The Thermal Effect on PLA And PLA / Curcumin Composite Properties under Positron Annihilation Lifetime Spectroscopy

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Abstract

   In this study, pure polylactic acid (PLA) and composite polylactic acid/ curcumin (PLA / Cur) were prepared by a suspension of ultrasonically agitated micrometer-sized curcumin powder, which was mixed with chloroform solvent under slow mechanical stirring and incorporated into the PLA. The resulting suspension was used to cast free-standing PLA / Cur composite films. The filler content was chosen to be 2.0 wt % curcumin. Physical properties (glass transition, temperature, mechanical and thermodynamic) were analyzed by Positron Annihilation Lifetime Spectroscopy (PALS), which is a unique tool for analyzing the defects of polymer materials. The free volume and holebility of PLA and PLA / Cur were studied in vacuum and temperature range of 283 to 353 K. Ortho-positronium (o Ps), life$^{(\tau_3)}$, and intensity$^{(I_3)}$ were measured as more sensitive parameters to determine free volume dimensions. The results of the thermodynamic property of PLA, examined with PALS technique, revealed a phase change of around 58 ºC. Also, an improvement was observed in the PLA / Cur structure with the addition of curcumin, by reducing nano-size defects.

Keywords: PLA; PLA Curcumin; Positron Annihilation Lifetime Spectroscopy; Parapositronium; Orthopositronium; free volume;hole fraction.

التأثير الحراري على حامض بولي لاكتيد والمركب بولي لاكتيد كركمين تحت التحليل الطيفي مدى الحياة لإبادة البوزيترون

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الخلاصه

في هذه البحث تم فحص بولي لاكتيد النقي و بولي لاكتيد كركمين .وذلك عن طريق الحصول على المحلول المعلق من مسحوق الكركمين وبولي لاكتيد المثير بالموجات فوق الصوتية مع مذيب الكلوروفورم تحت التحريك الميكانيكي البطيء وتم استخدام المحلول المعلق الناتج لصب أغشية رقيقة(فلم) من / PLA Cur باختيار محتوى الحشو 2٪ وزنا من الكركمين. لفحص الكميات الفيزيائية (التزجج ودرجة الحرارة

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وميكانيكية الجزيئات والديناميكية الحرارية)التي تم تحليل خصائصها بواسطة التحليل الطيفي العمري بأبادة
البوزترون .(PALS) وهي أداة فريدة لتحليل عيوب المواد البوليمرية .وقد تمت دراسة الحجم الحر والنسبة
الفراغية لـ PLA و Cur / PLA مابين درجات حرارية283 إلى 353كلفن .ان حياة ذرة أورثوبوزترونيوم
وشدتها (o Ps هي بارامترات أكثر حساسية لقياس أبعاد الحجم الحر . نتيجة لذلك، فإن الخاصية الديناميكية
الحرارية لـ PLA التي تم فحصها باستخدام تقنية PALS لاحظنا تغير طور في 58 درجة مئوية . وبإضافة
الكركمين تم ملاحظة التحسن في تركيب المركب بولي لاكتيد كركمين وذلك بتقليل عيوب الحجم الحرالنانوي.

1. Introduction

Polylactic acid is a widely used and rare material worldwide. To study this material and reveal its physical and chemical properties, the technique of PALS has been widely applied [1-3]. PLA and PLA / curcumin films were produced with thickness of 0.4mm. These films are important to investigate microscopic in terms of defects and free volume temperature dependence, as well as physical properties and mechanical behavior. The reason for using curcumin is the flexiblity and high mobility of its molecules, which reduces the microscopic size defect. PLA/curcumin composite has multiple and widely applied functions in various manufactures. Also, it has well known biological uses as antioxidant, anti-inflammatory, anticancer and wound healing, which were studied by Hezmaet *et al*., as well as pharmalogical activities, which were studied by Rachmawti *et al*. Also, Chen *et al*. studied blood compatibility and coagulation time properties of PLA/curcumin composite. Nanocapsules of this composite were investigated for cancer treatment by Alippilakkotte *et al*. İn the present study, pure polylactic and polylactic/curcumin composites were investigated by positron techniques, which were preferred to examine the free volume's dependence temperature and behavior. The aim of this study was to examine nanoscale polylactic acid material defects and investigate ways to minimize these defects. The free volume and nanometric defects were measured and compared between PLA and PLA / Cr composites. The need to find an approach to minimize these defects, as well as the holebility ratio, triggered this study and formed its purpose [4-7].

2. Theoritical part

When a positron captures an electron, a stable atom is formed. This atom is at bound state structure and is called positronium (Ps) [2]. The positron is the antiparticle of the electron (e⁻), indicated by (e⁺), and its magnetic moment is equal to that of the electron in quantity. The other features of positrons are almost identical to those of electrons. The positron is a member of the lepton group and follows to Fermi Dirac statistics [3]. Another feature of positrons is that they do not have strong interactions. It is very difficult to find a stable positron in nature. Positron, decay of weak neutron radioisotopes and gamma energy with greater than 1.05 Mev can occure through nuclear reaction such as double formation of rays. When a positron meets an electron, annihilation can occur and energy of $2mc^2$ or higher can be released in the form of gamma radiation, as in the following relation [3].

$$e^+ + e^- \rightarrow n\gamma \tag{1}$$

where n is the number of photons formed during the annihilation process. Positron and electron annihilation behavior can be explained by quantum electrodynamics. The interaction of conjugate particles can be classified according to their spin. İf the particles spin is antiparalel, the interaction is singlet $\left(^1S\right)$ and when they are parallel, it is triple $\left(^3S\right)$ [3]. Based on cross-section calculations, two photons (Para-Positronium) and three photons (Ortho-Positronium) between the electron and the free positron annihilation in spin interaction are accordance with the laws of physics. Positronium (Ps) has the same structure, wavelength and dimension as that of the hydrogen atom. The diameter of Ps is only two times that of Bohar radius (2a=1.06 $\overset{\circ}{A}$). The atom of Ps in polymer structures can occur in the free volume-hole fractions in the molecules, while it can occur in the free spaces or free volume cavities between molecules. Ps can occur at two basic energy levels. The first involves one-quarter of all positronium atoms and is called parapositronium (p-Ps), where electron and positron spins are opposite (anti parallel). Therefore, the total spin value is zero. The second energy level is called the orthopositronium (o-Ps), where the spins are parallel and the total spin value is 1.

Three different annihilation patterns have been observed experimentally so far; these are the photon, two photons, and three photons annihilations. According to momentum conservation, a photon

annihilation is possible with a third object to absorb the required recoil momentum [3]. One photon between the ^1S electron with atomic number Z the cross-section of free positron annihilation is:

$$\sigma_1 = \frac{4\pi r_o^2 Z^5 \alpha^4}{(\gamma+1)^2 \sqrt{\gamma^2-1}}\left[\gamma^2 + \frac{2}{3}\frac{\gamma+2}{\sqrt{\gamma^2-1}}\ln(\gamma+\sqrt{\gamma^2-1})\right] \qquad (2)$$

Here $\gamma = 1/\sqrt{1-(v/c)^2}$, r_o is electron radius , $\alpha = e^2/\hbar c$ is fine-structure constant, and v is positron velocity. The most common annihilation events are observed in two photon annihilations, the effective cross-section for which is described by the following relation:

$$\sigma_2 = \frac{\pi r_o^2}{\gamma+1}\left[\frac{\gamma^2+4\gamma+1}{\gamma^2-1}\ln(\gamma+\sqrt{\gamma^2-1})\frac{\gamma+3}{\sqrt{\gamma^2-1}}\right] \qquad (3)$$

While the effective cross-section for three photon annihilation is expressed as [3]:

$$\sigma_3 = \frac{4}{3\pi}(\pi^2-9)\alpha\sigma_2 \square 0.0027\sigma_2 \qquad (4)$$

Equation (4) shows the three photon annihilation cross-section, which can be neglected when compared with that of the two photons . But, the three photon annihilation is important in spin-interaction states, such as in orthopositronium atoms.
For the slow positrons in the PALS system have been [3].. $v/c << 1$, $\gamma \to 1$

$$\sigma_1 \to \frac{4}{3}\pi r_o^2 Z^5 \alpha^4 \frac{v}{c} \qquad (5)$$

$$\sigma_2 \to \pi r_o^2 \frac{c}{v} \qquad (6)$$

Since $\sigma_2 >> \sigma_1$, the two photon annihilation is dominant. With a numerical example to explain the positron published from ^{22}Na ,which is about 200Kev of kinetic energy to let for most polymer materials can get the Z atom number around 10. The ratio of σ_1/σ_2 has a value of about 10^{-6} orders[3]..

The positron annihilation velocity rate λ_i for the photon can be calculated by the following equation, where positron velocity is denoted by v, current electron number density is n, and the corresponding effective cross-section is σ_i.

$$\lambda_i = nv\sigma_i \qquad i = 1,2,3 \qquad (7)$$

Positron annihilation is higher in the electron-rich than in the electron-weak zone. The effective measurement of positron is a new technique in determining electron density in a substance.
The basic state wave function of the Ps atom can be easily calculated from the similarity between Ps and hydrogen atom:

$$\phi_{100}(r) = \pi^{-1/2}(2a_o)^{-3/2}e^{r/2a_o} \qquad (8)$$

where $a_o = \hbar^2/mc^2$ is the Bohr radius. Therefore, on the positron site, an electron probability density can arise, that is given by:

$$P_e = \left|\phi_{100}^2(0)\right| = \pi^{-1}(2a_o)^{-3} \qquad (9)$$

By substituting the value of electron propability density in equation (9) instead of electron number density in equatin (7), and given that the cross-section values of σ_2 and σ_3 are known from equation (6) for our slow positron system, then the annihilation velocity values of parapositronium and orthoposironium can be obtained. The reverse of annihilation velocity of (p-Ps) and (o-Ps) gives the theoretical annihilation lifetime of p-Ps in polymer. It is not affected by the environment and its value in vacuum is 125 ps. The annihilation lifetime of the o-Ps 's three photons has a value of 142 ns in vacuum [3]. Here, the time is three orders longer than the value of lifetime of p-Ps. Polymers generally have a chain structure of several thousands of angstroms in length molecules. These molecules called macromolecules because they are quite long [4]. The structural arrangement of a

simple macromolecule is called monomer, which consists of repetition of blocks. The binding force holding the monomers together is provided by covalent bonds, which are very strong. But neighboring macromolecules weak each other Van der Waals keep it with their force. Due to this weak force, the concept of free volume and space occurs in the microscopic size between the molecules of the polymer material [5]. Injecting positron in to a polymer material, ionization and electronic simulation it releases its energy to molecules making inelastic collisions such as thermal energy, they reach their levels in picoseconds order. Positron initially has a high energy that is mostly in the form of ionizing molecules, inhomogeneous in to very small volumetric dimensions along the path of movement creates ioniesd regions. After the positron releases its required energy, the positronium atom is formed by capturing an electron in a suitable free zone. However, a pick off annihilation of orthopositronium leads to decrease the life-time a few nanosecond of orthopositronium in molecular structure and pick off annihilation event predominate in o-Ps annihilation. In the pick-off process, the positron of o-Ps interacts with the neighboring electron with the opposite spin. The result is a two-photon annihilation. p-Ps annihilation lifetime is denoted as τ_1, o-Ps pick-off annihilation lifetime is τ_3, and the free positrons lifetime is τ_2. The annihilation events of each type are corresponding to I_1, I_3 and I_2 intensities, respectively [6-10]. The lifetime $\tau_3(o-Ps)$ is very sensitive to the dimension and size free volume cavities . Possible electron number density symbolically for orthopositroniums overlap of the positron wave functions in a lattice electron wave function and o-Ps integral as in [3].

$$n = \int_L \Psi_L^*(\vec{r})\Psi_+^*(\vec{r})\Psi_L(\vec{r})\Psi_+(\vec{r})d\vec{r} \qquad (10)$$

Based on the lattice interactive square well potential approach, and with the electron between wells and the density is taken as constant of ρ_o, then equation (10) is simplified to:

$$n = \rho_o \int_{\upsilon_o} \Psi_{Ps}^* \Psi_{Ps} d\vec{r} \qquad (11)$$

where υ_o is the volume outside the wells and Ψ_{Ps} is the mass of Ps In the wells wave function for centrral motion. By combining equations (6), (7) and (11), the pick-off annihilation rate for o-Ps atom will be as follows [3]:

$$\lambda_{pick-off} = \pi r_o^2 c\rho_o \int_{\upsilon_o} \Psi_{Ps}^* \Psi_{Ps} d\vec{r} \qquad (12)$$

Then we extract the wave function of o-Ps expression of the Schrodinger equation for spherical center motion in spherical polar coordinates, as follows:

$$\left[-\frac{h}{2m}\left(\frac{d^2}{dr^2} + \frac{2d}{rdr} - \frac{l(l+1)}{r^2} + V(r) - E_n \right) \right]\Psi_{Ps}(r) = 0, \quad \text{Where} \quad V(r) = \begin{cases} 0 & 0<r<R_O \\ \infty & r>R_O \end{cases} \qquad (13)$$

The basic state wave function solution is:

$$\Psi_{Ps} = \begin{cases} \dfrac{\sin(\pi r/R_o)}{(2\pi R_o)^{1/2} r} & 0 < r < R_o \\ \\ 0 & r > R_o \end{cases} \qquad (14)$$

Then the state energy eigenvalue of Ps is:

$$E_n = (n\hbar\pi)^2 / 2mR_o^2 \qquad (15)$$

The rate of annihilation requires electron density. It has been assumed that there is an electon layer cloud [11]. It is assumed that there is a homogeneous thickness electron cloud in the potential sphere wall, as represented by $\Delta R = R_o - R$, where R represents the free volume hole diameter . The thickness value for the known data was found to be $\Delta R = 0.1656\,nm$ and the velocity of o-Ps annihilation in this electron cloud layer is written as in below:

$$\lambda_{pick-off}(ns^{-1}) = 2\int_{\upsilon_o} \Psi_{Ps}^* \Psi_{Ps} d\vec{r} = 2 \times 4\pi \int_{\upsilon_o} |\Psi_{Ps}(r)|^2 r^2 dr \qquad (16)$$

By applying the wave function found in equation (15) , then substituting them in equation (17), then we obtain the velocity of annihilation and orthopositronium lifetime as in below [7]:

$$\lambda_{pick-off}(ns^{-1}) = 2\left[1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_o}\right)\right] \qquad (17)$$

The reverse of annihilation velocity of orthopositronium $\lambda_{pick-off}$ gives the lifetime of orthopositronium $\tau_3(o-Ps)$, as : $\tau_3(o-Ps) = 1/\lambda$

$$\tau_3(o-Ps) = \frac{1}{2}\left[1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_o}\right)\right]^{-1} \qquad (18)$$

Can be obtained by correlation with known cavity and cavity dimensions. The best fit of the polymer materials from Ps lifetime is obtained by positron lifetime spectroscopy to the free volume radius (R). The average free volume [8] is writeable as in below:

$$<\upsilon_f(\tau_3)> = 4\pi R^3/3 \qquad (19)$$

The thermodynamic behavior of polymer materials and blend materials were discussed in previous studies [9-10]. Also, a statistical theory with a measure of free volume hole fraction was developed. The theoretical hole fraction h_{th} can be extracted from the experimental P-V-T [3], as follows:

$$h_{th} = \int n(\upsilon_f)\upsilon_f d\upsilon_f = N <\upsilon_f>$$

$\to N = \int n(\upsilon_f)d\upsilon_f$ is the number of holes per unit volume, and $<\upsilon_f>$ average free volume is the hole size, $n(\upsilon_f)\upsilon_f$, υ_f and $\upsilon_f + d\upsilon_f$ holebility number in volume range density. The positron experiments suggested that $<\tau_3>$ may be related to $<\upsilon_f>$ and I_3, with the free volume density N can be taken proportionalıy as:

$$h_{Ps} = CI_3 <\upsilon_f(\tau_3)> \qquad (20)$$

where C is the ratio between o-Ps, intensity I_3, and cavity density. Obviously, C can be found from $h_{Ps} = h_{th}$. Equating the theoretical free volume fraction value to the experimental free volume fraction.

Usually, the constant C value for the polymer material is $0.0018(\overset{o}{A})^{-3}$.

3. Experimental Section

Using the PALS technique, measurements between two γ-rays were taken. The gamma beam value, that comes with the start signal to the 1274 keV γ beam, is determined as the signal spectrum of the birth of positrons. The gamma-ray value of 1022 keV, which comes after a few nanoseconds, is marked as the death of signal of the positrons annihilated by electrons in the material, or as a stop signal. The positron source was prepared by placing approximately 30 μCi ^{22}NaCl flowing solution on a thin aluminum foil (5 μm thick). The measurements were taken by sandwiching into the right and left sides of the source. The materials under investigation had to be of two mm thickness. Plastic scintillators, adhering to a 265 Ortec based Hamamatsu 2059 photomultiplier tube (PMT) that is operating at negative 2050 volts, were used because they are very sensitive to γ rays. These scintillators were set to positron start and stop signals at 1274 keV and 1022 keV, respectively. Two fixed fractional differential splitters (Ortec CFDD 583B) were used to detect timing signals. The Amplitude Transducer (TAC) was used for a time to convert different signals. The converted signals were fed to a multichannel analyzer (Ortec Model 919E Ethernim MCA). The spectroscopic data obtained from the MCA were analyzed using the RESOLUTION and PATFIT codes [12] to obtain the lifetime and free volume fraction density that reveal information about free volume. The resolution of the system was about 350 ps and the measurements were made by taking a million count for each temperature, as shown in Figure-1.
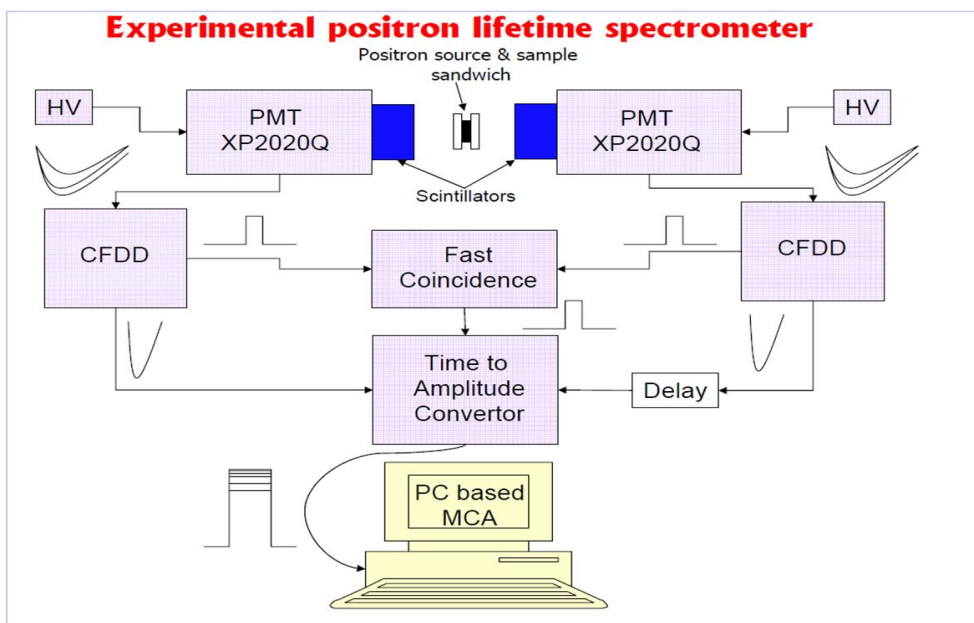
Figure 1- A schematic diagram of the positron annihilation lifetime spectroscopy system

It is worthy to note here that the positron and positronium parameters (parapositronium, orthopositronium, free positron, and intensities) were measured in the positronium lab in Istanbul, with a million positronn numbers for each temperature used.

4. Results and Discussion

The longest-lived component, o-Ps, with lifetime (τ_3) and intensity (I_3) were obtained from the analysis of the positron lifetime spectra. The o-Ps lifetime can serve as a measure of the free volume size. A Ps is considered to have an infinite spherical potential well of radius R. The relation (18) between the radius R and the o-Ps lifetime (τ_3) allows to find the average free volume in a spherical approximation,

where $R_0 = R + \Delta R$, with $\Delta R = 0.1656 \, nm$ is an adjustable parameter for a measure of electron layer inside the spherical potential well.

Properties of pure PLA and PLA/Cur composite

Table 1- Results of properties of PLA and PLA/Cur tested by using PALS technique, τ_1 is taken as 125 ps and fixed in all calculations. The intensities are normalized as $I_1 + I_2 + I_3 = 1$.

	T(°C)	τ_2(ns) (±0.003)	I_2(%) (±0.8)	τ_3(ns) (±0.01)	I_3(%) (±0.3)	R(Å) (±0.01)	f_υ(%) (±0.11)
PLA	10	0.382	75.67	2.07	15.28	2.91	2.84
	20	0.384	74.62	2.09	15.04	2.93	2.85
	40	0.374	80.01	2.17	15.3	2.99	3.10
	60	0.378	78.41	2.31	14.63	3.12	3.34
	70	0.380	77.19	2.34	14.83	3.14	3.47
	80	0.382	76.18	2.36	14.90	3.16	3.54
PLA Curcumin	10	0.376	71.76	1.82	14.74	2.67	2.13
	20	0.379	71.45	1.83	14.69	2.68	2.14

40	0.380	73.12	1.89	14.69	2.75	2.29
60	0.402	61.85	2.20	13.40	3.02	2.80
70	0.379	72.94	2.14	13.95	2.97	2.76
80	0.381	72.11	2.17	14.06	3.00	2.86

Using the PALS technique, the parapositronium lifetime spectrum was fixed and proven to have the value of $(\tau_1 = 125\,ps)$. The second component is orthopositronium, with lifetime (τ_3) and intensity (I_3). The third component is positronium, with lifetime (τ_2), that is formed from free positrons,, and intensity (I_2). Free volume radius and hole fraction could extract the free volume measurements for polylactic acid and polylactic acid curcumin hybrid, which were plotted against temperature values using the PATFIT program[12] .
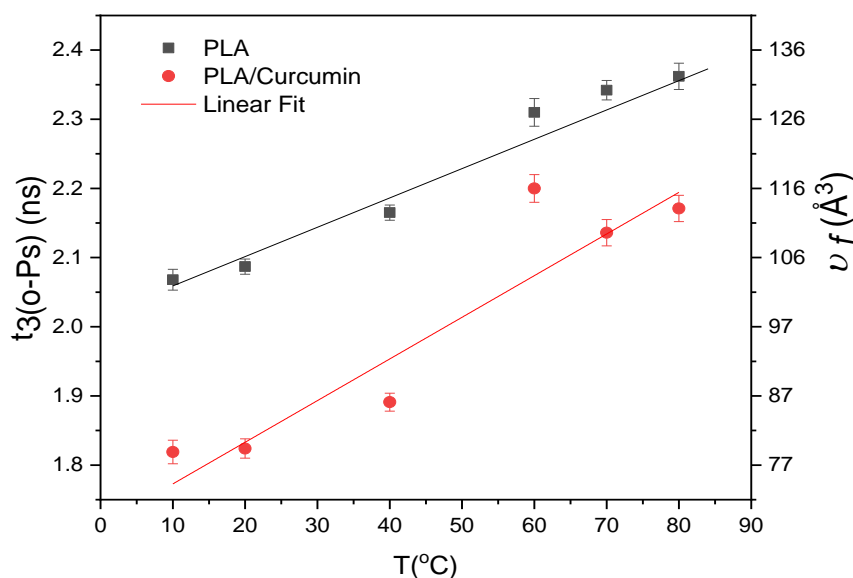

Figure 2- The o-Ps lifetime with the corresponding free volume versus temperature for PLA and PLA/Curcumin composite.

The lifetime and intensity of orthopositronium in the PALS system have an important role in measuring microscopic defects and free volume size. Figure-1 shows the o-Ps lifetime (left y-axis) corresponding to the free volume (right y-axis). These parameters are plotted for polylactic acid and polylactic acid curcumin hybrid as a measure of temperature. They showed a linear relationship with the pure polylactic acid and polylactic acid composite. However, there appears to be less increased values in the case of polylacticacid curcumin.
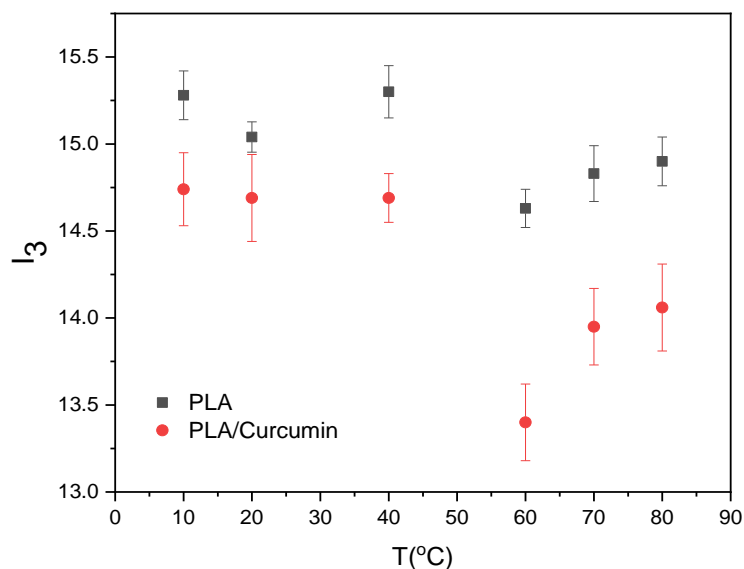
Figure 3- The o-Ps intensity versus temperature for PLA and cPLA/curcumin composite

The o-Ps intensities of polylactic acid and polylactic acid curcumin composite are associated with the number of hole free volumes [8-9]. It was found that there was a decrease in orthopositronium intensity of less than 60 ^{o}C, which was then increased relatively. Also, it was found that as the temperature increases, it causes an increase in free volume. There was a general decrease in orthopositronium intensities, as shown in Figure-3. .
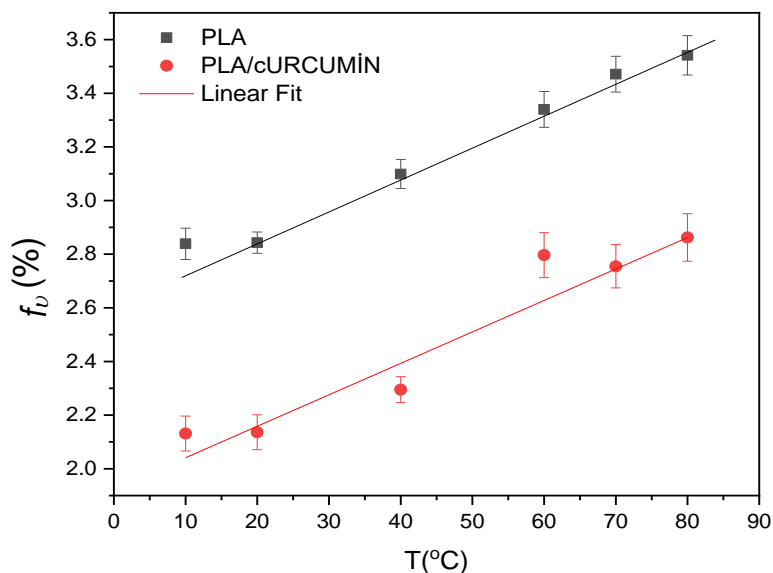

Figure 4-Free volume fraction versus temperature for PLA and PLA/Curcumin composite.

We also tested the free volume fraction versus temperature for the pure polylactic acid and polylactic acid / curcumin hybrid. When the temperatures increased, it caused an increase in the free volume fraction. A relatively less increase was observed in polylactic acid / curcumin hybrid compared with the pure polylactic acid. İn general, the relationship between free volume fraction and temperature was linear, as illustrated in Figure-4.
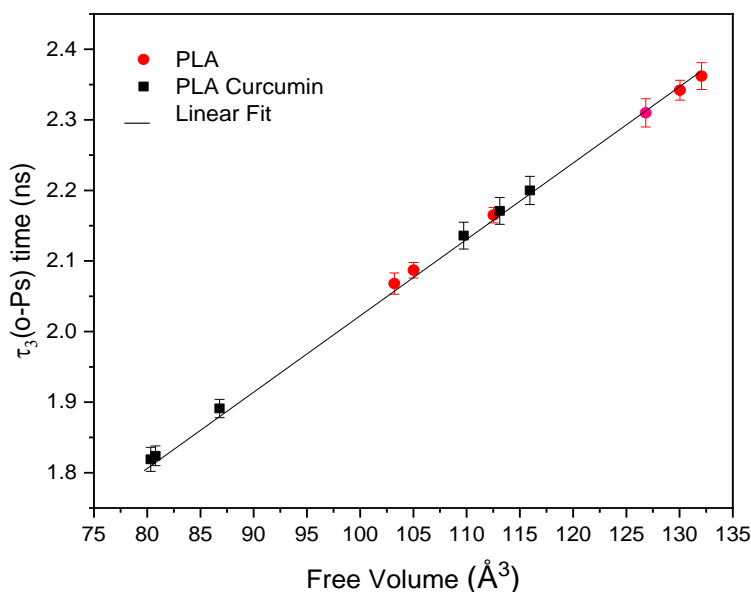
Figure 5-o-Ps life time versus free volume for PLA and PLA/Curcumin composite.

A linear relationship between free volume and o-Ps life was determined and the relationship between free volume and temperature was also found to be linear. Curcumines were used as additives to minimize the defects of the polylactic acid material. In order to determine the physical behavior, the temperature was increased to 353K and positronium parameters were measured. When we compared pure polylactic acid and polylactic acid / curcumin composite, the increase in free volume was less in the composite. The reason is the addition of curcumins that settle down in pores and free volume spaces [9] . . When the toughness of the material increases, the durability of the material will of course increase, as shown in Figure-5.

5. Conclusions

In this study, the thermodynamical properties of PLA, which has a wide application area, and its PLA/Cur composite, were examined with PALS technique to compare and analyze the hole fraction and free volume values. The o-Ps atom showed a lifetime value of 1-5 ns in the polymer structure. There was also a temperature dependence of the orthopositronium lifetime and intensity. The longest lifetime of orthopositronium atom on temperature gives information about the hole fraction and free volume dimension. Significant changes in thermodynamic properties were observed at a temperature of $58^{o}C$, as the polylactic acid underwent a phase change around this temperature; the orthopositronium lifetime τ_3 abruptly increased and its intensity I_3 suddenly decreased. The orthopitronium atom was very sensitive to hole fraction and free volume dimension. The orthopositronium lifetime and its intensity played a very important role in measuring the nanometric scale of hole fraction and free volume dimensions, as well as in determining the material defects .

When comparing pure polylactic acid and hybrid composite polylactic acid / curcumin, the relationship between hole fraction and free volume dimensions was found to be linear. There was a decrease in PLA / Cur defects and free volume dimensions. The reason is that curcumins tend to fill the nano-scale material hole fraction and free volume pores. PLA / Cur physical properties and mechanical behavior were improved in terms of imperfections. By adding curcumin to polylactic acid, material toughness and durability are increased. The thermodynamic properties of PLA/Cur showed that the hole fraction and free volume proportions were decreased. PLA/Cur material gained more durability by incorporating curcumin into PLA. According to our results, PLA /Cur composite will take its place in the health sector as a more effective medical material in wound healing.

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