POSITRON ANNIHILATION FOR CHARACTERIZING POLYMERIC MATERIALS

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Abstract. Positron annihilation spectroscopy (PAS) is reviewed as a powerful technique for characterizing a number of materials, emphasizing the case of polymers. The basic physics of positronium, positron and their interactions with matter are discussed, as well as the equipment required for a PAS experiment. A specific example, namely the grafting of low density polyethylene (LDPE) with acrylic acid (AA) and metacrylic acid monomers is used to illustrate the use of PAS for characterizing complex polymeric systems.

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1. Introduction

During the last few years, the so-called positron annihilation spectroscopy (PAS) has been successfully employed for characterizing a number of different materials, including a wide variety of polymers. As a result of these investi-
gations, it has been demonstrated that the characteristics of the ortho-positron annihilation (o-Ps) are very sensitive to the free volume that is a key characteristic of a polymer structure, since it has a definitive influence on many of their physical properties [1]. As a consequence, the characterization of the free volume is related to the thermal history of a polymer and is currently the subject of many interesting investigations [2].

The formation of positronium, its lifetime and its extinction mechanism, are determined by the physical and chemical conditions of the micromedia that surrounds it, this is why positronium can be used to study the properties of matter, at a nanoscale level in the same way that it is used to study the physical and chemical processes that take place within it.

Positron annihilation spectroscopy is a sensitive tool for the study of the nanostructure and the molecular movement in the polymer and its capability of measuring the characteristic free volume of polymers makes it a unique technique, since it is not intrusive, non-destructive and it is sensitive to the free volume at a molecular level. When the positron annihilation spectroscopy is combined with other techniques, new and important information can be obtained on the structure-properties relationship of the polymers.

The phase transitions and the molecular movements in polymers can be studied through various methods, including: differential sweep calorimetry (DSC), mechanical-dynamical methods, spectroscopy techniques such as RMN $^{13}$C and $^1$H, IR, Raman and X-ray diffraction [3]. The glass transition and fusion temperatures ($T_g$ and $T_m$, respectively) are determined by thermal methods, such as DSC, depending on the thermal history, cooling level and subsequent heating [4].

As it is well known, polymeric materials are of great importance to different areas of science and technology. Moreover, the development of new copolymerization techniques has contributed to the development of polymeric materials with special characteristics [5]. In the copolymerization the individual properties of each polymer component can be combined, resulting in new applications for these polymers. For example, the copolymerization by grafting has allowed to widen the perspectives in the development of new polymers [6]. Through this type of copolymerization, important materials in the field of biocompatible materials, are being innovated for the improvement of their compatibility with human tissue and organs [7, 8].

One of the most commonly used methods to prepare copolymers by grafting, is by ionizing radiation [9]. The ionizing radiation presents certain advantage over the conventional chemical methods to induce the copolymerization by grafting. The use of gamma radiation to induce the copolymerization by grafting, is one of the applications of the ionizing radiation in the treatment of polymeric materials [10].
In the present review of the use of PAS to characterizing polymeric materials, some actual examples of grafting systems were chosen as examples, namely low density polyethylene (LDPE) and the acrylic acid (AA) and the metacrylic acid monomers cases. As we shall discuss, the results reveal the existence of a correlation between variations of the positron annihilation parameters and the changes in the average size of the free volume and also depend on the phase transitions presented by the base polymer after its copolymerization by grafting. The formation process of the positronium is quite sensitive to physical and chemical changes that occur in the nanostructure of the polymeric material.

2. General Background: The Positronium and the Positron

The positronium is the bonded condition of a positron and an electron, and it is customary symbolized by Ps. The probability that the positron (antiparticle of the electron) could be combined (even with a very short lifetime) with an electron was first considered by Mohorovicic [11] in 1934. However, it was 17 years after that Deutch [12] experimentally detected this combination. Nowadays it is known as positronium. The name positronium was proposed by Ruark [13] in 1945 and later McGervey and Bennedetti [14] proposed the symbol Ps.

The positrons emitted as a result of $\beta^+$ decay, lose the major part of their kinetic energy during collisions with the atoms and molecules of the media. So, when their kinetic energy has diminished to a few electron-volts, they can be combined with electrons to form positronium. Thus, the positrons emitted in a system can be annihilated, either free or as a part of the positronium.

The probability of the formation of positronium and its lifetime, are highly dependent on the physical and chemical microstructure of the media where the positronium forms. These positron annihilation parameters can be determined through the measurement of the time elapsed between the emission of the positron and its subsequent annihilation, through a fast system of gamma-gamma coincidences.

The high sensibility of the positron to the nanometer-sized structure that surrounds it, has led to the use of techniques based on the positron annihilation for the investigation and characterization of polymeric systems. For example, the positron life interval technique has been used in the investigation of phase transitions, through the variation of the annihilation parameters (positronium life intervals and the formation probability of it) [15].

The study of the molecular solids through the positron life interval technique, is an interesting and extensive subject. Various authors have described the investigations about its application to different types of materials such as polymers, liquid crystals, liquid crystals and glassy metals [16]. These investigations have been focused to the study of the effects caused by some external
fields or the changes in the thermodynamic variables of these solids, through
the measurement of the positron annihilation parameters. The study of the ef-
facts caused by the gamma-ray irradiation, or by particle irradiation such as
electrons and neutrons on molecular solids has also been of great relevance.

3. Interaction of the Positron with Matter

The positron annihilation and the formation and decomposition of positronium
has been widely discussed in some papers [17,18] and in the proceedings of
the First International Conference on Positron Annihilation held in Detroit in
1965 [19], along with a great deal of works related to the subject [20–29].

As predicted by Dirac and discovered by Anderson in 1932, the positron \( e^+ \)
is the antiparticle of the electron \( e^- \), with the same mass \( m_0 c^2 = 0.511 \text{ MeV} \)
and the same charge, but positive charge \( e = 4.8 \times 10^{-10} \). In the original
experiments of the positron and the electron a phenomenon, previously un-
known, was observed: the annihilation accompanied by the gamma emission
of a quantum of energy, a characteristic process of the interaction between a
particle and its respective antiparticle.

When an electron-positron collision occurs, the annihilation may be accom-
panied by the emission of two gamma quanta or as in some rare cases (with
a probability of 1/373) of the three photons. The annihilation of one quantum
requires the participation of a third particle and its probability is negligible.

In bulk matter, a positron, with an initial energy in the order of keV, loses
great part of its energy during ionization and stimulation processes of the media
molecules, until it becomes an almost thermalized positron with energies in the
range of just a few eV. That is precisely when it can interact with an electron in
the media, transforming mass and energy of both particles into electromagnetic
energy. This process is known as annihilation and it can be schematically
illustrated as follows:

\[
Ee^+ + Ee^- \rightarrow E\gamma .
\]

During the process, a certain number of gamma photons are emitted, de-
pending on the relative orientation of the positrons and electrons spins: an
even number of photons (most probably two), when the spins are antiparallel
(singlet state), and an odd number of photons (most probably three), when the
spins are parallel (triplet states). In the first case, the two photons are emitted
in opposite directions, each one with energy of 0.511 MeV. On the other hand,
the three photons lie within a plane and the sum of their energies is 1.022 MeV.

The interaction process of the positron may be preceded by the formation of
a linked positron-electron state, known as positronium (Ps). The probability of
the formation of the Ps mainly depends on the chemical and physical structure of the media where the positron is found [30].

4. Positronium

The positronium mass is 1/920 of the mass of a hydrogen atom and its reduced mass is \( \mu_{\text{Ps}} = \frac{m_0}{2} \), or half the mass of the H atom, \( \mu_H = m_0 \). Consequently, the ionization potential of positronium for the base state 1s is half of H and is equal to \( V_{\text{Ps}} = 6.77 \text{ eV} \).

\[
V = e^4 \frac{\mu Z^2}{2 \hbar^2 n^2}, \quad \mu = \frac{m_0}{2}, \quad Z = 1, \quad n = 1.
\]

The distance between the negative and positive charges in the H atom is defined as the radius of Bohr’s first orbit: for the positronium it is the double in magnitude and very close to 1.06 Å (for \( n = 1 \)). However, for the positronium this distance is not the radius but the diameter of the atom itself.

The positronium exists in two base states (1s; \( n = 1 \)) depending on the relative orientation of the spins of particles \( e^+ \) and \( e^- \); the triplet state or ortho-positronium \( ^3\text{Ps} \) (3s1) or o-Ps with parallel spins of \( e^+ \) and \( e^- \), and on the other hand, the singlet state or parapositronium \( ^1\text{Ps} \) (1s0) or p-Ps with antiparallel spins of \( e^+ \) and \( e^- \). The resulting spin of the o-Ps is \( J_T = 1 \). Nevertheless, three sub-states are possible, each one with a different value for their magnetic quantum number (\( m = +1, 0, -1 \)). For p-Ps, \( J_S = 0 \) and \( m = 0 \). According to the statistic weight of the p-Ps it is one third that of the o-Ps; however, in the formation of the positronium the triple atoms count with 75\% in all cases and the single atoms only count with 25\%.

The positronium lifetime in free space is finite and like the positron, physics conservation laws (energy, momentum, etc.) control its interaction. In agreement with the different rules of selection, the p-Ps is annihilated with the emission of two gamma quanta, whereas the o-Ps emits three photons. So, the intrinsic lifetime of the singlet atoms is much shorter than that of the triplet atoms. The p-Ps lifetime in vacuum is equal to

\[
\tau = 2 \frac{\hbar^2}{m_0 e^2} \frac{1}{c^2} = 1.25 \times 10^{-10} \text{ s}.
\]

While the lifetime of o-Ps is \( \frac{9\pi}{4} (\pi^2 - 9) \frac{\hbar c}{e^2} = 1115 \), this value indicates that o-Ps is 1115 times bigger than p-Ps and its value is \( \tau_T = 1.4 \times 10^{-7} \text{ s} \).
Due to the fine coupling of state 1s of the Ps atom, the energy of o-Ps exceeds that of the p-Ps according to the relation:

\[
\Delta W = W^\text{p} - W^\text{o} = \frac{7e^2}{12\hbar c} m_0 c^2 = 8.4 \times 10^{-4} \text{eV.}
\]

In strong enough external magnetic fields, it is not the total momentum \(J\), but the magnetic quantum number \(m\) the significant quantum number, and the conditions \(m = 0, J = 1\) and \(m = 0, J = 0\) are intermixed; then the annihilation fractions by two gamma quanta are increased from 25 to 50\% (in a vacuum). The external field alter the energies of sublevels with \(m = 0\), increasing this energy for \((m = 0, J = 1)\) and decreasing the energy according to \((m = 0, J = 0)\) states through the relation

\[
\Delta W = \frac{\Delta W}{2} \sqrt{1 + \chi^2}
\]

where:

\[
\chi = \frac{2e\hbar}{m_0c} \frac{H}{\Delta W} = 2.7 \times 10^{-2} \text{H (kGauss).}
\]

But there is no effect on the energy in the \(m = \pm 1\) states. The probability of annihilation by three Ps gamma then can be reduced by the transition of a magnetic dipole \((m = \pm 1) \rightarrow (m = 0)\), in a high frequency electromagnetic field with a resonance frequency given by the relation \(\nu = \frac{\Delta W}{2\hbar} (\sqrt{1 + \chi^2} - 1)\). For a field of approximately 10 kG, the frequency \(\nu\) is approximately equal to 3000 MHz; thus, the first investigations conducted by Deutsch [31] on extinction were the first experiments on radiospectroscopy of the positronium with which the value of \(\Delta W\), with a great precision, was obtained.

The characteristics of the base states of the positronium are summarized in Table 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>para-positronium</th>
<th>ortho-positronium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>p-Ps</td>
<td>o-Ps</td>
</tr>
<tr>
<td>Spin’s relative orientation</td>
<td>Antiparallel</td>
<td>Parallel</td>
</tr>
<tr>
<td>Formation’s relative probability</td>
<td>1/4</td>
<td>3/4</td>
</tr>
<tr>
<td>Intrinsic life spans</td>
<td>0.125 ns</td>
<td>140 ns</td>
</tr>
<tr>
<td>Most probable annihilation mode</td>
<td>2 photons</td>
<td>3 photons</td>
</tr>
</tbody>
</table>

As can be seen in Table 1, the properties of the o-Ps, especially its lifetime in relation to the p-Ps, make it the most adequate type for the interpretation of
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the chemical and physical characteristics of the media where the annihilation occurs. Thus, in condensed matter and as a result of various interactions, the o-Ps lifetime is reduced to a few nanoseconds. This issue constitutes the basis of the Positron Lifetime Technique within the Positron Annihilation Spectroscopy.

5. Basic Differences Between Hydrogen and Positronium [32]

The positronium atom can participate in substitution, addition and oxidation reactions, and chemically acts like hydrogen, but as a result of its principal difference in mass, the structure of the compounds formed, its formation energies and the kinetics of the chemical reactions are very different for H and Ps.

If a molecule of the type HA (A = arbitrary atom) is considered as a molecule of two nuclei, then similarly PsA = e⁺A⁻ is characterized as a one nucleus molecule. Thus, for example an A atom has layers mixed with electrons and positrons. This has a strong effect on the bonding energy. For example, if the bond energy of molecular hydrogen is close to 4.5 eV, then such energy has been estimated to be 0.657 eV for HPs and 0.11 eV [33] for Ps₂.

Any molecule of type PsA would be less stable than HA, due to value zero of the vibrational energy, from which the dissociation energy quantified must be increased with the addition of the reduced mass μ of the molecule. In the beginning \( h\omega_0 \frac{1}{\sqrt{\mu}} \), but the relation \( \frac{(h\omega_0)_{PsA}}{(h\omega_0)_{HA}} \) almost never gets to the value:

\[
\sqrt{\frac{\mu_{HA}}{\mu_{PsA}}} \approx \sqrt{\frac{m_{Ps}}{m_{Ps}}} \approx 30.
\]

Nevertheless, any substitution reaction in which the hydrogen atom is replaced with Ps, HA + Ps \( \rightarrow \) PsA + H, must be an endothermic process.

The ionization potential of hydrogen is twice greater than that of the positronium, consequently the oxidation of Ps by H in the gaseous phase must be a strong exothermic process: \( H^+ + Ps \rightarrow He^+ + 6.8 \) eV. However, since hydration heat (particularly solvation heat) of the proton gets close to 11 eV, very far from that of the positron (its tentative value is 1.5–2.0 eV as in the case of the electron), the oxidation of Ps in a water solution is an endothermic process and is proved to be \( H_{aq} + Ps_{aq} \rightarrow H_{aq} + e_{aq} (\approx 2.5 \) eV).

The electronic affinity of an H atom (0.75 eV) exceeds that of the positronium, which has an estimated value of 0.2 eV. When we compare the reaction data of H and Ps, we must consider the difference between their heats (endothermic reaction heat is the minimum activation energy possible), pre-exponent coefficients (the thermal velocity of the positronium is approximately 30 times greater than that of H) and the diffusion coefficients, which in the
case of positronium in different solutions reach values of \( D \approx 3 \times 10^{-4} \text{ cm}^3\text{s}^{-1} \) [17].

We must also consider the tunnel effects of light particles such as the Ps, particularly under those conditions when the transitions are practically impossible for H atoms. It has been found that [36, 37] the values of "tunnel temperatures" \( T_{\text{tun}} \), are a way under the tunnel transitions that predominate exponentially over the Arrhenius behavior, for example, the transitions over the barrier \( T_{\text{tun}} = \frac{\hbar}{k \pi d} \sqrt{\frac{E}{\mu}} \), where \( k \) is the Boltzmann constant, \( \mu \) is the reduced mass of the tunnel system and \( d \) and \( E \) are width and height of the potential barrier.

For the free positronium the tunnel temperature \( T_{\text{tun}} \) is approximately 30 times that of H and frequently of hundreds of degrees. Consequently, the gaseous phase reactions with positronium in a tunnel mechanism without activation are highly probable.

The tunnel effect is not the only consequence of the wave properties of Ps associated with its small mass and the consequently greater wave de Broglie wavelength \( \lambda \). For a thermalized Ps atom at room temperature \( \lambda \) is approximately equal to 9 Å and the effective section of the processes that involve the positronium atom, in a beginning, can reach values of \( 4 \pi \lambda^2 \approx 10^{-3} \text{ cm}^2 \).

Another difference between H and Ps reactions is caused by the Ps’ smaller mass so the transition of electrons between Ps and other atoms cannot be regarded as an adiabatic process, unless accompanied by a change in the distance between the positron and the other atom nucleus.

Finally, the smaller mass of the Ps produces a special type of excitation during the endothermic substitution involving the Ps atom (Ps+AB \( \rightarrow \) APs+B), and this excitation widely differs from that of the H atom, but it is very close to the excitation for the dissociative electronic seizing effect (e\(^-\)+AB \( \rightarrow \) Ae\(^-\)+B). The cross sections of such reactions for the Ps and the e\(^-\) have a maximum which significantly decreases as the energy increases over the threshold value for a quantity equal to that of quantum vibration of the AB molecule [38].

From the above discussion it is clear how difficult is to translate the results for the Ps to reactions involving H; nevertheless, this allows to foresee new ways to apply the Ps techniques in chemistry, which we will discuss throughout this paper.

6. Models for Positronium Formation

One of the main challenges for the study of Ps physical chemistry, is to satisfactorily explain the mechanism of its formation. There exists controversy among the models proposed, and the following are the most accepted.
6.1. Ore Model

Ore proposes that the Ps formation occurs when the positron directly “captures” the media molecules, within the defined energy interval, which is known as Ore interval (39). This process can be represented as

\[ e^+ + M \rightarrow Ps + M^+ . \]

The limits of the Ore interval depend on the ionization energy and excitation of the media molecules \((V_i)\) and the ionization energy (link energy) of the Ps. \(V_i\) gives the upper limit: \(E_{\text{max}} = V_i\) and the low limit is \(E_{\text{min}} = (V_i - 6.8)\) eV, where 6.8 eV is the bonding energy of Ps. The formation probability of Ps is greater for those positrons whose kinetic energy is found within the limits of the Ore interval. The rest of the positrons only produce ionization and excitation for the free media molecules, annihilating themselves without forming Ps (Fig. 1).

![Fig. 1. Diagram representation of the Ps formation and extinction processes, that illustrates the Ore model and its possible deflection](image)

The validity of this model is limited almost exclusively to monatomic gases. In condensed matter factors as dissociation energies and intermolecular forces require another type of treatment to determine the ore interval for the formation of Ps [40].

6.2. “Spur” Model (conglomerate)

In 1974 Mogensen [41], proposed an alternative model to that of Ore’s, considering the fact that a positron, in its path through the media, is capable of producing a “spur” (conglomerate; a group of intermediate reactive species), when it ionizes the molecules that finds along its way (Fig. 2). According to
this model, Ps is formed in the final part of the "conglomerate", between one of the created electrons in it and the incident positron, as illustrated below:

(1) \( e^+ + M \rightarrow e^+ + e^- + M^+ \)

(2) \( e^+ + e^- \rightarrow Ps \)

The formation reaction of the Ps competes with all those reactions that occur between the radical or ionic species with the electrons or positrons within the "spur", as long as the kinetic energy value of the positron is higher than \( (V_i - 6.8 \text{ eV}) [42] \), the lower limit of the Ore interval. This model is capable of explaining the experimental results obtained in the liquid phase. However, it does not exclude the validity of the Ore model.

**Fig. 2.** Diagram representation that shows the "spur", produced during the last positron ionization process (a) the combined kinetic energy of any electron positron pair is greater than the coulomb attraction force, (no positron is formed); (b) the kinetic energy of an electron positron pair is less than the coulomb attraction force (positron is formed). The total electron and positron energies, \( (E^-, E^+) \), \( I \) is the positron ionization potential

The formation process of Ps is so complex, especially in solids, that none of the former models have been able to explain satisfactorily and in a quantitative manner, many of the experimental results obtained.

The interaction between the positron (or positronium) and matter, can be investigated throughout two fundamental phenomena: the inhibition of the o-Ps formation and the extinction of the o-Ps formed.
6.3. Inhibition of the Positronium Formation

The inhibition of the Ps formation, that is, the diminish of its formation intensity, may be treated on the basis of the exposed models. That is if we take the Ore model or the “spur” model as a basis, the inhibition will be understood as a diminish of the positron energy even under the lower limit of the Ore interval, or, as an seize effect of the Ps ($e^+ + e^-$) forerunners within the “spur”.

As it was previously mentioned, the Ore model implies that all the positrons that have kinetic energy within the Ore interval produce Ps. That is, the formation process of the Ps, must compete with other processes that can cause the moderation of the Positronium, within energies below the inferior limit of the Ore model. The most important are the elastic and inelastic collisions with the media molecules. The inhibition process of the Ps formation also includes the seize of the positrons when these are added to the subtraction of the AB molecule:

$$e^+ + AB → ABe^+ \text{ or } A + Be^+$$

If the formation of the compound occurs above or within the Ore interval, the seized positrons are no longer available for the formation of Ps, thus decreasing its performance.

7. Interaction of the Positronium with Matter

In condensed media, the Ps annihilation mechanism and its lifetime, are greatly modified as a result of the diverse interactions with itself. This way, the lifetime of o-Ps goes from 140 ns, in free space, to a few nanoseconds in matter. The responsible processes of this phenomenon are known as extinction processes and mainly depend on the physical and chemical characteristics of the media. The extinction processes are:

1. Extinction by pick-off;
2. Extinction by spin conversion;
3. Extinction by chemical reactions.

The most common of these processes is the extinction by pick-off process, which can be applied to all substances, independently from their nature or properties.

The spin conversion process and the chemical reactions only occur in certain types of substances, for example: oxidant, paramagnetic and other substances [43]. These processes properly constitute the Positronium Chemistry.
8. Extinction by Pick-off

As it has been mentioned, the lifetime of Ps is sensibly decreased when it interacts with matter. This process is known as extinction by pick-off of the Ps and consists of the positron, that forms the Ps, is annihilated with an electron (of contrary spin) of the media’s electronic cloud and not with the one that it is associated with. This consequently annihilates the o-Ps via the emission of only two gamma photons and that its lifetime decreases. The p-Ps has a very short lifetime (0.125 ns) to be affected by this process.

The degree of annihilation by pick-off, \( \lambda_p \), is given by the following relation [31]:

\[
\lambda_p = \frac{1}{\tau_p} = \pi r_0^2 c N_{\text{eff}}
\]

where \( N_{\text{eff}} \) is the effective number of electrons by volume unit, \( \tau_p \) is the o-Ps lifetime in the media, \( r_0 \) is the classic radius of the positron or electron, \( c \) is the light speed.

As it can be seen, the annihilation degree by pick off depends on the electronic properties of the media. It has been proved that, in this type of extinction, the positronium interacts with media’s molecular electronic cloud

\[
\lambda_p = \frac{1}{\tau_p} = \frac{N_A}{M \rho \nu \sigma_p}
\]

where \( N_A \) is the Avogadro number, \( M \) is the molecular weight of the media, \( \rho \) is the density of the media, \( \nu \) is the positron’s velocity in the media, \( \sigma_p \) is the efficient section of the annihilation by pick-off.

However, some of these parameters, like \( \nu \) and \( \sigma_p \), cannot be calculated directly. That is why, there have been many attempts to establish a relation between the degree of annihilation by pick-off \( \lambda_p \) and the characteristics of the material in which the annihilation occurs.

In the mid-50’s it was thought that for the molecular solids there had to be a relation between the degree of annihilation by pick-off and the changes in the materials density, by temperature or pressure variation. It was proposed that, in a molecular solid, the positronium was found in the molecular interstices in a way that the atoms that surrounded it performed a repulsion force over it. Thus, the lifetime of Ps depends on the free that’s available to avoid this repulsion [39].

9. Positronium in Molecular Solids

The formation of positronium in molecular solids has not been studied well enough as it has been in liquids. In a solid, the formation of Ps seems to
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depend on the same elements as in liquids, on the chemical structure of that solid. However, for a solid, the quantity of free space between the molecules seems to play a fundamental role. Thus, the Ps will be formed with greater intensity in a less dense structure than in a denser structure [44]. The free space between the molecules plays an important role in the lifetime variation of the Ps. The greater the free space available for Ps, it will "feel" less molecular electrons. For example, to explain the lifetime variation of o-Ps $\tau_2$ with pressure, Wilson [45] has proposed a model in which, the Ps is found always in regions of low density in the material and that's related to $\tau_2$ with density change. On the other hand, the influence of flaws on the Ps lifetime has been studied.

The positronium will tend to be trapped in the studied materials flaws, which offers major space in the material even when they are under concentrations in the order of ppm. A clear example of the Ps trapping in the structure cavities, has been the ice case [44]. At temperatures under $-100^\circ$C, Ps annihilates very fast. However, when cavities are induced in the ice, heating it up from $-100^\circ$C to $50^\circ$C or by the addition of an HF solution, some of the Ps are trapped in the cavities before their annihilation. Apparently, the trapping happens under low flaw concentrations, of the order of ppm, as we mentioned before. In the majority of the molecular crystals, the flaw concentrations are much greater than the ppm levels, that is why one must wait until the Ps is completely trapped in such crystals before it is annihilated. However, it is unknown whether Ps is completely trapped in such flaws or if it can move in the crystal through the, for example, tunnel from cavity to cavity.

10. Free Volume Model

The observations of different authors about the relation between the o-Ps lifetime and molecular structure of the media, back in the fifties [39] was summarized in a model proposed by Brandt, Berko and Walker [46]: the free volume model. This model correlates the o-Ps $\tau_2$ lifetime, with the available free volume in the material's network, for the formation and extinction of the o-Ps. That is, the o-Ps lifetime increases with the free volume. An increase of the free volume in the system means less overlap of the wave functions of the positron (that forms the o-Ps) and of the media electrons.

To understand the concept of free volume, it can be defined as a unit of volume:

\[
\text{unit of volume} = \text{free volume}(V_f) + \text{excluded volume}(V_{exc})
\]

Where the excluded volume is the high-density electronic region within the unit of volume and therefore, it is not available to be occupied by the positronium.
or Ps. Then, the free volume can be written as

\[ V_f = \text{unit of volume} - V_{\text{exc}}. \]

In an extension of their original model, Brandt et al [47] established a dependency of the formation intensity of the Ps with the free volume. According to this model, the formation probability of Ps is greater in those substances that have greater free volume up to a certain critical value.

11. Annihilation of the Positron in Polymers

The study of the positron annihilation in the polymers has attracted great attention in the last few years [2, 48–56]. This is due to two main circumstances: the polymers are a good model system for the investigation of the Positronium atom in solids and, on the other hand, the positron studies can be a useful tool for the analysis of the polymeric materials microstructure.

The positron annihilation spectroscopy has been used in studies of various physical-chemical systems, in which can be included the polymeric materials. As a result of these investigations, it has been demonstrated that the characteristics of the annihilation of the ortho-Positronium are sensitive to free volume present in polymers. Free volume can be understood as the volume within the polymeric structure that is not occupied by molecules and that has a great influence on the physical properties of the polymers. Consequently, since the free volume characterization is related to the mechanical and thermal history of the polymer, its investigation is of great interest. The use of the Positronium Annihilation Spectroscopy in the free volume characterization is unique, since it is a non-destructive technique and is sensitive to a free volume in a molecular level. When this technique is combined with other conventional measurements, it can offer very useful information related to the structure/properties relationships of the polymers [58].

The use of polymers in industrial applications requires a basic understanding of their properties. A key problem in this sense is the relation between the macroscopic mechanical properties (impact strength, elastic modulus) of the polymers and the holes of free volume present in these at an atomic scale of just a few angstroms [9]. The existence of free volume in polymers has been stated for over more than three decades [57]. The explanation of the viscoelastic properties in the polymeric materials is based on the theory of free volume [60], which describes the kinetic and dynamical behavior of the polymeric molecules and the holes of free volume in the matrix.

Besides the great efforts during the last decade to understand the physical-chemical properties of free volume, limited information of the holes size, concentration and its form was obtained. In fact, there are no direct experimental
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observations of these parameters. Among the techniques that have been used in this type of microanalysis we can find the Positronium Annihilation Spectroscopy [61,62] photochromic and fluorescent spectroscopy [63, 64] and X-ray diffraction [65]. The diffraction method gets complicated when the size of the hole is less than 10 Å, while the other two methods induce additional perturbations, that is why the information can only be considered as approximate. The Positronium Annihilation Spectroscopy is capable of obtaining the most important properties of the free volume holes directly in the polymeric materials [66].

Unlike the majority of the analytic tests, which require some material to be injected in the system under study in an external way, the Positronium is, by nature, spread internally in the holes after it has been thermalized in a polymeric material. Due to this unique characteristic, the Positronium Annihilation Spectroscopy can be regarded as an analytic in situ technique. This technique has the advantage of a great sensibility especially in the determination of the free volume holes in the polymers and in the solids surface. In Fig. 3, the in situ characteristic of the Positronium Annihilation Spectroscopy is presented for a polymeric material.

![Ps localization diagram in the free volume holes of a polymer before it’s annihilation](image)

The vast majority of the engineering polymers are amorphous, such that positrons present a tendency to form Ps in this type of materials. The polymer specialists have used the interaction of Ps with the micromedia of the polymeric material, as a basis for the measurement of free volume, glass transition temperatures, metallic ion effects on the chemical architecture and the effects of chemical additives over the physical properties of polymers [58].

12. Experimental Section

In the present paper, copolymers by grafting of low-density polyethylene systems were prepared grafted with acrylic acid and metacrylic acid. Ionizing γ-radiation and an indirect grafting method were employed. The phase tran-
sitions that occur were studied in these systems by positronium annihilation spectroscopy, using the positron life interval technique.

12.1. Materials and Reactives

For the experiments, a low density polyethylene was used, provided by ABA Industry, the monomer acrylic and metacrylic acids and the Mohr salt (ammonium ferrous sulfate) were from Aldrich Chemical Company Inc and were used without previous purification. The water used was distilled. The polyethylene, monomer and Mohr salt chemical structures used, are shown below:

chemical structure of polyethylene
\[ -(\text{CH}_2=\text{CH}_2)\_n \]

chemical structure of monomers
\[ \text{CH}_2 = \text{CH} - \text{COOH} \quad \text{CH}_2 = \text{C} (\text{CH}_3) \text{COOH} \]
acrylic acid
metacrylic acid

chemical structure of ammonium ferrous sulfate (Mohr salt)
\[ \text{FeSO}_4 (\text{NH}_4) _2 \text{SO}_4 6\text{H}_2\text{O} \]

The experimental part consists of two main stages. A difference in the polymeric substrate used, was the thickness of the film, in one case it was 0.05 mm and in the other case it was 0.20 mm. The glass transition temperature \( T_g \) published for the LDPE is of \(-121^\circ C\) and a fusion temperature \( T_m \) that ranges from 105 \(^\circ C\) to 120 \(^\circ C\), with a density of 0.920 g/c.c. and a fluid index of 2. For the monomers, a \( T_g \) of 106 \(^\circ C\) is published, with a density of 1.051 g/ml for the AA and 228 \(^\circ C\) with a density of 1.015 g/ml for the MAA. The fusion temperature in both cases was not published due to their amorphous character [67].

12.2. Preparation of Polymer Samples

The selected polymer, for all the experiments, was prepared as a film. This film was cut in different sizes, 1 cm \( \times \) 0.6 cm for the experiments with the PAL and 2 cm \( \times \) 2 cm for the absorption experiments. In the first case, once the samples were ready, we placed them one on top of the other until we had a minimum thickness of 2.5 mm to insure that the positrons interacted effectively with the material.
12.3. Absorption Experiments

The original LDPE (ABA Industry) in a film form with two different thicknesses (0.05 and 0.20 mm), was cut in small sheets of 2 × 2 cm, which were separately introduced in vessels each containing 10 ml of a solvent (n-hexane, benzene, chloroform, water, and ethyl acetate) with the purpose of studying its absorption level. In the same way, the absorption percentage for each one of the pure and solution (1:1) monomers was determined with the purpose of establishing the appropriate conditions to continue with the grafting experiments.

All the samples were previously washed with ethanol to eliminate all contamination that could be present on the material surface, afterwards, these were placed on a stove at a temperature of 60 °C during 30 minutes, until they were totally dried, and finally they were placed on a vacuum drier during 24 h. Once this operation was completed, the initial weights for each of the sheets to be used, were determined at room temperature and were placed in glass vessels containing AA or MAA solution with concentrations varying from 100 % to 0 % of pure acid, at ten units steps. Afterwards, they interacted during different contact times: 1–12, 24, 48, 72, 96 and 120 hours; this was achieved without a light source to avoid the homopolymerization of the monomer. Then, the samples were removed from the vessel and dried with filter paper and immediately weighed. For the samples placed in the pure solution, the same procedure was employed.

The absorption percentage was determined according to the following equation:

\[ \%A = \frac{P_f - P_i}{P_i} \times 100 \]

where \( \%A \) is the absorption percentage, \( P_f \) — sample’s final weight and \( P_i \) — sample’s initial weight.

12.4. Grafting Experiments

The method used for the copolymerization reaction was the indirect or pre-irradiation method, which, in previous investigations [68], demonstrated to be the only method that could provide the required grafting percentages, within the interval needed for our investigation, and that offers superior technical advantages over the direct method.

The sample irradiation took place in a Gammacell-220 built by Atomic Energy of Canada Limited, with a nominal activity of 11840 Ci of Co until September 21\textsuperscript{st} 1974. In Fig. 4, its external characteristics are shown. The Gammacell-220 is a cobalt 60 \( \gamma \)-irradiation unit, which basically consists of a cylindrical source permanently locked up in a lead armor, a cylindrical vessel,
and a mechanism to move the cylindrical vessel upwards or downwards in the center of the source. The vessel has a chamber, 20 cm height by 15 cm diameter dimensions, in which the samples are placed externally.

![Fig. 4. Gammacell-220 general diagram](image)

The preparation of the samples was carried out as follows: 5 sheets of each density, previously weighed, were placed in test tubes of approximately 6 cm long and 1 cm wide. The vials were degassed and vacuum-sealed to be irradiated afterwards. The irradiation was made at room temperature at a dose rate of 1.05679 Kgy/h (Kilogray per hour), at a dose rate of 30 Kgy for all samples.

Later, once the irradiation period was almost finished, the samples were stored during 72 h in liquid nitrogen before carrying out the grafting reaction. The vials were opened while they were still frozen in a gloves box with a nitrogen atmosphere, with the purpose of avoiding the irradiated polymeric substrate to be in contact with the media oxygen, and to avoid the free radicals formed to react with it and form peroxides.

Once the samples were opened, the acid solution composed of 50% of the monomer, 50% water and 0.25 g of Mohr’s salt, freshly prepared and with nitrogen bubbling. The salt was added with the purpose of eliminating homopolymerization, an unwanted reaction originated during the grafting process. The vials were sealed again before introducing them in a hot water bath at a constant temperature of 80°C. After the contact times were completed for each sample, these were taken out of the vials, were placed separately in 250 ml glass and washed with enough distilled water. Afterwards, they were placed in distilled water, which was heated up to boiling point during approximately 8 hours and finally we applied Soxhlet extractions with the ethyl acetate; both treatments were carried out to eliminate monomer and homopolymer excess.
that could exist in the samples. Later, the samples were dried in the stove at a temperature of 60 °C and finally they were introduced in the vacuum drier during 24 h. Once this procedure was concluded, the samples were weighed and we determined their grafting percentage with the following formula:

\[
\%I = \frac{P_f - P_i}{P_i} \times 100
\]

where \(\%I\) is the absorption percentage, \(P_f\) — sample’s final weight and \(P_i\) — sample’s initial weight.

13. Obtaining the Positron Lifetime Annihilation Spectrum

The positron annihilation spectrum with a summit height of approximately 25 000 counts, was obtained at temperature steps of 5 °C, through an adequate temperature range to mainly locate the transitions of every copolymer system under research, obtaining at least three spectra per temperature step.

14. Positron Source

The radioactive sources most commonly used to produce positrons are Cu and Na. The maximum energy of the resulting positrons from the \(\beta^+\) decay of Cu is \(E = 0.65\) MeV and the average lifetime of this isotope is \(T_{1/2} = 12.8\) h. This means that the sources must be frequently changed, but the most significant advantage of copper is that high intensity sources with any configuration can be rapidly obtained by reactor irradiation; if copper is irradiated during a few hours within a thermic neutron flux of approximately \(10^{12}\) n/cm², you can get a Cu source with specific activities of hundreds of millicuries per gram. Such sources are necessary for angular correlation experiments, where high resolution angular instruments are used.

In our case, the positron source used in the positron life interval technique is Na, whose decay diagram is shown in Fig. 5. The positron life interval is measured as the elapsed time between the 1.28 MeV photon detection and the 0.511 MeV photon detection, that is a result of the positron annihilation process.

A thin nickel sheet was used as a support for the positron source, on whose surface was placed a drop of NaCl solution carrier free (from Amersham), which was evaporated on the sheets surface. The activity of the source used was approximately 25 mCi.
15. Gamma-gamma Coincidence Fast System

The obtention of the positron annihilation life interval spectra, was achieved using a gamma-gamma coincidence fast system, with a resolution (FWHM) of 0.3712 ps and its time calibration of 0.547 ns/channel. This equipment, including its resolution and calibration conditions, has been detailed in previous investigations [69, 70].

In Fig. 6, a typical gamma-gamma coincidence fast system block diagram is shown. The system consists of two flashing plastic detectors (Naton 135), which receive the gamma photons at 1.28 and 0.511 MeV values from the radioactive Na decay and from the positron annihilation process, respectively. Two constant fraction discriminators (TCFD) are connected with the detectors, which select the photons depending on their energies, this way, the 1.28 MeV photons pass through the TCFD-1, whose slit filters pulses with energies ranging from 0.8 to 1.3 MeV.

The discriminators are connected to a coincidence unit (CU) and to a pulse height-to-time converter (PHTC). The PHTC is used to measure the time interval between the 1.28 MeV photon detection and the 0.511 MeV of annihilation.
When it simultaneously receives a coincidence unit signal, a new pulse is generated with amplitude proportional to the measured time interval. The output pulse distributions from the PHTC are stored in a multichannel analyzer and are registered in memory in different channels according to its height, thus representing the positron life interval distributions.

16. Results: Positron Life Interval Spectra

The positron life interval spectra obtained, were solved in three components with the PATFIT [71] computing program; the short life component, in which the para-positronium (p-Ps) annihilation processes and the free positrons are involved; this component has an associated life interval \( \tau_1 \) (ns), a formation probability \( I_1 \) (%), and an annihilation velocity \( \lambda_1 = 1/\tau_1 \) (ns\(^{-1}\)). The intermediate component is related to the positronium or positron annihilation process in the polymer crystal network flaw [72] whose parameters are: \( \tau_2 \) (ns) for the life interval, \( I_2 \) (%) for the formation intensity and the annihilation velocity \( \lambda_2 \) (ns\(^{-1}\)); and the long life component, associated with the extinction formation of the ortho-positronium (o-Ps) in the amorphous regions in the polymer, are associated with the following parameters: \( \tau_3 \), \( \lambda_3 = 1/\tau_3 \) and \( I_3 \). These last parameters are the most important ones, because its analysis will determine the physical-chemical characteristics of the media where the positron annihilation occurs.

\[
N = D \exp(-\lambda_1 t) + C \exp(-\lambda_2 t) + B \exp(-\lambda_3 t)
\]

Fig. 7. Positron lifetime spectrum in the PEBD, in which the three components to be solved are shown, using the PATFIT computer program

In Fig. 7, a life interval spectra is shown, representing the \( N \) coincidence time distribution, that comes from the positron annihilation processes. Mathematically, the spectra could be analyzed as the sum of exponentials:
where $N$ is the number of accumulated coincidences, $D$, $C$ and $B$ are the slope intercepts of each component at the zero time axis.

17. Concluding Remarks

Positron annihilation spectroscopy has been scarcely exploited as a powerful technique for characterizing complicated polymeric systems, such as copolymers of blends, which are of technological interest. As it is well known, polymers have the unique characteristic, as compared to other materials, of their relatively large free molecular volume, responsible for many of the amazing characteristics of polymers and its measurement is critical for both theoretical and technological purposes. The advantages of PAS are its ability to detect nanometer-scale changes in the materials, its non-intrusive character and the possibility of a high degree of accuracy. Finally, it is worth mentioning that some very interesting basic science in the area of the interaction of positron with matter, remains to be discovered.

References

17. V. Goldanskii. Physical Chemistry of Positron and Positronium (Nauka, Moscow 1968) (in Russian); At. Energ. Rev. 6 (1968) 3.