA

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[11]–[15]. It is known that polystyrene (PS) is an important material in both academic research and industry. PS has a simple chemical structure that consists of both unsaturated aromatic ring and saturated aliphatic chain [16]. Studies have shown that the surface modification of PS, especially the chemical reactions occurred at the unsaturated and saturated bonds. Recently, attention has been paid to modification of PS with respect to micro-fluidics, cell culture and electronic applications. In most works, the effects of gamma or laser treatments on alterations in the polystyrene have been investigated [17]–[19]. Physicochemical changes in this layer, induced by the gamma or laser radiation, have also been reported [20][21].

This work focuses on the effects of over exposure gamma irradiation of polystyrene by chemical, morphology and optical properties of polystyrene nanosphere at various time of exposure. The samples were characterized by means of Fourier Transform Infrared (FTIR), Raman spectroscopy, Scan Microscopy (SEM), Atomic Force Microscopy (AFM) and Ultra violet-visible spectrometer (UV-Vis) measurements. The optical energy band gaps and number of carbon atoms deduced from transmittance spectra are discussed.

2. Experiment

2.1. Methods and characterization

The p-type Silicon wafer was cut into 1 x 1 cm^2 and the wafers were treated in piranha solution (H_2SO_4:H_2O_2 =3:1) for 45 min at 80 ℃, the substrates were then rinsed in deionized water and dried with nitrogen before use [5]. Polystyrene nanospheres with a mean diameter of 500 nm and a concentration of 10 wt% in solution were purchased from Sigma Aldrich and was used without further purification, to achieve a large-area hexagonal close-packed nanosphere monolayer, the PS nanosphere solution was diluted to be 2 wt% with deionized water, then about 10 μL PS nanosphere suspensions with the concentration of 2 wt% was dropped on silicon wafer and allowed to dry at room temperature before gamma irradiation treatment. The gamma irradiation was performed at room temperature in air atmosphere using a Cesium-137 (Cs-137) source and irradiation times were taken as 1-5 hour.

FTIR analysis was performed using a Perkin Elmer FTIR Spectrometer LR 64912C, N3896 equipped with a universal Attenuated Total Reflectance (ATR) sample stage. The sample molecular structure was determined within the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. Raman spectroscopy was carried out using XploRA plus Raman microscope Horiba scientific with 532 nm line of a He-Ne laser as the excitation source. The laser power was maintained at a lower value to avoid laser induced heating of the sample. Roughness of the samples was studies using Atomic Force Microscopy (AFM) XE-100 Park systems. The measurement was carried out using non-contact mode under the room temperature conditions with scan size of 5 μm x 5 μm, high resolution 256 pixels x 256 pixels. Morphology of the samples were obtained using Scanning Electron Microscope (Hitachi SU1510) and coated with platinum before characterization. The optical energy band gap of irradiated PS and non-irradiated PS thin films were studied using the optical transmittance spectra recorded on the samples with the help of UV-Vis-NIR double beam spectrophotometer. The optical transmittance spectrums of samples were recorded in the range of 320-900 nm wavelengths.

2.2. Data analysis

2.2.1. Optical energy band gap.

The optical energy band gap can be estimated by calculating the optical absorption coefficient (α) from transmittance data obtained using the following relation:

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right), \tag{1}$$

where T is the transmittance and d is the film thickness. The thin film under study has an absorption coefficient (α) obey the following relation for high photon energies ($h\nu$). The energy band gap was estimated by assuming direct and indirect bands using Tauc`s equation:

$$\alpha h\nu = B\left(h\nu - E_g\right)^n \tag{2}$$

where E_g is the band gap of the samples, $h\nu$ is the photon energy, B is band tailing parameter that depends on the electron-hole mobility and n is a constant which determines the type of transition ($n = 1/2$ and $(3/2)$ for direct allowed and forbidden transitions $n = 2$ and 3 for indirect allowed and forbidden transitions respectively) [22], [23].

2.2.2. Number of carbon atoms (N)

The number of carbon atoms (N) in a cluster is correlated to the optical band gap (E_g) The number carbon atoms per conjugated length N was calculated by modified Tauc`s equation [24]*:*

$$N = \frac{2\pi\beta}{E_g} \tag{3}$$

where 2β is the energy of a pair of adjacent π sites and β is taken to be ~2.9eV as it is associated with the $\pi \rightarrow \pi^*$ optical transition in the $-C=C-$ structure [1][24].

3. Results and discussions

3.1. Chemical properties

The molecular structures of both irradiated and non-irradiated polystyrene with gamma irradiation are performed using FTIR and Raman spectroscopy. FTIR spectra of non-irradiated PS and irradiated PS are shown in figure 1 at various at various time of exposure (a-f). FTIR spectrum of non-irradiated PS have characteristic band at 3100 - 3000 cm^{-1} corresponds to the =C-H stretching due to the aromatic ring, peaks at 2924 and 2846 cm^{-1} is attributed to the symmetrical and asymmetrical stretching vibration of CH_2, bands at 1602, 1490 and 1447 cm^{-1} correspond to stretching vibration of the C=C bond on the benzene ring, band at 1023 cm^{-1} correspond to C-O and bands at 902 cm^{-1} is assigned to the C-H out-of-plane bending vibration of the benzene ring [25]–[27]. Irradiated PS bands are found to be affected, bands reduced in intensity and become broader compared with non-irradiated PS which indicate the structural changes as a result of gamma irradiation. It's clearly shown that intensity of

band at 1602 cm^{-1} for samples (b-f) reduced due to gamma irradiation and also the band at 2924 cm^{-1} shifted 2951 for 2hr, 2979 cm^{-1} for 3hr and 3044 cm^{-1} for 5hr.

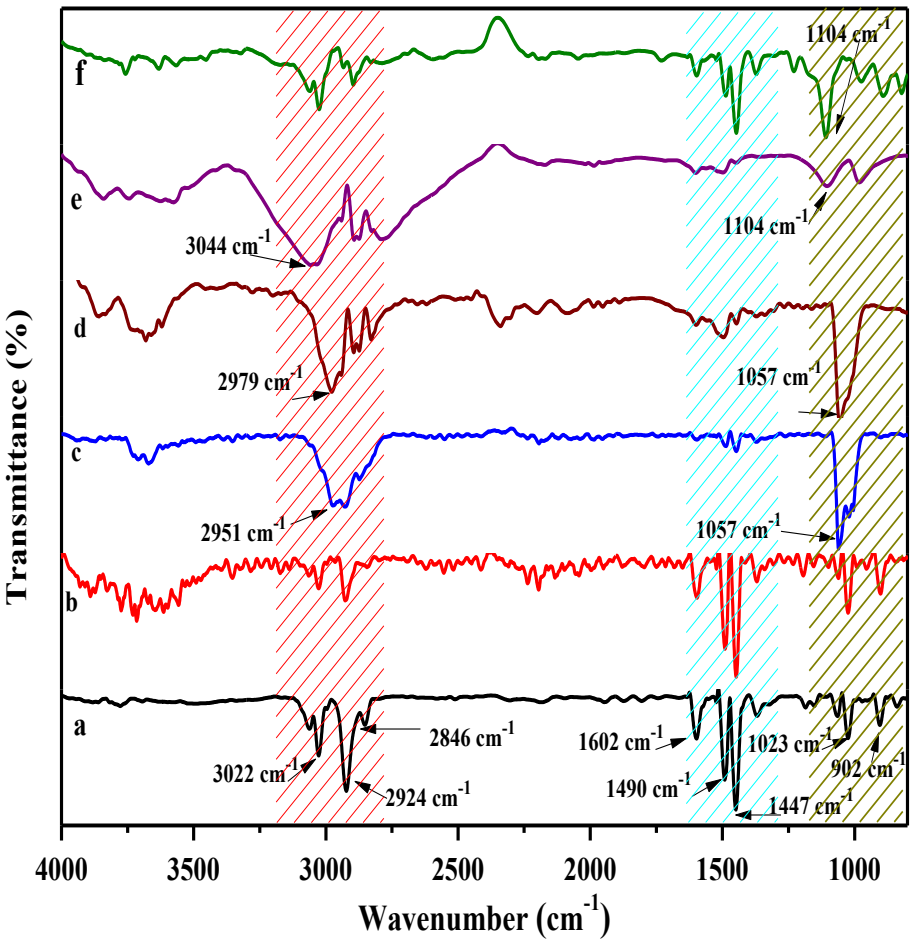

Figure 1. FTIR spectra of polystyrene at various time of exposure (a) non-irradiated PS, (b) 1hr, (c) 2hr, (d) 3hr, (e) 4hr, (f) 5hr gamma irradiation.

Raman analysis was performed using Raman micro spectrometers in backscattering geometry. Raman spectroscopy is a quick and non-destructive technique to analysis mainly carbon samples. Figure 2 (a-f) shows the Raman spectra of both non-irradiated and irradiated PS with gamma irradiation at different interval of time. Spectra peaks of polystyrene are present at 1002 cm^{-1} correspond to the aromatic breathing, peaks at 1030 cm^{-1} assigned to C-H bending, peaks at1602 cm^{-1} modes are the most intense band correspond to the C=C aromatic ring stretching and peak at 620 cm^{-1} assigned to ring deformation [28]–[32]. The non-irradiated PS spectrum reveals that peak at 1602 cm^{-1} is due to stretching of benzene rings, and increase intensity as the irradiation time increases.

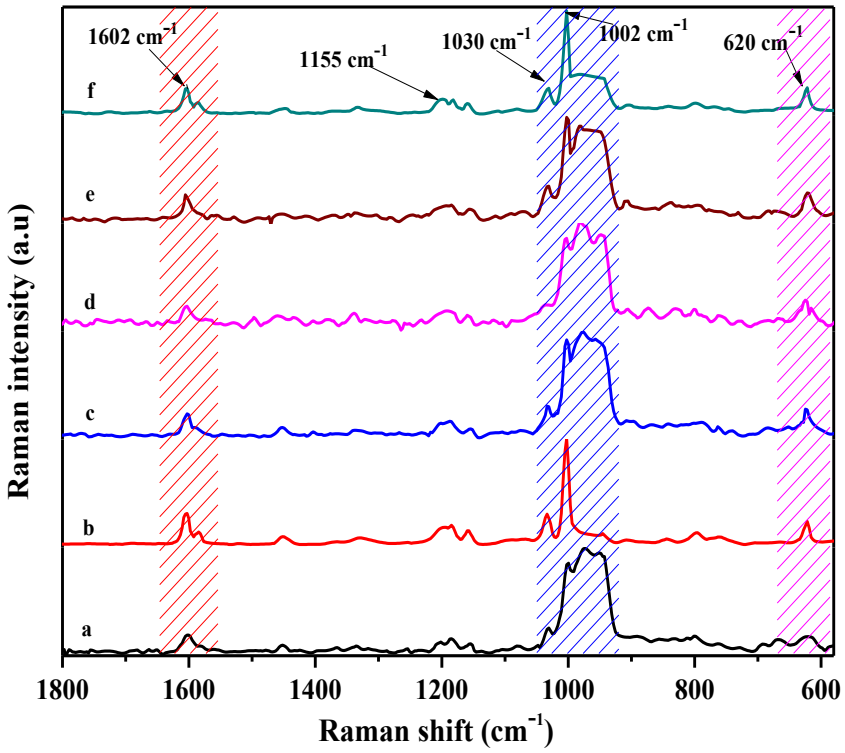

Figure 2. Raman spectra of polystyrene at various time of exposure (a) non-irradiated PS, (b) 1hr, (c) 2hr, (d) 3hr, (e) 4hr, (f) 5hr irradiation.

3.2. Morphology properties

Figure 3 (a-f) show top views of SEM images obtained for both non-irradiated and irradiated polystyrene respectively. Figure 3a shows the non-irradiated surface morphology of the PS film, it can be seen that a self-assembled monolayer of PS coated clearly formed in hexagonal shape arrangement on the silicon substrate. After irradiation at different time of exposure it revealed that the average diameter of individual PS beads reduced in size and shape, as the time of irradiation increase from 1-5 hours. However the original hexagonal lattice was maintained and become more carbonaceous material due to fragmentation formed between PS beads and also create gap in void. As reported in previous work, [4][5][33] the carbonization of polymers will produce volatile gases and the volume of polymers will decrease obviously due to loss of atoms [34]. Therefore evolution of the gap between each polystyrene bead as illustrated in figure 3(b-f).

Atomic force microscopy is a powerful tool for identify both surface morphology of the thin films and obtain information about the roughness, height asymmetries values such as the skewness and kurtosis of the films. The average roughness, root mean square (rms) and height asymmetry values are measured using a software analysis from AFM instrument and the results obtained are depicted table 1. It is appear from the table 1 that average roughness of the samples increases as the exposure time increases.

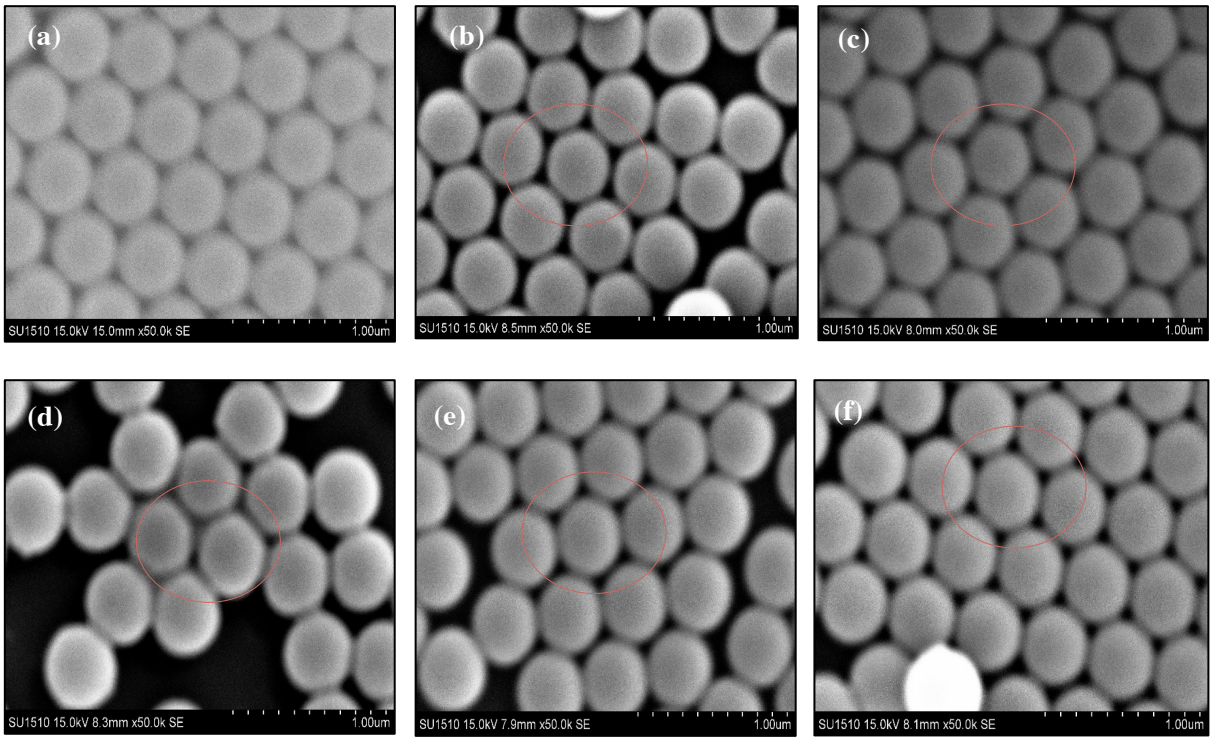

Figure 3. SEM images of polystyrene at various time of exposure (a) non-irradiated PS (b) 1hr (c) 2hr (c) 3hr (d) 4hr (e) 5hr gamma irradiation.

Figure 4 shows the AFM images obtained from both non-irradiated and irradiated polystyrene at various time of exposure. Figure 4a show that for non-irradiated PS many sharp and regular present over the whole substrate surface. The case is different for 3-5hr gamma irradiation their AFM images show significant change in topography compared to 1hr, 2hr and non-irradiated PS these could be caused by overexposure of gamma irradiation [35]. AFM results are also accorded with SEM results and optical measurements, and further confirm the enhancement of the chemical resistance of PS by gamma irradiation resulted to the formation of carbonaceous material.

Table 1: Statistical parameters of the irradiated polystyrene thin films at various time of exposure

Statistical parameters	Samples					
	Pure PS	1hr	2hr	3hr	4hr	5hr
Averege roughness (nm)	20.4	22.15	20.3	144.1	147.8	126.5
RMS roughness (nm)	23.8	30.5	27.6	162.5	166.9	153.9
Skewness S_{sk}	0.29	1.88	0.98	0.56	-0.48	0.87
Kurtosis S_{ku}	2.39	9.31	4.896	1.84	1.82	2.63

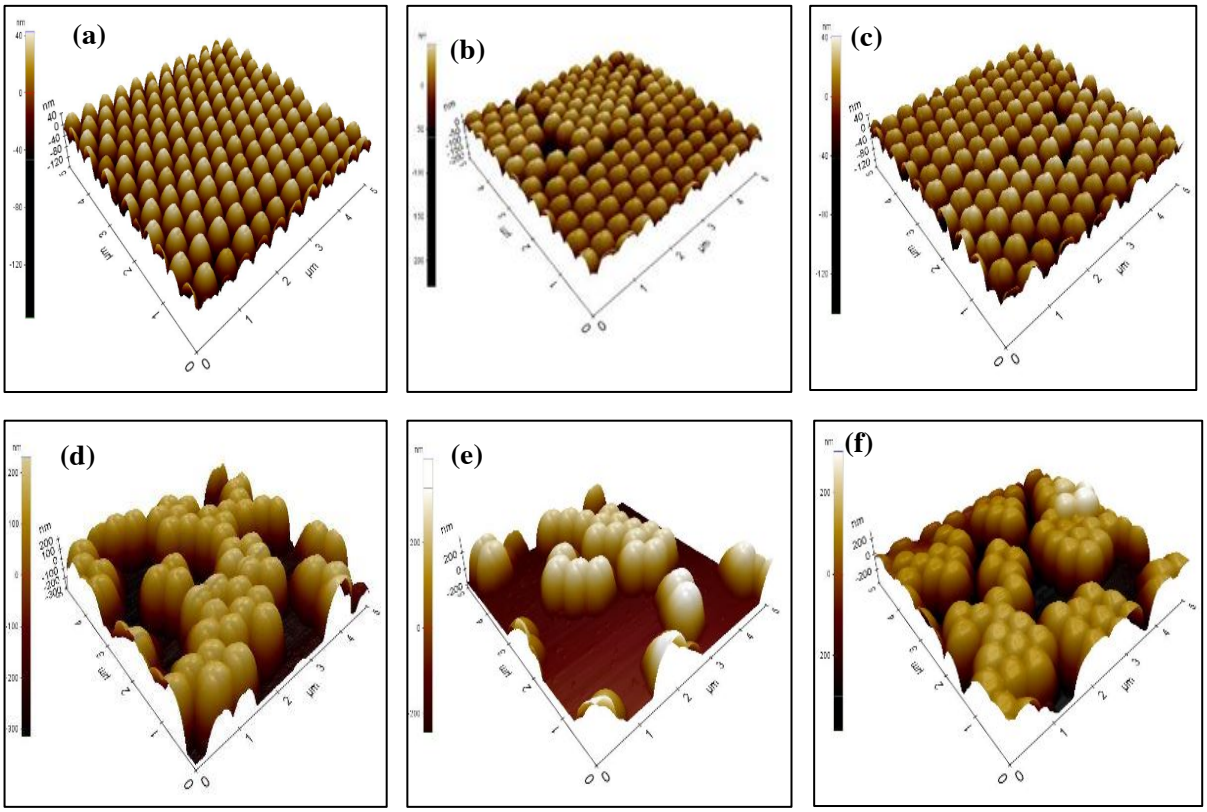

Figure 4: Atomic force microscopy images obtained from polystyrene at various time of exposure (a) topography of non-irradiated PS (b) topography of 1hr (c) topography of 2hr (c) topography of 3hr (d) topography of 4hr (e) topography of 5hr gamma irradiation of PS deposited on silicon substrate.

3.3. Energy band gap

The values of E_g at different time of exposure were estimated by extrapolation of the linear part of the plots to $(\alpha h\nu)^2 = 0$ from the curve of $(\alpha h\nu)^2$ versus $h\nu$ in the high absorption range are shown in figure 5. The values of energy band gaps (E_g) were listed in table 2. From results, the values of the optical energy band gap decreased with increase in time of exposure as observed in figure 5. This decrease in the optical energy values is due to creation of carbon enriched clusters to the partial evolution of hydrogen molecules. Also may be due enhanced diffusion rate of π-electron in the forbidden energy level of polymer formation of defects or creation of carbonaceous cluster. The results are in agreement with the results obtained by Sharma et al. [23].

Table 2: Show the values of estimated energy band gap and number of carbon atoms (N) in a cluster of both irradiated and non-irradiated polystyrene

Samples	Value of estimated energy band gap (eV)	Number of carbon atoms (N) in a cluster
PS	2.02	9
1hr	1.97	9
2hr	1.82	10
3hr	1.80	10
4hr	1.79	10
5hr	1.72	11

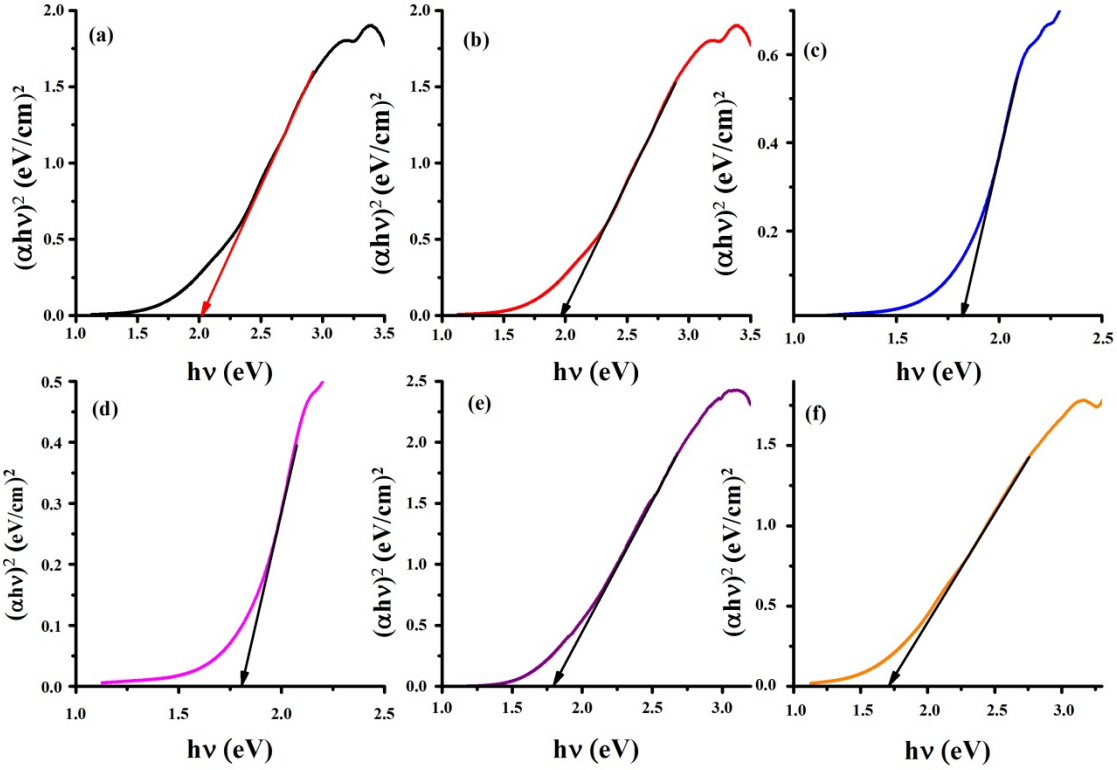

Figure 5: Energy band gap of polystyrene at various time of exposure (a) non-irradiated PS (b) 1hr (c) 2hr (c) 3hr (d) 4hr (e) 5hr gamma irradiation.

3.4. Number of the carbon atoms

The number of the carbon atoms increases with increasing irradiation time as depicted in table 2. This is attributed to the breakage of C-H bonds upon irradiation and the collapse or escape of hydrogen as hydrogen molecules, however, carbonaceous clusters are supposed to rich with charge carriers that enhance the optical properties in radiation bombarded polymers and they also influence the electrical conductivity of such materials [36].

4. Conclusions

Polystyrene nanosphere was successfully prepared by drop coating method onto substrate and treated by gamma irradiation different time (1-5 hours) with constant dose of 30 kGy. In this work, the overexposure of PS by gamma irradiation was systematically changing the morphology, chemical and optical properties of the samples. It was observed that irradiated samples reduce the average particles diameter and change the roughness of the samples as the irradiation time increases. The chemical properties revealed that the chemical resistance of PS by gamma irradiation resulted to the formation of carbonaceous material. The optical band gap of the thin films decreased with the increasing gamma irradiation time and polystyrene gradually undergoes crystallization from its amorphous state.

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