

Positron Spectroscopy of Free Volume in Poly(vinylidene fluoride) after Helium Ions Irradiation

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Abstract Free volume is an extremely important intrinsic defect in polymers. Structurally, free volume is the randomly distributed holes in the polymer molecular chain segments. In proton exchange membrane fuel cells, free volume is also the space needed for the directional conduction of protons. Irradiation by α particles to grafting sulfonated poly(vinylidene fluoride) (PVDF) is one of the methods to produce proton exchange membrane with good proton channel rate. Positron annihilation lifetime spectroscopy was used to study the free volume size at different absorbed dose levels from 0.13 MGy to 0.65 MGy. Measurement method of positron annihilation lifetime spectroscopy for PVDF based on ^{44}Ti positron source was developed. For low dose irradiation at 0.26 MGy, a decrease in free volume and practically unchanged crystallinity were observed. Further increase of absorbed dose range from 0.26 MGy to 0.39 MGy led to an increasing crystallinity with the same free volume level. For the absorbed dose from 0.39 MGy to 0.65 MGy, crystallinity was decreased but free volume remained almost constant.

Keywords Positron annihilation; Free volume; XRD; Poly(vinylidene fluoride); Helium ions; Connection; Degradation

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INTRODUCTION

The research and application of irradiation effects on polymers have been paid with more and more attention. The chemical changes of polymers caused by absorbed doses are not significant. However, the induced changes of physical and mechanical properties of polymers are significant. Regardless of cross-linked or degradable polymers, their inherent physical, chemical, and mechanical properties can be severely damaged when the absorbed dose is high to a certain degree, which causes materials unusable.^[1–4] Therefore, radiation stability or radiation resistance is one of the important properties of polymers, especially when polymers are used in the nuclear reactor or aerospace industry. Positron annihilation lifetime spectroscopy (PALS) is the only sensitive method for studying the microstructure—the parameter of free volume with atomic size of amorphous polymers.^[5–8] Using the method of PALS, it was found that the influence of radiation on polymers is related to the type of radiation, the type of polymers, as well as the irradiation power. For example, El Keriem^[9] investigated effect of low γ -irradiated dose on the structure of cellulose triacetate films and found that the intensity of *ortho*-positronium component (I_3) showed an increase from 0 kGy to 10 kGy. Such an

increase of I_3 is mainly due to the presence of carbonyl groups, which are formed during irradiation.^[10] With a further increase in the dose up to 15 kGy, I_3 decreased gradually and then approached to a constant of 25 kGy, which is well known for γ -irradiated polymers.^[11] Such behavior may indicate that the stability in the structure has been achieved. Zhou and his collaborators^[12] obtained results on the change of free volumes in γ -irradiated polytetrafluoroethylene (PTFE) and polyethylene (PE). It was found that, from 0 kGy to 300 kGy, the crystallinity of PTFE increased continuously and the size of the free volume decreased gradually, while in polyethylenes both parameters showed the opposite behavior depending on the dose. Jassim and his collaborators^[13] investigated the properties of free volumes in β -irradiated high density polyethylene (HDPE). It was indicated that both free volumes and I_3 increased at a dose lower than 1.5 Gy, followed by a decrease to a constant volume at a dose of 1.5 Gy to 12 Gy. These studies indicate that many factors influence the characteristics of the interaction between radiation and substances, one of which is the radiation resistance of polymers. Possessing high resistance to different types of radiation, polymers show a structural change only at a high radiation dose (several hundred kGy), otherwise the polymer structure has no changes and approaches to a stable state even at a sufficiently low radiation dose (several Gy).

Positron annihilation technique is one of the sensitive tools for investigating microscopic defects and phase trans-

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ition of materials. In normal positron spectroscopy, the positron energy is in the order of MeV and the depth of injection in the sample is deep for the research of average defect density in the material. In order to achieve this goal, it is usually required that the amount of annihilation positrons in the sample should be no less than 50% of the amount of positrons emitted from the positron source. This places stringent requirements on the positron source and the thickness of sample. The positron emitted by ^{22}Na performs a maximum energy of 0.545 MeV, the injection depth of which in metal is usually from 0.3 mm to 1 mm, and is from 1 mm to 2 mm in a polymer material with a small density.^[14] ^{44}Ti is a high-energy positron source that produces positrons with a maximum energy of 1.47 MeV, the injection depth of which will be deeper in the polymer material compared to positrons emitted by ^{22}Na . Poly(vinylidene fluoride) (PVDF) is a material used to prepare modified proton exchange membranes.^[15–17] Due to the working environment, the thickness is required to be in the range of 20–100 μm (a greater ohmic overpotential will be generated if it exceeds this range).^[18–20] Since the positron energy produced by ^{44}Ti is in the order of MeV, and the thickness of PVDF is very small, only a few positrons are annihilated in PVDF, and most of the positrons penetrate the film without annihilation. In order to annihilate 50% of positrons in PVDF and not to use positron moderators for cost savings, we propose a method to make the annihilated positron percentage in PVDF close to 50% in this work, which is in good agreement with the requirements of the PALS method.

Herein, PALS and XRD are combined with free volume theory to study the influence of helium ions irradiation on the microstructure of PVDF, so as to reveal the relationship between the microstructure changes and absorbed dose.

DEVELOPMENT OF PALS MEASUREMENT METHOD FOR POLYMERS BASED ON ^{44}Ti POSITRON SOURCE

The principle of positron annihilation method is to estimate the concentration of defects by calculating the proportion of positrons that are trapped in different defects. In the case where the total number of emitted positrons is constant, according to statistics, the more the number of positrons trapped in the material, the larger the statistical total, and the closer the statistical results are to the true state of the experimental sample.

The transfer profile or the path of positrons through the material is calculated using the LYS-1 program, which is based on a multi-scattered model.^[21,22] For calculation, only the linear absorption coefficient, backscatter factor, and material thickness are required.

Linear absorption coefficient is:^[23]

$$\alpha_+ = \frac{12.6Z^{0.17}\rho}{E_{\max}^{1.28}} \quad (1)$$

where Z is the atomic amount of the substance; $E_{\max}$ is the maximum positron energy (MeV); ρ is the density of the substance ($\text{g}\cdot\text{cm}^{-3}$).

Backscatter coefficient is:^[24]

$$R = 0.42\lg Z - 0.146 \quad (2)$$

In positron annihilation measurements, in order to ensure that all positrons are annihilated in the measured material, the sample and the radioactive source must adopt a “sandwich” structure, that is, the same sample is placed on both sides of the source. In addition, in order to make a great amount of incident positrons stay in the material, an ordinary method is to make the thickness of the sample greater than the incident depth of positrons. For PVDF polymers with small thickness, to increase the amount of annihilated positrons in films, the following two models are developed in Fig.1, while the positron source is ^{44}Ti , which emits positrons with a maximum energy of 1.47 MeV.

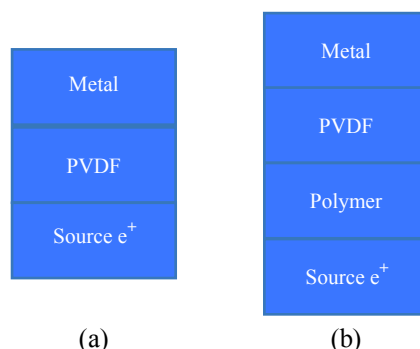


Fig. 1 (a) One side of “sandwich” structure of two-layer model: source e^+ + PVDF (first layer) + metal (second layer); (b) One side of “sandwich” structure of three-layer model: source e^+ + polymer (first layer) + PVDF (second layer) + Pb (third layer)

According to the equations (1) and (2), in order to obtain the linear absorption coefficient and backscatter coefficient of each layer, it is necessary to know the energy of positrons that reach the surface of each layer. This requires that the energy loss of positrons in each layer must be known, which can be determined by braking ability of each layer for positrons.

The energy loss of positrons in substance is divided into two types, the collision loss and bremsstrahlung energy loss. The collision loss of positron energy is determined by the following formula:

$$\left(-\frac{dE}{dx}\right)_{\text{col}} = \frac{2\pi r_e^2 m_e c^2}{\beta^2} N_A \frac{Z_2}{A} \times \left[\ln\left(\frac{\beta^2}{1-\beta^2} \frac{\varepsilon}{2(I^*/m_e c^2)^2}\right) + F^+(\varepsilon) \right] \quad (3)$$

where Z_2 is the atomic amount of the substance; r_e is the classical radius of an electron (cm); m_e is the mass of an electron (g); N_A is the Avogadro constant; a is the atomic mass of substance (a.e.m); c is the speed of light ($\text{cm}\cdot\text{s}^{-1}$); I^* is the average excitation energy of the substance's atom (erg); v is the positron velocity ($\text{cm}\cdot\text{s}^{-1}$); $\beta = \frac{v}{c}$; $\varepsilon = \frac{T}{m_e c^2}$; T is the kinetic energy of a positron (erg); $F^+(\varepsilon)$ is the function for positrons.

$$F^+(\varepsilon) = 2\ln 2 - \frac{\beta^2}{12} \left[23 + \frac{14}{\varepsilon+2} + \frac{10}{(\varepsilon+2)^2} + \frac{4}{(\varepsilon+2)^3} \right] \quad (4)$$

The bremsstrahlung energy losses of positrons are related to the bremsstrahlung energy losses of electronics. In the Born approximation without taking shielding into account, the calculation of the braking ability caused by the radiation of electrons with non-relativistic energies gives the following result:

$$\left(-\frac{dE}{dx}\right)_{\text{rad}} = \frac{16}{3} \times 3.44 \times 10^{-4} \frac{Z_2(Z_2+1)}{A} T_0 \quad (5)$$

where T_0 is the kinetic energy of electrons (MeV); A is the atomic mass of substance (a.e.m);

For the relativistic case:

$$\left(-\frac{dE}{dx}\right)_{\text{rad}} = 3.44 \times 10^{-4} \frac{Z_2(Z_2+1)}{A} T_0 \left(4 \ln \frac{T_0}{0.255} - \frac{16}{3}\right) \quad (6)$$

The loss of positron energy to radiation can be calculated by loss of electrons *via* multiplying them by the function (7):

$$\eta\left(\frac{T_0}{Z_2^2}\right) = \begin{cases} 0, & x \leq -8 \\ \frac{1}{2} + \frac{1}{\pi} \arctg(0.415x + 0.0021x^3) \\ + 0.00054x^5, & -8 < x < 9 \\ 1, & x \geq 9 \end{cases} \quad (7)$$

where $x = \ln(7.52 \times 10^6 \frac{T_0}{Z_2^2})$, T_0 in GeV.

The total energy losses of positrons on per unit path (total braking ability) are equal to the sum of energy losses due to collisions and radiation:^[25]

$$-\frac{dE}{dx} = \left(-\frac{dE}{dx}\right)_{\text{col}} + \left(-\frac{dE}{dx}\right)_{\text{rad}} \quad (8)$$

Table 1 shows the amount of annihilated positrons in PVDF using different metals as the material of the second layer.

Table 1 Results of calculation for the two-layer model “source e^+ + PVDF (first layer 20 μm) + metal (second layer)”

Materials	Linear absorption coefficient	Backscatter coefficient	The amount of annihilated positrons in the first layer (%)
Al	33	0.23	20.40
Fe	107	0.34	23.00
Ni	123	0.35	23.28
Cu	124	0.35	23.28
Zn	100	0.36	23.56
Zr	95	0.40	24.74
Nb	126	0.41	25.06
Sn	111	0.44	26.04
Pb	188	0.51	28.70

It can be seen from Table 1 that in the two-layer model, the maximum amount of annihilated positrons in PVDF was obtained using Pb as the material of the second layer, which has the largest backscattering coefficient among all the metals listed.

Since the location of Pb behind the PVDF film allows the most significant increase in the amount of annihilated positrons in a PVDF film, it is necessary to settle calculation for the model “source e^+ + PVDF (first layer) + Pb (second layer)” with different thicknesses of the PVDF film (Table 2).

Table 2 Results of calculation for the model “source e^+ + PVDF (first layer) + Pb (second layer)”

PVDF thickness (μm)	The amount of annihilated positrons in a PVDF film (%)
50	28.70
70	36.90
100	46.94

In three-layer model, a polymer is placed on layer 1 in order to hold back the positrons. Three different polymers are taken for calculation: polyethylene (PE, C_2H_4), PVDF ($\text{C}_2\text{H}_2\text{F}_4$), and Teflon (PTFE, C_2F_4). Tables 3 and 4 show the amount of annihilated positrons in PVDF using C_2H_4 , $\text{C}_2\text{H}_2\text{F}_4$, and C_2F_4 as the material of the first layer with various thicknesses.

From the data shown in Tables 3 and 4, the larger the proportion of hydrogen atoms in the polymer (first layer), the smaller the thickness of the polymer (first layer), the larger the thickness of PVDF (second layer), and the larger the amount of annihilated positrons in PVDF (second layer).

In order to increase the amount of annihilated positrons in a PVDF film, two models were developed, different from one another in the amount of layers. The first model is the two-layer model. In this model, the maximum amount of positrons annihilated in the PVDF film was obtained using lead (Pb) as the material of the second layer, which has the greatest backscatter coefficient among all the metals considered in this work. With a 100 μm thickness of PVDF film, the amount of annihilated positrons is 46.94%. The second model is the three-layer model. The essence of this model is that any material should be placed on the first layer in order to reduce positron energy. In comparison with the three-layer model, the two-layer model allows obtaining a larger amount of annihilated positrons in a PVDF film. The disadvantages of the three-layer model are as follows.

(1) The braking ability of polymers (the first layer) is in the range of $1 \times 10^{-4} \text{ MeV} \cdot \mu\text{m}^{-1}$ to $4 \times 10^{-4} \text{ MeV} \cdot \mu\text{m}^{-1}$, then the energy losses of the positrons in the first layer are:

$$\Delta E = \frac{dE}{dx} \times h_1 \leq (4 \times 10^{-4} \text{ MeV} \cdot \mu\text{m}^{-1}) \times (100 \mu\text{m}) = 0.04 \text{ MeV} \quad (9)$$

The energy of the positrons emitted from the source ^{44}Ti :

$$E_1 = 1.47 \text{ MeV} \quad (10)$$

The energy of positrons incident on the second layer (PVDF film):

$$E_2 = E_1 - \Delta E \geq 1.47 \text{ MeV} - 0.04 \text{ MeV} = 1.43 \text{ MeV} \quad (11)$$

It is observed that polymer materials hardly reduce the energy of positrons. When the thickness of the second layer (PVDF) is increased to 100 μm , the maximum amount of annihilation positrons in the PVDF film is only 40.80%.

(2) As already mentioned above, the smaller the thickness of the polymer (first layer), the greater the amount of annihilated positrons in the PVDF film (the second layer), *i.e.* with a polymer thickness of zero, the maximum amount of annihilated positrons in a PVDF film (the second layer) is observed, and this is a two-layer model.

So, in this study, the two-layer model is used in the experiment of PALS analysis.

Table 3 Results of calculation for the three-layer model “source e⁺ + polymer (first layer) + PVDF (second layer) + Pb (third layer)” with a thickness of the second layer of 50 μm

Polymer	Thickness of the first layer (μm)	Braking capacity of the first layer (MeV·μm ⁻¹)	The energy of the positrons falling to the second layer E ₂ (MeV)	The amount of annihilated positrons in the second layer (%)
Polyethylene (C ₂ H ₄)	50	2.76 × 10 ⁻⁴	1.46	24.60
	70	2.76 × 10 ⁻⁴	1.45	24.44
	100	2.76 × 10 ⁻⁴	1.44	23.30
PVDF (C ₂ H ₂ F ₂)	50	3.88 × 10 ⁻⁴	1.45	22.24
	70	3.88 × 10 ⁻⁴	1.44	20.10
	100	3.88 × 10 ⁻⁴	1.43	17.92
Polytetrafluoroethylene (PTFE, C ₂ F ₄)	50	3.41 × 10 ⁻⁴	1.45	19.46
	70	3.41 × 10 ⁻⁴	1.45	17.80
	100	3.41 × 10 ⁻⁴	1.44	17.70

Table 4 Results of calculation for the three-layer model “source e⁺ + polymer (first layer) + PVDF (second layer) + Pb (third layer)” with the thickness of the second layer of 100 μm

Polymer	Thickness of the first layer (μm)	Braking capacity of the first layer (MeV·μm ⁻¹)	The energy of the positrons falling to the second layer E ₂ (MeV)	The amount of annihilated positrons in the second layer (%)
Polyethylene (C ₂ H ₄)	50	2.76 × 10 ⁻⁴	1.46	40.80
	70	2.76 × 10 ⁻⁴	1.45	40.40
	100	2.76 × 10 ⁻⁴	1.44	37.80
PVDF (C ₂ H ₂ F ₂)	50	3.88 × 10 ⁻⁴	1.45	37.00
	70	3.88 × 10 ⁻⁴	1.44	33.68
	100	3.88 × 10 ⁻⁴	1.43	29.36
Polytetrafluoroethylene (PTFE, C ₂ F ₄)	50	3.41 × 10 ⁻⁴	1.45	32.74
	70	3.41 × 10 ⁻⁴	1.45	29.96
	100	3.41 × 10 ⁻⁴	1.44	24.98

EXPERIMENTAL SET-UP

Sample Preparation and Irradiation

The sample under investigation was the F-2M (PVDF) film with a thickness of 20 μm produced by “Fluoropolymer” (St. Petersburg). The R-7M accelerator of physicochemical institute of Tomsk Polytechnic University was used as a source of ionizing radiation producing a beam of helium ions with energy 27 MeV discharged into the air. Absorbed dose rate was 0.26 MGy·min⁻¹, while total absorbed doses were 0.13, 0.26, 0.39, 0.52, and 0.65 MGy. The corresponding sample codes are PVDF0, PVDF0.5, PVDF1, PVDF1.5, PVDF2, PVDF2.5, respectively.

PALS Analysis

A conventional fast-fast coincidence spectrometer with a time resolution of 240 ps was used for PALS measurements.^[26,27] In PALS spectrum, about 3–5 million counts were accumulated. The PALS spectra were analyzed into three components (τ₁, τ₂, and τ₃) with their intensities (I₁, I₂, and I₃) using MELT. At present, several computer programs with various mathematical models have been developed to obtain the spectrum of PALS. PATFIT-88,^[28] considering the spectrum of PALS as a convolution of superposition of multiexponential components with the instrument's resolution function, estimates the parameter values based on the method of semi-linear least squares. LifeTime10^[29] obtains the PALS spectrum the same as PATFIT-88, but estimates the parameter values using non-linear least squares. CONTIN^[30,31] considers the spectrum of PALS as a convolution of the resolution function and Laplace transform

function, while the continuous spectrum of PALS is obtained through the inverse Laplace transform. The MELT program^[31,32] also allows one to obtain a continuous distribution of positron time, analyzing the spectrum of PALS based on the maximum entropy principle. Unlike other spectrum analysis programs, the program MELT has the following advantages: (1) application of the program for filtering Poisson noise and application of the filtered solution as the initial solution of MELT allow obtaining a more stable result; (2) there is no requirement to measure the reference spectrum, and a low number of counts (generally 1 million counts) makes it possible to get a stable solution.

XRD Analysis

X-ray diffraction studies were performed with CuKα radiation (0.154 nm wavelength) using XRD-7000S diffractometer (Shimadzu, Kyoto, Japan) in Bragg-Brentano geometry from 30° to 80° with the scan speed of 10.0 (°)·min⁻¹, the sampling pitch of 0.0143°, the preset time of 42.972 s at 40 kV and 30 mA. The diffraction patterns were collected using OneSight (Shimadzu, Kyoto, Japan) wide-range array high speed detector with 1280 channels.

RESULTS AND DISCUSSION

Results of PALS Analysis

In high molecular weight polymers, positrons not only directly annihilate with electrons, but also form a metastable state “positronium” with electrons, followed by annihilation. There are two basic states of positronium: (1) *para*-positronium (*p*-Ps), the spins of the electron and the positron

are antiparallel, the intrinsic lifetime of *p*-Ps in vacuum is 125 ps; (2) *ortho*-positronium (*o*-Ps), the spins of electron and positron are parallel, and the intrinsic lifetime of *o*-Ps in vacuum is 140 ns. Due to the fact that the positronium size is only 1.06 Å and most *o*-Ps are formed in free volumes with subsequent annihilation, the measurement of *o*-Ps annihilation parameters allows obtaining information about the microstructure of high molecular weight polymers, while the lifetime and intensity show the size and quantities of the free volume, respectively.^[33]

A high molecular weight polymer is a complex system. Generally, it is considered that in a high molecular weight polymer there are two regions: crystalline and non-crystalline. The free volumes are distributed in the non-crystalline region. Thus, there are several mechanisms of positron annihilation in solid polymers: pick-off annihilation of *o*-Ps, self-annihilation of *p*-Ps, annihilation of free positrons in the crystalline region, and annihilation of positrons in various capture states. Attention should be paid to the fact that in practical polymers, there are many different capture states, for example, in a non-crystalline region there is a capture state with a long lifetime component, the value of which is close to the lifetime of *o*-Ps and in the crystalline region there is possibly the capture state with a short lifetime component, the value of which is close to the lifetime of *p*-Ps. In spite of many possible types of capture states, in the practical work of analyzing the PALS spectrum, the model of the three lifetime components allows obtaining a good processed result, in this case, τ_1 is the lifetime of *p*-Ps and positrons annihilating in the capture states with a short lifetime, τ_2 is the lifetime of free positrons annihilating in the crystalline region, τ_3 is the lifetime of the pick-off annihilation of *o*-Ps and positrons annihilating in the capture states with a long lifetime. τ_2 only depends on the crystalline part, whereas only the non-crystalline region affects τ_3 . As a result, the model of the three lifetime components satisfies the requirement to study the change of free volumes that exist only in the non-crystalline region. Table 5 shows the lifetimes of the three components and their corresponding intensities.^[34]

According to the principle of quantum mechanics, Tao and Eldrup obtained a relationship between the radius of a spherical free volume and the lifetime of *o*-Ps:^[35]

$$\tau_3 = \tau_0 \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} \quad (12)$$

where τ_3 is the lifetime of *o*-Ps in free volume; τ_0 is the lifetime of *o*-Ps in the electron layer surrounding the free volume, $\tau_0 = \frac{1}{2}$ ns; R is the radius of the spherical free volume; ΔR is the thickness of the electron layer formed on external electrons of free volume, on which annihilation of *o*-Ps occurs, $\Delta R = 0.1656$ nm.

Free volume is

$$V = \frac{4}{3}\pi R^3 \quad (13)$$

It can be seen from Fig. 2 that I_3 does not change with absorbed dose below 0.26 MGy, since PVDF has a high radiation resistance. In the range of 0.26–0.39 MGy, the intensity I_3 decreases, whereas with further increase in the absorbed dose, the intensity I_3 increases. This can be explained by the fact that at a low absorbed dose the main process that occurs when α particles interact with high molecular weight chains of PVDF is the connection of chains. With a further increase in the absorbed dose, degradation of chains predominates over connection of chains, which leads to an increase in the non-crystalline region. It is known that the energy of C–C bond is 332 kJ·mol^{−1}, C–H bond is 414 kJ·mol^{−1}, and C–F bond is 489 kJ·mol^{−1}. As a result, it is believed that the connection and degradation of the molecular chains of PVDF is mainly carried out by the formation and decomposition of the C–C bonds.

It can be seen from Figs. 3 and 4 that at an absorbed dose below 0.26 MGy, the free volume decreases rapidly, and it is noted that in this range of absorbed dose the crystallinity does not change obviously. This behavior is explained by the characteristics of the connection and degradation processes of the molecular chains of PVDF, which are presented in Fig. 5. At a low dose, segments of molecular chains in the non-crystalline region begin to move and are prepared for connection with each other (processes a and b). In this process, a redistribution of space occupied by free volumes and segments of molecular chains occurs in such a way that several segments enter the free volume and leave in their place with a new free volume. As a result, the proportion of non-crystalline region is not changed, but the size of the free

Table 5 The lifetimes of the three components and their corresponding intensities

Absorbed dose (MGy)	$\tau_1 \times 10^{12}$ (s)	$\tau_2 \times 10^{12}$ (s)	$\tau_3 \times 10^{12}$ (s)	Free volume $\times 10^3$ (nm ³)
0	121	315	1292	37.90
0.13	127	318	1259	35.57
0.26	134	322	1227	33.36
0.39	126	314	1235	33.90
0.52	121	318	1229	33.49
0.65	122	321	1246	34.67
Absorbed dose (MGy)	I_1 (%)	I_2 (%)	I_3 (%)	Crystallinity (%)
0	41.2 $\pm$ 0.7	51.3 $\pm$ 0.7	5.7 $\pm$ 0.1	90
0.13	41.3 $\pm$ 0.7	51.1 $\pm$ 0.6	5.8 $\pm$ 0.1	89.81
0.26	43.2 $\pm$ 0.9	49.5 $\pm$ 0.9	5.6 $\pm$ 0.1	89.84
0.39	42.5 $\pm$ 0.8	50.8 $\pm$ 0.7	5.1 $\pm$ 0.1	90.88
0.52	42.6 $\pm$ 0.7	50.4 $\pm$ 0.6	5.4 $\pm$ 0.1	90.32
0.65	42.0 $\pm$ 0.7	50.7 $\pm$ 0.6	5.7 $\pm$ 0.1	89.89

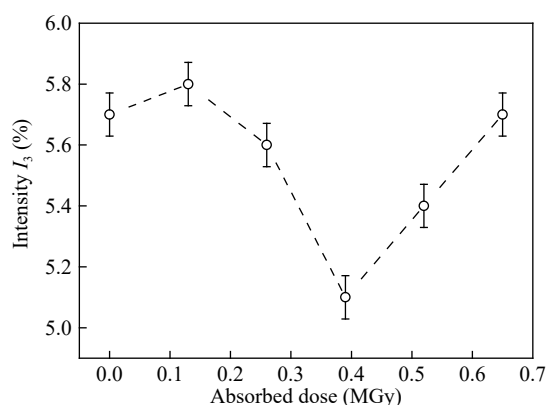


Fig. 2 Dependence of intensity I_3 on absorbed dose

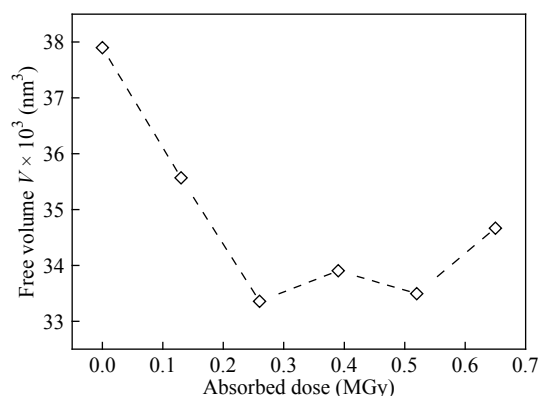


Fig. 3 Dependence of free volumes on absorbed dose

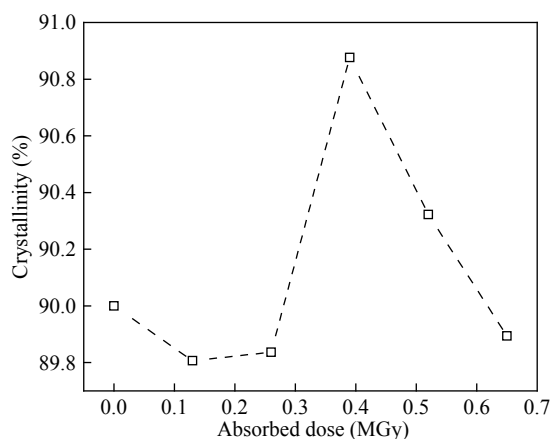


Fig. 4 The crystallinity from the absorbed dose, determined by the ratio $I_2/(I_2 + I_3)$

volume decreases. In the range of 0.26–0.39 MGy, the discrete previous segments of the molecular chains, having entered in the free volumes, begin to connect and transform into ordered long molecular chains, which leads to the growth of the crystal region with an unchanged size of free volumes in PVDF (process c). In the range of 0.39–0.65 MGy occurs the reverse process of process (c) (process d). It should be noted that not only are new connected molecular chains degraded, but also the inherent (“old”) long molecular chains in the crystalline region. It is for this reason

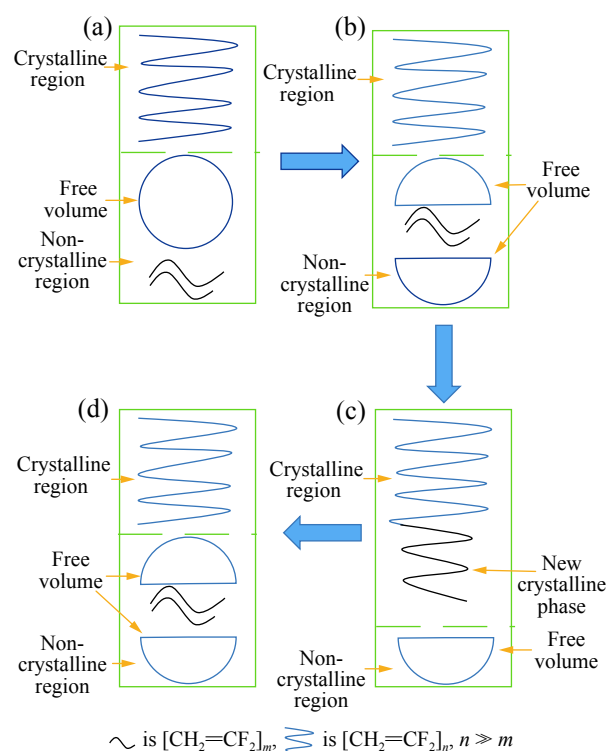


Fig. 5 Process of connection and degradation of molecular chains of PVDF under irradiation of helium ions

on that an increase in the non-crystalline region and in the size of free volumes is observed at a high absorbed dose.

Results of XRD Analysis

The XRD patterns of PVDF samples irradiated with different doses are shown in Fig. 6. It is found that the peak of the highest intensity is about 20° , which is a characteristic peak of the crystalline phase. This means that the main part of PVDF is occupied by the crystalline phase, and also explains the low intensity of τ_3 obtained by PALS method. Based on the XRD patterns, the dependence of diffraction angles (Fig. 7) and distance between crystal planes (Fig. 8) on the absorbed dose can be obtained.

From Fig. 7, there is an obvious shift of Bragg diffraction peak change at dose of 0.39 MGy. This is explained by that at dose 0.39 MGy in the amorphous region a new crystalline phase is produced,^[36] as shown in Fig. 5(c), which results in crystalline modification change. As the absorbed dose increases, the new crystalline phase is gradually destroyed (as shown in Fig. 5d), and the Bragg diffraction peak gradually returns to its original state.

According to Fig. 8, at a low absorbed dose (< 0.26 MGy), d does not change, while at the absorbed dose of 0.26–0.39 MGy, d decreases. With subsequent increase of the absorbed dose, d increases. This result coincides with the dependence of I_3 on the absorbed dose obtained by the PALS method (Fig. 2). This is explained by the definition of free volume as the vacant part of the polymer that is not occupied by molecular chains. Obviously, the unoccupied space increases as d increases and I_3 correspondingly increases.

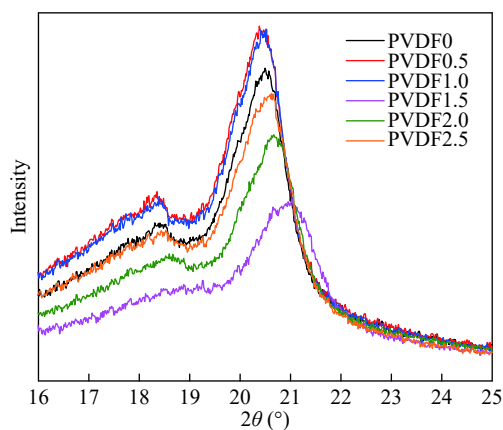


Fig. 6 XRD patterns of PVDF samples

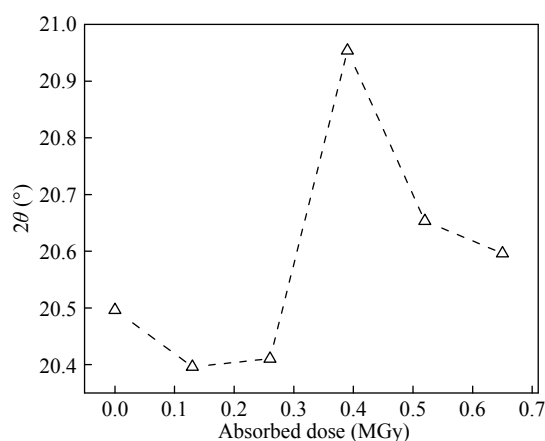


Fig. 7 Dependence of 2θ on the absorbed dose

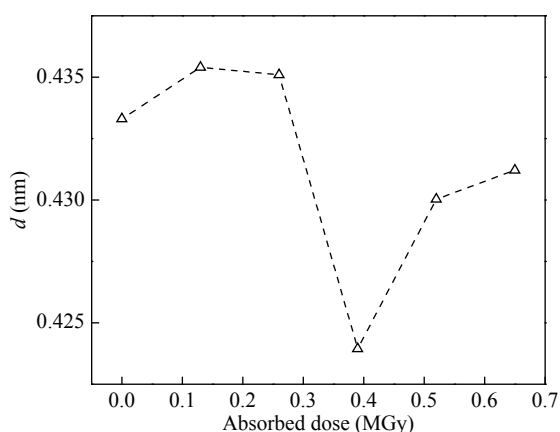


Fig. 8 Dependence of d on the absorbed dose

CONCLUSIONS

Analyzing the test results measured by different methods, it can be concluded that PVDF has a high resistance to radiation, and after PVDF is irradiated by helium ions, connection and degradation take place at the same time. Under different doses, the reaction mechanism is different. At an absorbed dose less than 0.26 MGy, a decrease in the free volume is observed, while the crystallinity is practically unchanged. In the absorbed dose range of 0.26–0.39 MGy,

an increase in the crystallinity and no significant change in the free volume are observed. With a further increase in absorbed dose, a continuous decrease in the crystallinity is observed, while when the dose is raised to 0.52 MGy, there is no significant change in the free volume, and a further increase in the dose to 0.65 MGy leads to its insignificant growth. This is due to the movement and connection of segments of molecular chains in the non-crystalline region at a low absorbed dose and the degradation of long molecular chains at a high absorbed dose. Therefore, it is determined that the absorbed dose of 0.65 MGy has exceeded the maximum damage dose of the PVDF material, at which degradation of the intrinsic crystal region of the polymer begins to occur. The results of XRD analysis confirmed the results obtained by PALS method. Interpretation and analysis of data are based on the theory of connection or degradation of molecular chains (formation or decomposition of C—C bonds) in PVDF.

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