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Comparative Effect of Gamma Irradiation on the Nano-Free Volume and Electrical Properties of PVA/PEG/Reduced Graphene Oxide Nanocomposites

M. Mohsen[1], A. Ashry[2], A.M. Ismail[2], F. El-Sayed[2], D. M. Abd El-Maqsoud[2], K.R. Mahmoud[3]
(1)Physics Department, Faculty of Science, Ain Shams University, Cairo, Egypt.
(2)Physics Department, Faculty of Education, Ain Shams University, Roxy, 11711, Cairo, Egypt
(3)Physics Department, Faculty of Science, Kafrelsheikh University, 33516, El-Gaish Street, Kafr El-Sheikh,

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Reduced graphene oxide (RGO) doped polyvinyl alcohol/ polyethylene glycol (PVA/PEG) films were prepared by solution casting technique and exposed to 100 kGy gamma radiation. The structural modifications in the samples before and after irradiation were studied using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry DSC. The free volume holes V_f determined from the ortho-positronium (o-Ps) lifetime (τ_3) measured by the positron annihilation spectroscopy (PALS) is found to decrease from (84.52 to 67.24Å^3) and from (85.67 to 78.21 Å^3) for nonirradiated and irradiated samples respectively with increasing the nanoscale RGO filler content into the polymer matrix. The resulting decrease of the free volume holes size due to this incorporation could be explained by both the formation of hydrogen-bonding and crosslinking between RGO and PVA/PEG blend as confirmed by XRD and FTIR measurements. This also caused a decrease in the concentration of free volumes F_r for both nonirradiated and irradiated samples. The increased D.C. electrical conductivity with increasing RGO volume fraction (0–0.265) suggests a conductivity chain formation through the nanoparticle aggregation. The deduced Ln σ is found to be positively correlated with the probability of free annihilation of positrons I_2 trapped at crystalline-amorphous interfaces. The D.C. conductivity results could be successfully fitted using the model suggested by Miyamoto and Shibayama. The critical free volumes for the charge carriers transport has been deduced to be 80.34 and 82.16Å^3 for nonirradiated and irradiated samples respectively.

Keywords: *Nanocomposites; Reduced graphene oxide; γ-radiation; Free volume; Positron annihilation; D.C. conductivity*

Introduction

Over recent years, polymer nanocomposites have become the subject of extensive studies due to their promising novel properties compared to their individual components. Polymer blending and doping with nano-sized fillers will result in new nanocomposites with enhanced physical properties such as electrical and thermal conductivity, chemical stability, flexibility and easy processability [1-5]. Polyvinyl alcohol (PVA) is a semi-crystalline, water soluble and biodegradable polymer which has potential application owing to its stability and easy processability. The carbon chain backbone of PVA contains OH-groups, which serve in hydrogen bonding between neighbouring chain segments and allows homogeneous dispersion of numerous nanofillers [5,6]. Polyethylene glycol (PEG) is a water-soluble polymer and has a wide range of applications. The PEG chain was able to provide a micromer, that could be used in vinyl copolymerization, hydrogel system and surface modification. PEG has been considered a promising phase-change material for thermal energy storage and temperature control because of its relatively large heat of fusion, congruent melting behaviour, non-corrosiveness and wide melting point range [1].When both PVA

Corresponding author: donamy1510@yahoo.com

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and PEG are mixed, an interaction between them is expected through the formation of hydrogen bonds to form perfectly compatible and miscible blend. Reduced graphene oxide (RGO) is one of the most attractive nano-materials, because of its excellent electrical, thermal, mechanical, optical properties, and high transparency with high specific surface area[7]. It can be obtained in large quantities by the chemical reduction of graphene oxide which is synthesized by the oxidization and exfoliation of graphite. The produced RGO sheets must improve dispersibility in many polymer matrices and organic solvents. Due to the partial re-aggregation of the RGO sheets during processing, the surfactant agents or ultrasonic treatment are usually used to re-disperse the RGO sheets in the polymer matrix [6,7]. Gamma-radiation (γ-rays) plays an important role in altering and improving the properties of polymers and it is a useful technique to crosslink or degrade the desired component polymer or to fix the blend morphology through free radical formation at the boundary surface in the polymer blend phase [8]. It is well known that the exposure of polymers to γ-rays induces changes in structure and morphology and hence in chemical and physical properties. The irradiation of polymers (such as PVA and PEG) generates several charged species, ions, free radicals and induces either scission or cross-linking or both [9]. Bearing in mind that gamma-irradiation reduces the production cost and avoid the use of chemical cross-linkers [10]. Defects in polymer and polymer nanocomposites are in the form of atomic scale local free volume holes. The presence of these holes in semicrystalline polymers, such as PVA and PEG, increases the crystalline phase density at the expense of the amorphous phase density. This in turn influences the mechanical, electrical, optical and thermal properties of these polymers.

One of the most important techniques in measuring free volume size, concentration and distribution in polymers is positron annihilation lifetime spectroscopy (PALS). When positrons are injected into polymers, they lose their energy through elastic collisions and finally annihilate with electrons. Several annihilation mechanisms are possible, namely annihilation of free positrons with orbital electrons, pick-off annihilation of positrons which have formed ortho-positronium (o-Ps), self-annihilation of para-positronium (p-Ps), and possibly, annihilation of positrons which have formed a bound state with the molecules of the system. Furthermore, the decay rates corresponding to some of the mechanisms may vary within the system depending on the local environment. The lifetime (τ_3) and the intensity (I_3) of the long-lived component in polymers are contributed by the ortho-positronium (o-Ps), which has a close relationship with the size and concentration of the free volumes. PALS is an ideal nuclear non-destructive technique for the detailed study of polymers and polymer blends as well as nanocomposites [11,12]. In this work, the authors aimed to synthesize RGO doped polymer composite based on PVA and PEG using the solution casting processing method and study the effect of the different percentages of RGO on the physical properties of the PVA/PEG blend before and after exposure to 100 kGy of γ-radiation. In addition, a correlation is established between the obtained structural and electrical properties with the nano-scale free volume properties measured by the positron annihilation spectroscopy (PAS).

Experimental details

Materials and sample preparation

(PVA) used in this study was purchased from Alpha chemika co.(India) with an average molecular weight (Mw) of 125,000 g mol^{-1}. (PEG) had an average Mw of 6000 g mol^{-1} and was purchased from Nice Chemicals Co.(India). The synthesis of (RGO) was achieved by the chemical reduction of graphene oxide using two different reducing agents. The starting graphene oxide was prepared using Hummer's method [13]. Graphene oxide was then chemically reduced using hydrazine hydrate and sodium borohydride [14,15]. The obtained RGO was in the form of powder with average particle size length of 1 to 3 µm and thickness of 1 to 5 nm.

PVA/PEG/RGO nanocomposites with a composition of 75% PVA and 25% PEG and loaded with different volume fractions of RGO (0 – 0.265) were prepared using solution casting method. PVA powder was initially dissolved in distilled water at 70 °C with a magnetic stirrer for 24 h till a clear and homogeneous solution is obtained. Then PEG powder was dissolved in distilled water at room temperature in a separate glass beaker. The PVA and PEG were mixed together using a magnetic stirrer at room temperature for 4 h. RGO - powder was also dispersed in distilled water in a separate beaker by a magnetic stirrer for 6 h. The RGO- solution and PVA/PEG composites were mixed together by vigorously stirring for 6 h until the uniform dispersion of graphene in the polymer matrix is obtained. Finally, PVA/PEG/RGO solution was casted onto a glass Petri dish and dried in a hot air oven at 40 °C for 5 h. The thickness of the obtained composite films was in the range of (0.22 – 0.36 mm).

Measurements

Positron lifetime measurements were performed using a fast-fast coincidence spectrometer (ORTEC) [16,17] with a resolution of ~350 ps, which was determined using a ^{60}Co source at room temperature. The positron source was 15 mCi of ^{22}Na deposited on a thin Kapton foil and placed between two sandwiched samples. In general, 2-3 measured spectra for each pair of samples differed by a total number of elementary annihilation events in the range of 1-1.5 million counts. The obtained spectra were analysed by LT computer program of Kansy[18], with a suitable correction for the positrons annihilated in the Kapton. The measured positron lifetime annihilation (PAL) spectra were resolved into three components. The first lifetime component (τ_1, I_1) is attributed to the self-annihilation of p-Ps and the free annihilation of positrons in the bulk. τ_1 has very weak interaction with the environment so it was kept fixed during the analysis. The intermediate lifetime component (τ_2), having intensity I_2, is associated with annihilation of positrons trapped by defects present in the crystalline regions and positrons trapped in the crystalline–amorphous interface regions of the polymeric material. The longest lifetime component (τ_3) is related to the annihilation of ortho-positronium (o-Ps) by “pick off” in free volume sites present in the amorphous region of the solid matrix. The intensity (I_3) is a measure of o-Ps formation probability, and the concentration of free volume holes [11,19,20,21].

The o-Ps lifetime (τ_3) directly correlates with the size of the free volume holes by using the Tao–Eldrup semi-empirical equation [22,23]; the cavity hosting of Ps is assumed to be a spherical void with effective radius R. The relationship between τ_3 and radius R is as the following:

$$\tau_3 = 0.5\left[\frac{\Delta R}{R+\Delta R} + \frac{1}{2\pi}sin\left(2\pi\frac{R}{R+\Delta R}\right)\right]^{-1} \qquad (1)$$

where the units of R and τ_3 are Å and ns, respectively and ΔR =1.656 Å for polymers and is derived from fitting the observed o-Ps lifetimes in molecular solids with known hole sizes. Furthermore, the fractional free volume F_v is evaluated in terms of the o-Ps intensity I_3(which correlates with the concentration of free volume holes) and the size of free volume hole ($V_f = \frac{4\pi R^3}{3}$) by the equation:

$$F_v = C\, V_f\, I_3 \qquad (2)$$

where C is a proportionality constant. Jean et al. have estimated the value of $C = 0.0018$ nm^{-3} using many polymers. The value of C cannot be used for all the polymers due to variation in their chemistry and hence, the relative fractional free volumes calculated using C = 1 nm^{-3}[24]. Usually, we use relative fractional free volume F_r where,

$$F_r = \frac{F_v}{C} = V_f I_3 \qquad (3)$$

All these components were determined by the fit's variance ranged from 0.96 to 1.14. The experimental errors for the PAL parameters τ_3, I_3, determined over multiple measurements, were found to be 25 ps and 0.86%, respectively.

X-ray Diffraction (XRD) pattern and crystalline structure of the prepared samples were determined from X-ray Diffractometer (Philips xpert MPD) equipped with Cu Kα as a radiation source of (λ = 1.54Å). Fourier transform infrared spectra (FTIR) measurements were collected using Nicolet instrument (Model 6700, USA) in the absorbance mode at a resolution of 4 cm^{-1}.Differential scanning calorimetry (DSC) thermograms were carried out at the temperature range from 0°C up to 400 °C by using Shimadzu 50, differential scanning analyzer with a scanning speed of 5°C/min, with a heating rate of 10°C/min under nitrogen atmosphere. D.C. electrical conductivity measurements were performed on samples in the form of discs of radius of (5 mm) and thickness of about (0.22 - 0.39 mm). Conductive silver paste was applied on the flat surfaces of the samples for proper contact with the electrodes of the D.C. electrical circuit; the electrical resistivity was measured by using a digital electrometer - Keithley 6512. Gamma Irradiation of the samples with dose of 100 kGy, was carried out in a ^{60}Co γ-cell (Indian gamma cell - Gu 4000 A) at the National Center for Radiation Research and Technology, Cairo, Egypt. Irradiation was carried out under atmosphere at a dose rate 1.553 kGy/h.

Results and Discussion

Positron annihilation lifetime spectroscopy (PALS)

Lifetime spectra for the samples of PVA/PEG doped with different amounts of RGO before and after exposure to 100 kGy of γ-radiation have been analysed using LT program to obtain free volume parameters $\square_3$ and I_3. $\square_3$ is found to decrease from (1.849 to 1.645 ns) and from (1.862 to 1.776 ns) for nonirradiated and irradiated samples respectively with increasing the nanoscale RGO filler to the polymer matrix. Fig. (1) shows V_f and F_r that were calculated by using eq. (1) and eq. (3) respectively as a function of RGO volume fraction. It is noticed, that V_f decreases from (84.52 to 67.24 Å^3) and from (85.67 to 78.21 Å^3) for nonirradiated and irradiated samples respectively. This can be explained by either the formation of hydrogen-bonding or a crosslinking between RGO and PVA/PEG blend, which lead to a weak decrease in F_r or the concentration of free volumes [2,25] for both nonirradiated and irradiated samples. The decrease in F_r is caused by restriction on the segmental motion of the PVA/PEG/RGO composites [26]. Also, the irradiated samples have higher values of V_f than those of the nonirradiated samples while the values of the irradiated F_r are lower than those of the nonirradiated ones which can be explained as the γ-radiation inhibits the formation of o-Ps due to cross linking, resulting in decreasing the o-Ps concentration F_r. However, the dissociation of the hydrogen bonding, that are formed between RGO and PVA/PEG results in increasing V_f [11,19,25]. The presence of nanofillers in polymer matrix is found to affect the free volume characteristics since the nanoscale offer a large surface area for interaction with the organic polymer matrix. This leads to creation of a spatial region of finite thickness (interphase) around the nanofillers with the altered free volume characteristics. The free volume available in interphase region mainly depends on the interaction between polymer molecules and the nanofillers. In case of semicrystalline polymers, nanofillers can act as nucleating agents reducing the chain mobility [24]. This leads to a decrease in the free volume in the polymer matrix. Depending on the type of polymer and nanofillers, the chain packing required for crystallization of the polymers may be disrupted due to the presence of the nanofiller. This would lead to expected decrease in crystallinity as will be confirmed by XRD and FTIR measurements. Fig. (2) shows a decrease in τ_2 from (0.5322 to 0.4078 ns) and (0.517 to 0.4205ns) for nonirradiated and irradiated samples respectively with increasing the RGO content respectively due to the crosslinking. However, the probability of free annihilation of positrons I_2 trapped at crystalline-amorphous interfaces increases.

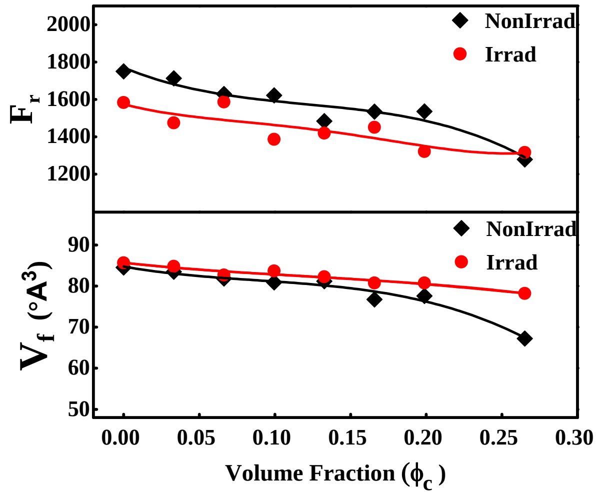

Fig. (1): The dependence of (a) V_f and (b) F_r on the RGO volume fraction before and after irradiation

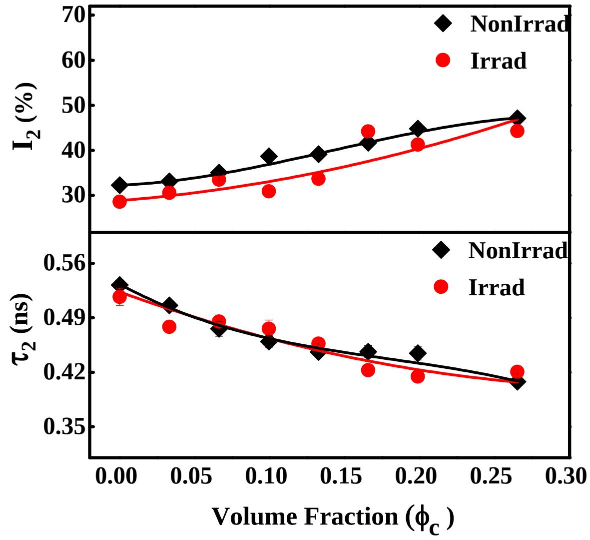

Fig. (2): The dependence of (a) τ_2 and (b) I_2 on the RGO volume fraction before and after irradiation

X-ray Diffraction (XRD)

XRD diffractograms of PVA/PEG filled with different amounts of RGO before and after exposure to γ-irradiation of 100 kGy are shown in Fig.(3). These patterns show two characteristic diffraction peaks at 2θ = 19.59° and 23.14° corresponding to PVA and PEG, respectively followed by few weak signals at higher angles. These features are indicative of a semi-crystalline polymer [27]. No detection of peak corresponding to reduced graphene oxide (RGO) which could be due to the low volume fraction of the fillers in the composites and indicates a complete exfoliation of the graphene layers, and homogeneous dispersion in the PVA/PEG matrix with no restacking of the layers after drying [28]. The XRD results of PVA/PEG filled with different amounts of RGO before and after exposure to 100 kGy of γ-radiation are shown in Table (1).

The observed changes in the diffraction patterns with adding RGO and exposure to γ-irradiation can be quantitatively studied in terms of the degree of crystallinity, χ_c%, which can be calculated from the following equation [29]:

$$\chi_c\% = \frac{\Sigma A_{cryst}}{\Sigma A_{cryst}+\Sigma A_{amorp}} \qquad (4)$$

where, A_{cryst} and A_{amorp} are the fitted areas of the crystal and amorphous phases respectively. The variation of χ_c **%** as a function of RGO content for nonirradiated and irradiated samples is shown in Fig.(4). From this figure, it's obvious that the degree of crystallinity χ_c% decreases with the incorporation of RGO and this can be explained by the formation of hydrogen bonds between RGO and the polymer matrix resulting in the crosslinking between polymer chains and RGO nanoparticles. However, the exposure of samples to 100 kGy γ-radiation is seen to be sufficient to break these hydrogen bonds and consequently increase the crystallinity rather than that of the nonirradiated samples. The variation of the degree of crystallinity χ_c% is shown to be consistent with the changes in the free volume size V_f as seen in Fig.(5). The complexation due to hydrogen bonds between the polymer chains and RGO nanoparticles leads to the formation of crosslinks entanglements and filling the open free volume holes and hence a decrease in both crystallinity and free volume takes place.

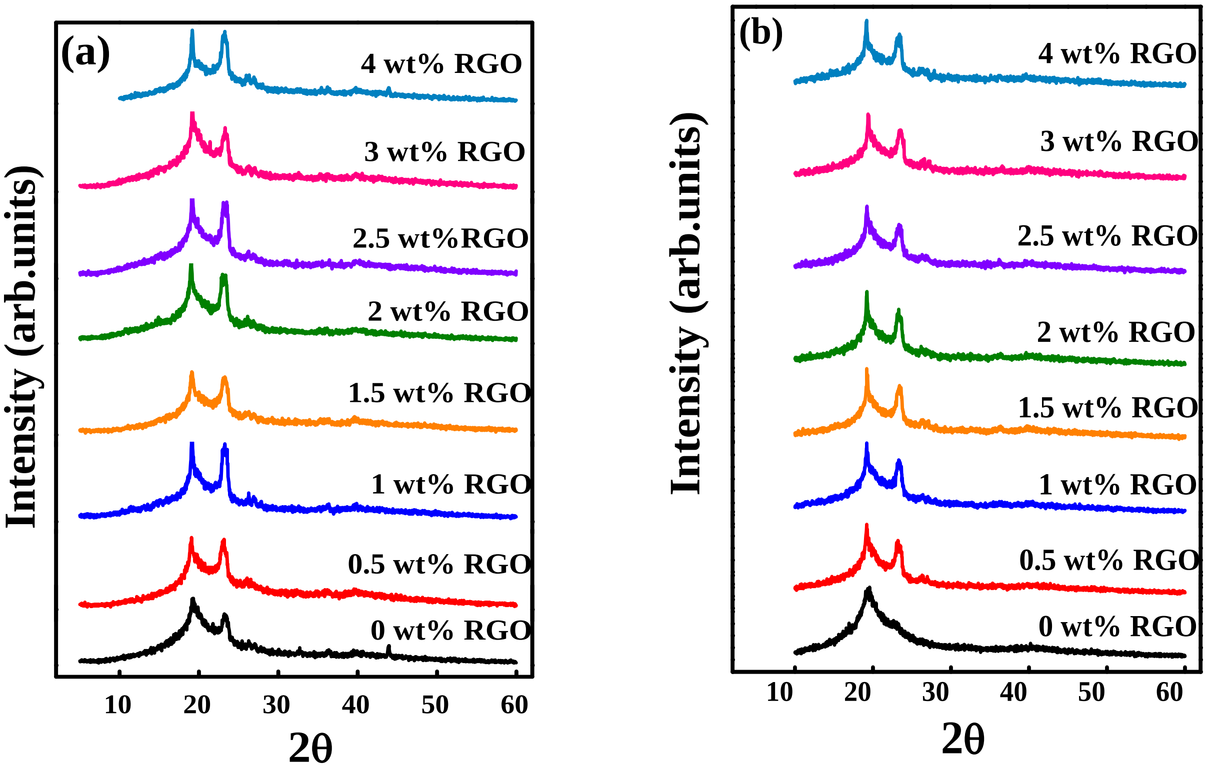

Fig. (3): XRD diffractograms for (a) nonirradiated and (b) irradiated PVA/PEG samples doped with different amounts of RGO

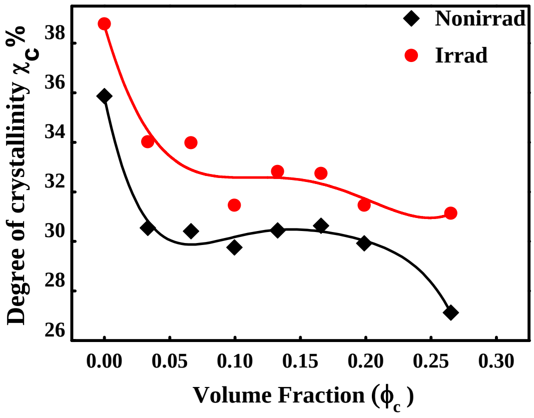

Fig. (4): The dependence of χ_c % on the RGO content for nonirradiated and irradiated samples

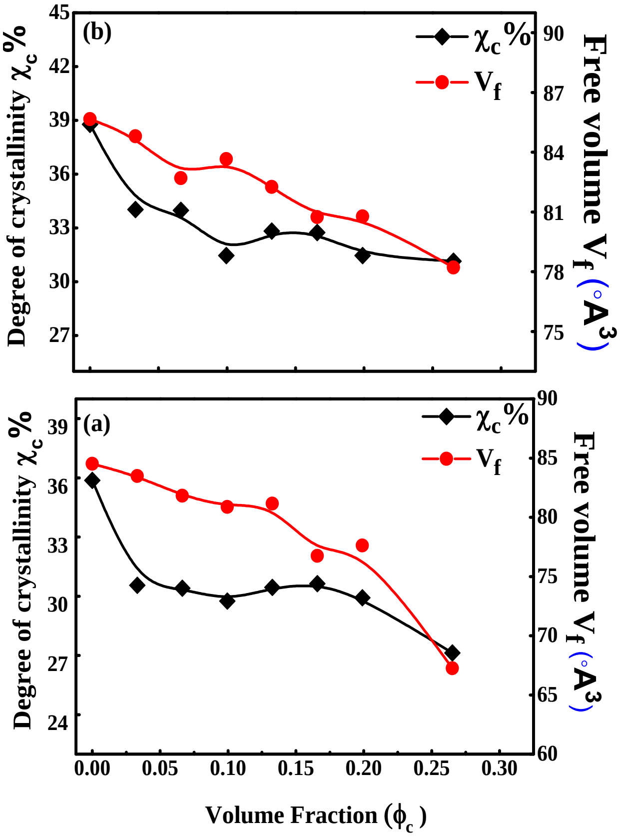

Fig. (5): The variation of χ_c % and V_f with the RGO volume fraction for(a) nonirradiated and (b) irradiated samples

The inter chain distance (d) in the polymer crystalline phase can be calculated from the XRD patterns using the position of the maximum of the first diffraction peak and Bragg's law:

$$d = \frac{n\lambda}{2\,sin\theta} \qquad (5)$$

The values of d agree with the values of the diameter of the nanopores (D) that are calculated from positron annihilation data, within the experimental error. Here the average distance between amorphous segments is the diameter of the nanopores (D = 2R), whose value can be estimated from the PALS results using equation (1). The estimated results of D and d are listed in Table (1). It's found that there's a slight difference between the values of d and D of these methods[30]. This slight difference may be due to the fact that, PALS method is sensitive not only to the static open volume holes but also to the holes living for short times, while the XRD measurements give the average distance between molecules.

. Fourier Transform Infrared (FTIR) Spectroscopy

The infrared (IR) spectrum of PVA/PEG polymer blend doped with different amounts of RGO before and after exposure to γ-radiation at a dose of 100 kGy are shown in Fig. (6). The waves of the absorption bands together with their structural assignments are listed in Table (2). The O-H stretching vibration region which is the most characteristic feature of alcohols and esters is found to be broad and strong band located between 3382 and 3620 cm^{-1}resulting from the stretching vibration of hydroxyl group with strong hydrogen bonding. Two strong peaks at 2949 and 2869 cm^{-1} are the characteristic bands of asymmetric and symmetric aliphatic C–H stretching respectively [31-34]. An absorption band due to C=O stretching of the ester group of the nonirradiated PVA can be seen between 1642 and 1743 cm^{-1}. Whereas the characteristic infrared peak of C=C appeared at 1571 cm^{-1}. The C=C may be a result of crosslinking results from heating the polymer through sample preparation. The values of C=O and/or C=C indicate the presence of hydrogen bond with oxygen of C=O group [34,35]. Two absorption peaks were observed at 1483cm^{-1} which is assigned as CH$_2$ bending vibration and 1371cm^{-1} which is associated to the deformation vibration of C–CH$_{3.}$ The absorption shoulder at 1247 cm^{-1}is arising from CH$_2$ wagging. The absorption band at 1010 cm^{-1}arises from the C–O stretching vibration while the band at 809 cm^{-1} results from C–C stretching vibration.CH$_2$ rocking was found at 901 cm^{-1} and OH wagging was found at 701 cm^{-1} and

Table (1): The XRD parameters, the inter chain distance (d) and the diameter D from positron annihilation and the degree of crystallinity χ_c% for nonirradiated and irradiated samples

RGO volume fraction (ϕ_c)	Nonirradiated				Irradiated			
	2θ PVA	**2θ PEG**	**d (Å)**	**D (Å)**	**2θ PVA**	**2θ PEG**	**d (Å)**	**D (Å)**
0	19.59	23.12	4.188	5.445	19.58	22.98	4.188	5.470
0.033	19.71	23.01	4.180	5.423	19.46	23.18	4.180	5.451
0.066	19.33	23.2	4.208	5.387	19.46	23.25	4.208	5.406
0.099	19.59	23.15	4.188	5.366	19.49	23.313	4.188	5.427
0.132	19.17	23.07	4.238	5.372	19.44	23.28	4.23	5.396
0.165	19.39	23.19	4.211	5.273	19.50	23.26	4.211	5.363
0.198	19.56	23.14	4.191	5.293	19.76	23.44	4.191	5.364
0.265	19.74	23.17	4.171	5.046	19.30	23.21	4.171	5.306

C–O bending vibration was found at 543 cm^{-1}[32-34]. The incorporation of RGO affects the -OH stretching band which is located between 3382 cm^{-1} and 3620 cm^{-1} as it became weaker and new sharp peaks have been created. It is known that both the -OH stretching and the –C–OH stretching bands are sensitive to the hydrogen bonding degree. So that, this behaviour has been attributed to the formation of hydrogen bonding among the hydroxyl groups in the polymer and RGO. Furthermore, the band assigned to the –C–OH stretching (around 1010 cm^{-1}) displayed a similar behaviour, as it shifted towards higher values of wave numbers with increasing in its relative intensity which indicates and ensures the hydrogen bonding formation between the -OH in the polymer blend and the oxygenated groups remaining in RGO [33,36]. Another feature has been induced which is that the relative intensity of the band at 1571 cm^{-1}increases with the increase of RGO content which may be attributed to the crosslinking results from heating through sample preparation and anew absorption band at 1651cm^{-1}grew at the expense of the absorption band at 1642cm^{-1}which was found to decay with increasing RGO content. The addition of RGO decreases the crystallinity of the polymer Fig. (6). The band around 1111 cm^{-1} has already been related to the crystallinity of the polymer blend. The relative intensity of this band decreases as the amount of RGO increases showing the same trend described by the shifts of the C–OH and -OH bands. These results may reinforce the hypothesis for the existence of hydrogen bonding between the polymer and the filler, to the detriment of hydrogen bonding among polymer chains, that diminishes the crystallinity [32,36]. From Fig.(6), it's clear that we have two structural mechanisms, which appeared after the exposure to γ-radiation : the first is the disappearance of the absorption peak at 1571 cm^{-1}for the 0 wt% RGO sample, which can be attributed to some sort of –C=C–structure deformation and/or chain scissions of the polymer. The second is the appearance of the -OH stretching band, which is located at 3382 cm^{-1} becoming weaker sharp peaks and ensures the dissociation of the hydrogen bonding among the hydroxyl groups in the polymer and between the polymer and the RGO. Furthermore, the band assigned to the –C–OH stretching also has been decayed. Also, it seemed that the irradiation increases the crystallinity since the intensity of the band around 1111 cm^{-1}which is correlated to the crystallinity has been increased and became sharper than the nonirradiated ones. This result is in good agreement with those of XRD pattern [3,32]. Fig.(7) shows a simple illustration of how the residual carbonyls and hydroxyl group son RGO forms hydrogen bond with PVA/PEG chains resulting in molecule-level dispersion of RGO in the polymer matrix and strong interfacial adhesion between them. On the other hand, in the γ-radiation process, high-energy γ-rays interact with PVA/PEG molecules leading to chain session and produce electrons, ions, free radicals and excided molecules. Another important effect of γ-radiation is the breaking of hydrogen bonding structure between RGO and PVA/PEG chain segments that lowers the crosslinking role of RGO filler.

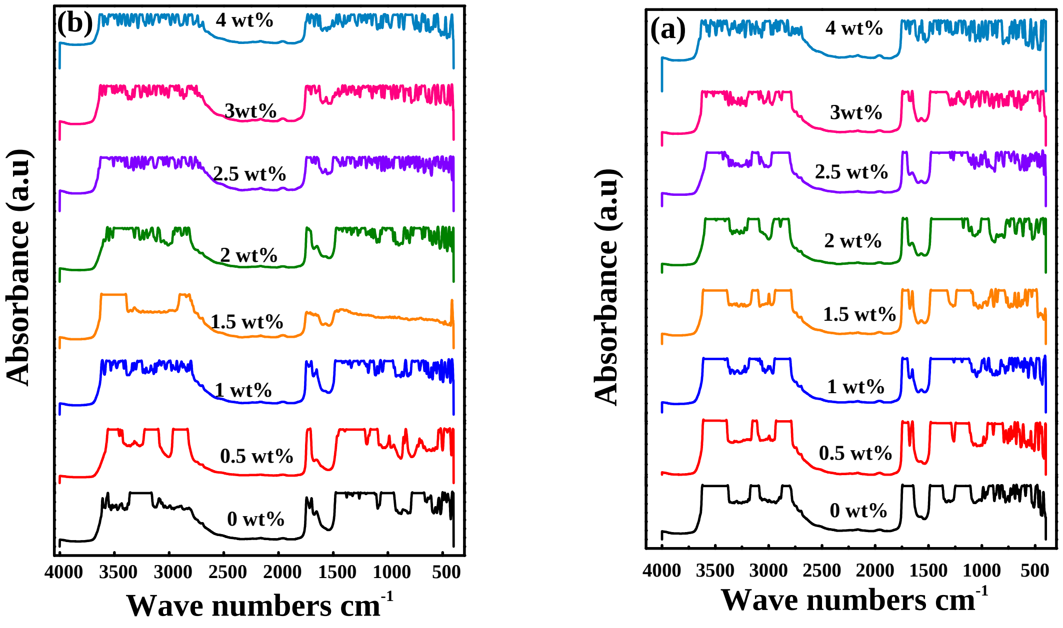

Fig. (6): FTIR spectrum for (a) nonirradiated and (b) irradiated PVA/PEG samples filled with different amounts of RGO

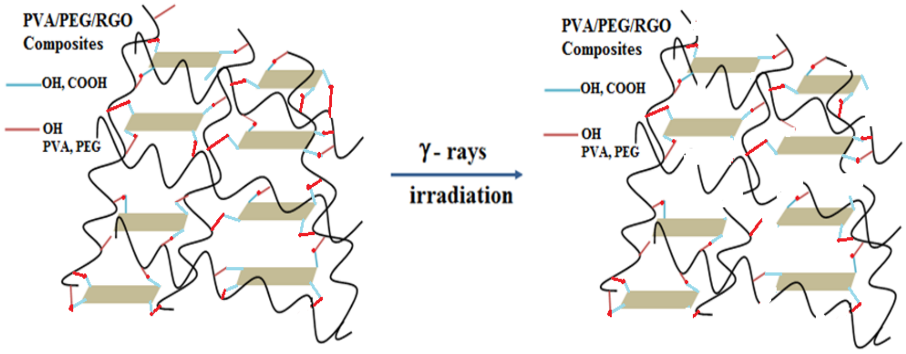

Fig. (6): Fig. (7): Proposed structure of PVA/PEG/RGO composite before and after irradiation with γ-rays

Table (2): The obtained IR absorption bands and their assignment of the nonirradiated pure PVA/PEG

Assignment	Band position(cm^{-1})
OH stretching	3382-3620
CH2 assymetric stretching	2949
C–H symmetric stretching	2869
C=O stretching	1743
C=O stretching	1642
Conjugated C=C stretching	1571
CH2 bending vibration	1483
C–H symmetric stretching	1371
CH2 wagging	1247
C–O stretching vibrations	1010
CH2 rocking	901
C–C stretching	809
OH wagging	701
C–O bending vibrations	543

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) thermograms of PVA/PEG doped with different amounts of RGO before and after exposure to 100 kGy of γ-radiation are shown in Fig(8).The glass transition temperatures, T_g are observed in the range of (64–53 °C). The values of T_g were found to be in the same range after irradiation. See Table (3). It's also seen that the addition of RGO causes an increase in the T_g temperatures compared to that of the pure PVA/PEG, which could be ascribed to the semi-crystalline nature of the PVA in which high physical interactions between the polymer chains exist besides the hydrogen bonding between the RGO layers and the polymer matrix[32]. The DSC thermograms also showed an endothermic peak that assigned to the melting of crystalline fraction of the polymer blend [30]. The melting temperatures (T_m) was measured at the position of the peak maximum and it shows that the T_m shifts towards lower values with the addition of the RGO which reflects in a decrease in the crystalline thickness because of the physical crosslinking[31] and the formation of hydrogen bonds between the polymer matrix and RGO.

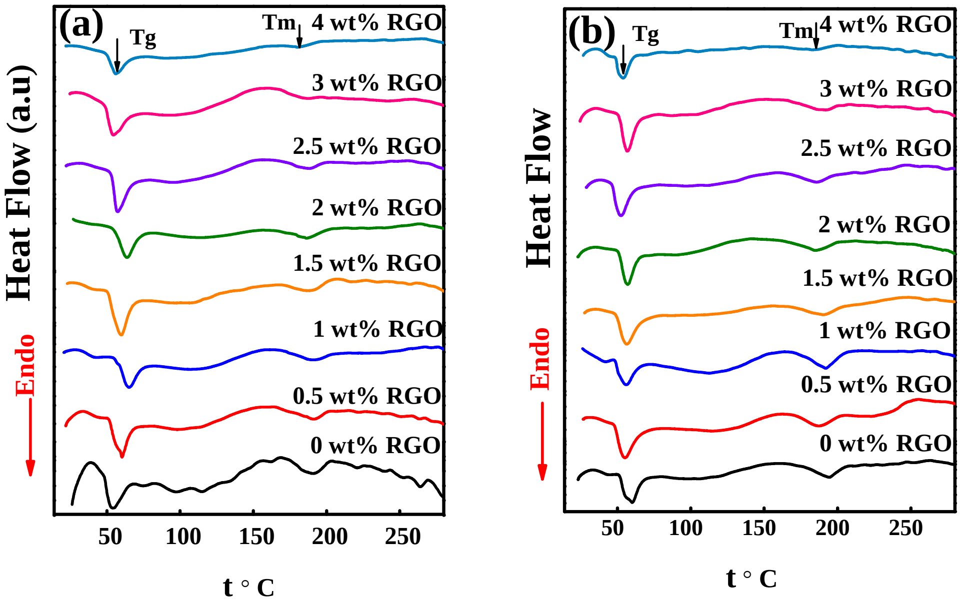

Fig. (8): DSC thermograms for (a) nonirradiated and (b) irradiated PVA/PEG samples doped with different amounts of RGO

Table (3): The values of glass transition temperatures (T_g) and melting temperatures (T_m) for nonirradiated and irradiated samples

RGO volume fraction (ϕ_c)	Nonirradiated		Irradiated	
	T_g °C	T_m °C	T_g °C	T_m °C
0	53.737	190.592	60.14	194.55
0.033	60.18	191.17	55.27	187.13
0.066	64.16	191.586	56.14	191.98
0.099	59.36	187.91	56.3	190.65
0.132	62.5	185.3	57.15	184.93
0.165	57.023	188.015	52.46	185.61
0.198	54.39	187.24	56.65	191.98
0.265	55.99	179.51	54.04	182.27

D.C. Electrical Conductivity

The dependence of the D.C. electrical conductivity (σ) of PVA/PEG polymer on the RGO volume fraction before and after exposure to γ-radiation is shown in Fig.(9). At very low loading of the filler, a slight increase in the conductivity is observed. As the filler content is increased, in a certain region which is called the percolation region, the conductivity increases rapidly by many orders of magnitude. At sufficiently high content, the conductivity reaches a value which is approximately equal to the conductivity of the filler [7,30]. In fact, when the amount of loading is increased in the polymer matrix a discrete chain structure is formed in the nanostructure holes and the conductivity begins to be observed. On further increase of loading, a continuous conductive network forms by physical contact of the filler particles through which the charge species can move from one end to the other end under an electrical field showing a stable conductivity. So, at higher content, at or above the percolation limit (when continuous conductive networks are already formed), the conductivity of the composite mainly depends on the conductivity of the filler particles rather than on their ability to form a continuous conductive network through aggregation. Thus, the conductivity depends on the structure, particle size, surface area and the porosity of the filler at or above the percolation limit [20,37,38]. Also, the irradiated samples gave low values of conductivity since, irradiation broke the physical bonding that are formed by the RGO and the polymer matrix.

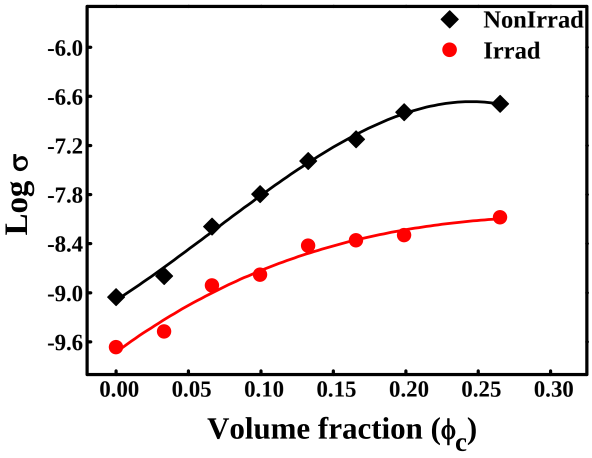

Fig. (9): The dependence of D.C. electrical conductivity on the filler volume fraction(ϕ_c)

The D.C. conductivity of polymer systems where one phase is an insulating polymer matrix and the other phase is conducting filler particles can be predicted by different theoretical models.

Voet model

Voet model is associated with the possibility of non ohmic electrical conduction in polymer-filler conducting composite systems where the conducting fillers are incorporated in the insulating polymer matrix. The concept is that the electrical conduction in polymer composite system not only takes place through inter particle contact; rather, it also takes place due to theelectronic emission occurs between adjacent conducting particles where the inter particle gap is smaller than or equal to 10 Å. Thus, the non ohmic conduction (electronic emission) also governs the electrical conductivity in polymer composite systems. The equation based on Voet model is given as follows [39]:

$$\log \sigma = k\,(\phi_c)^{1/3} \qquad (6)$$

Where σ is the conductivity of the polymer composite system, k is a constant and ϕ_c is the volume fraction of filler. The plot of log σ against $(\phi_c)^{1/3}$ should be a straight line. Fig. (10) exhibits that initially the increase in conductivity with the increase in $(\phi_c)^{1/3}$ is slow followed by sharp increase in conductivity at a critical point. Then the increase in conductivity becomes marginal with the further increase in volume fraction of filler. This type of phenomenon has been explained earlier based on percolation theory. The critical value $(\phi_c)^{1/3}$ at which there is sudden increase in conductivity is coinciding with the percolation threshold of this composite system. As a result, Voet model is not applicable to the entire range of the volume fraction of filler; especially, at and beyond the percolation threshold. Actually, what is happening here is that before percolation the conductive particles are separated from each other and hence the electrons are hoped from one conductive site to another which account for non ohmic conduction in the composite system. Thus, it is observed that the Voet model is applicable before the percolation threshold. At and beyond the percolation, due to the direct contact between the particles, the electrons do require jumping from one conductive site to another, and hence Voet model is not applicable in this region [40].

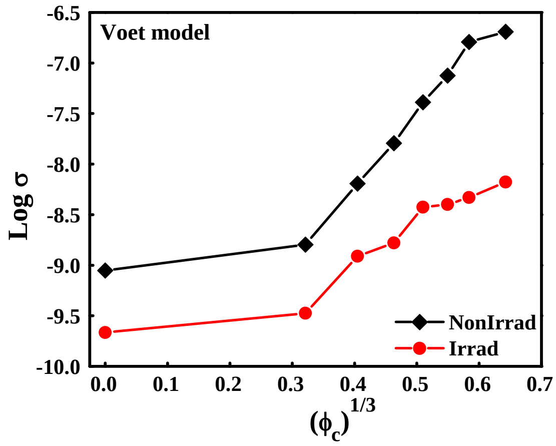

Fig. (10) Theoretical plot of Log σ based on Voet model

Chodak and Krupa model

The data collected from The D.C. conductivity measurements were fitted with the empirical formula [41]

$$\log\frac{\sigma_c}{\sigma_m} = B(1 - e^{-a\phi_c})^n \qquad (7)$$

where, B, a and n are adjustable parameters, $\sigma_c$is the electrical conductivity of composites, σ_m is the electrical conductivity of polymeric matrix and ϕ_c is the volume fraction of filler. An inflexion point (ϕ_i) of this dependence which was identified with percolation concentration (ϕ_p) is determined via curve fitting procedure according to the following equation:

$$\phi_i = \phi_p = \frac{\ln(n)}{a} \qquad (8)$$

and the parameter B can be approximately expressed as

$$B = \log\left(\frac{\sigma_{c,max}}{\sigma_m}\right) \qquad (9)$$

Where $\sigma_{c,max}$ is the electrical conductivity of composites at maximum experimentally used concentration of the filler. The ratio (σ_c/σ_m) of the PVA/PEG /RGO composites as a function of the volume filler content (ϕ_c) is shown in Fig. (11). The points represent the experimental data and the solid line shows the empirical fitting curve obtained by applying Eq. (7). The parameters B, n, a are listed in Table 4.The results show that there is a slight difference between the experimental and the calculated for both nonirradiated and irradiated samples.

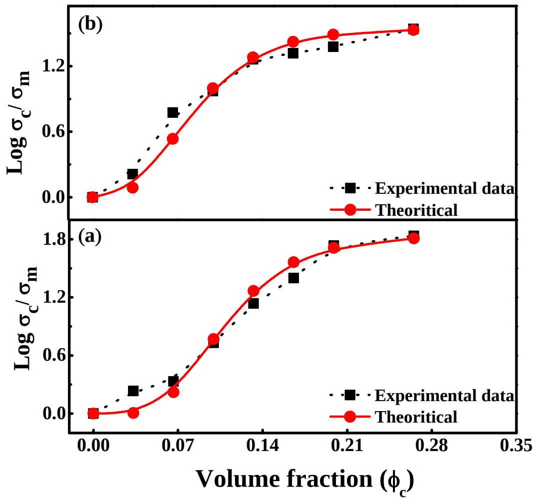

Fig. (11): The relation of log (σ_c/σ_m) of the PVA/PEG composites as function of the RGO volume fraction (φ_c) for (a) nonirradiated and (b) irradiated samples

Table (4): The values of the Chodak and Krupa model parameters for nonirradiated and irradiated samples

Parameter	Non-irradiated	Irradiated
B	1.83356	1.54
a	25	20
n	5	5
Φ_p	0.06437	0.08047

Correlation between I_2 and Ln σ

Figure (12) shows a positive correlation between Ln σ and the intensity I_2 which corresponds to the fraction of free positron annihilation with the free electrons at the polymer–filler interface, and this can be treated as the measure of electrical conductivity for both nonirradiated and irradiated composites. This can be explained due to the incorporation of RGO nanoscale filler, that leads to an increase in conducting path resulting in increasing the conductivity. The motion of charge carriers is impeded at the crystalline–amorphous interface region at higher dopant concentrations. Adding more filler will increase the free electron density and consequently the electrical conductivity. Accordingly, new positron annihilation sites are created, which lead to increase in I_2[20,38].

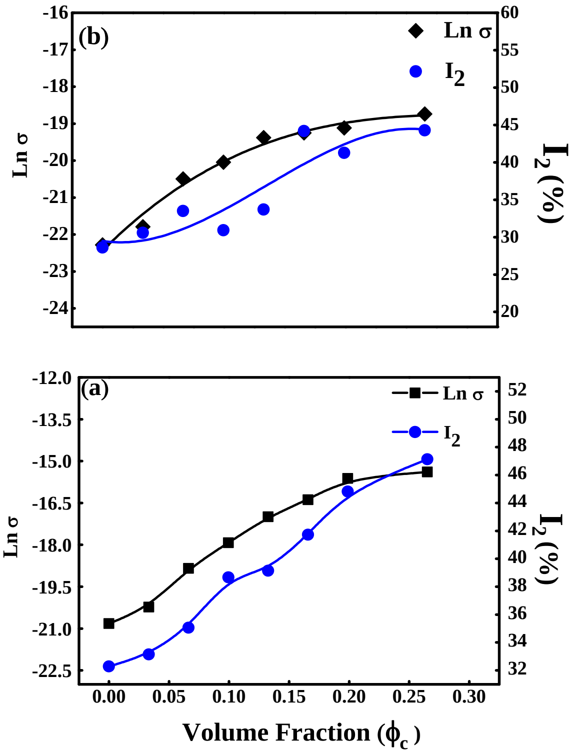

Fig. (12): The relation of Ln (σ) and I_2 of the PVA/PEG/RGO composites as a function of the volume filler fraction (φ_c) for (a) nonirradiated and (b) irradiated samples

Correlation between V_f and Ln σ

The electrical conductivity of polymer nancomposites under a relatively low applied electric field is affected strongly by the structural factors of the polymers. The conduction process in polymer nanocomposites is explained in terms of the movement of charge carriers/ions regulated mainly by the distribution of the free volume holes (V_f). To correlate the free volume induced ionicand electrical conductivity, it is more appropriate to consider the model suggested by Miyamoto and Shibayama [42,43]. The variation of ionic and electrical conductivity with the incorporation of nanofiller requires minimum hole size for ion transfer called critical free volume (V_i^*). Therefore, it is important to estimate the minimum hole size necessary for ion transfer in the polymer matrix. The dependence of DC electrical conductivity(Ln σ) on free volume size (V_f) is given by the following equation[38,44]:

$$\sigma = \sigma_0 \exp\left\{-\left[\frac{\gamma V_i^*}{V_f}\right]\right\} \qquad (8)$$

where V_i^* and V_f are the minimum hole size necessary for ion transfer due to the thermal fluctuation of free volume (critical free volume) and average size of free volume cavities respectively. σ_0 is the pre-exponential factor and γ is the numerical factor to correct the overlap of the free volume. The variation of (Ln σ) with the reciprocal of free-volume ($1/V_f$) is as shown in Fig. (13). The deduced value of critical free volume V_i^* for the charge carriers/ion transport in PVA/PEG/RGO polymer nanocomposites is equal to 80.34 and 82.16 Å^3 for nonirradiated and irradiated samples respectively.

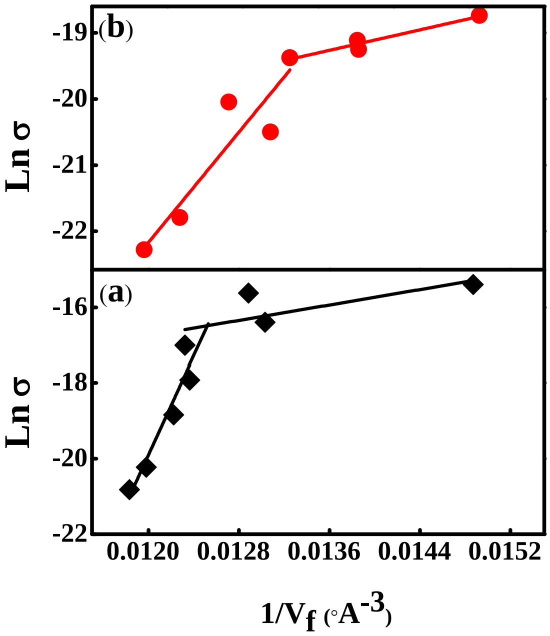

Fig. (13): The variation of (ln σ) as a function of the reciprocal of the free volume, ($1/V_f$) of PVA/PEG/RGO polymer nanocomposites for (a) nonirradiated and (b) irradiated samples

Conclusion

The effect of addition of RGO in amounts of (0–4 wt%) on the properties of free volume holes (I_3, τ_3, V_f and F_r) in PVA/PEG composites have been studied. The probability of positron annihilation at interface, I_2 and in free volumes I_3 is determined by PAL. A correlation is established between the variation of free volume parameters and some structural and electrical properties of the PVA/PEG /RGO composites before and after irradiation with γ-rays. The results can be summarized as follows:

- V_f decreases from (80 to 70 Å^3) and from (80 to 75 Å^3) for nonirradiated and irradiated samples respectively with increasing the RGO volume fraction of the filler.F_r also decreases with increasing the filler content due to inhibition of o-Ps formation. This could be explained by the reduction in the degree of crystallinity (χ_c%) due to crosslinking and the hydrogen-bonding as deduced from the FTIR spectra. Irradiation with gamma tends to break hydrogen bonds between RGO and PVA/PEG chain segments and lowers the crosslinking role of RGO filler.

- The probability of free annihilation at composite- filler interface (I_2) increases with the filler content, due to the enhancement of the electron density. This explains the positive correlation between ln σ and (I_2).
- XRD showed that the degree of crystallinity (χ_c%) decreases with increasing the RGO content, which is positively correlated with the variation of the free volume size V_f.
- The dependence of the data for DC electrical conductivity (Ln σ) on free volume size V_f could be successfully fitted using the model suggested by Miyamoto and Shibayama. From the variation of the electrical conductivity, ln σ with $1/V_f$, the critical free volumes for the charge carriers' transport has been deduced to be 80.34 and 82.16 Å^3 for nonirradiated and irradiated samples respectively.
- The results of DSC thermograms were used to determine the melting temperature of the crystalline phase T_m and T_g. It turned out, that T_m shifts towards lower values due to the addition of RGO, while T_g shifts towards higher values. This is in accordance with the reduction in the degree of crystallinity (χ_c) due to crosslinking and the hydrogen-bonding.
- The inter chain distance (d) determined by XRD and the D value calculated from positron annihilation data shows a slight difference since the PALS method is sensitive not only to the static open volume holes but also to the holes living for short times, while the XRD measurements give the average distance between molecules.

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