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PROJECTO MEFT

**PALS – Setup optimisation and application to
macromolecular materials characterisation**

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1 Introduction

One of the fundamental structural aspects in soft condensed matter is the free volume structure which exists in the interior of matter. This includes vacancies, pores, holes, voids and other structures, which appear due to irregular packing, density fluctuations and topological constraints. The free volume structure can have great influence in a material's physical, chemical and mechanical properties. Probing and characterising it is therefore of fundamental importance. One of the techniques that is currently well-recognised as a powerful and versatile tool for direct measuring of these micro to sub-nanometer structures, whether in terms of existence, concentration or size of free volumes in matter, is Positron Annihilation Lifetime Spectroscopy, or PALS [1].

PALS was developed in the late 1960s as part of a series of nuclear spectroscopy techniques based on the process of annihilation of positrons with electrons in matter [2]. In the particular case of PALS, the elapsed time between the implantation of positrons into the material being tested and the emission of the gamma radiation resultant from the positron-electron annihilations are measured. The lifetime of positrons depends on the state of the positron upon annihilation. In fact, the lifetime is different for the ones which annihilate in the bulk of the material, the ones which form a bound-state with a molecular electron, known as positronium (defined in section 4.1.2), and also depends on the material's free volume structure where the annihilation takes place, involving both positrons or Ps atoms. Furthermore, for the ones which annihilate in free volumes, their lifetime is also dependent on the geometry and size of these volumes. Therefore, the lifetime of the positron alone or the positron in the Ps atom can then be used to determine the free volume size and corresponding concentration and distribution in the sample.

Earliest PALS investigations were devoted to the study of defects in metals and alloys, which then were extended towards semi-conductors and non-metals. Nowadays, it experiences constant improvements in the measuring methods, finding applications in all kinds of materials, with uses in a number of technologically important fields. In particular, an improvement of the technique to investigate macromolecular materials and biological systems is being increasingly reported [3]. PALS presents four great advantages that make it a very suitable and useful method for the intended analysis: it is a non-destructive technique, allowing subsequent use and studies of an examined material; it alone provides a complete study of the material's free volume characteristics, in a wide range of temperatures; it can probe both near-surface and in depth regions and even layered structures; and the PALS experimental setup can operate unattended and for long periods of time, which facilitates and accelerates the process of analysis.

In our case, in this work on "PALS – Setup optimisation and application to macromolecular materials characterisation", after an optimisation of a PALS based spectrometer, this will be used in the characterisation of the morphology and structure of advanced polymers and hybrid materials. These materials have been developed by GREI for special applications, such as human tissue repair and conservation of cultural heritage artefacts. The application of PALS to the characterisation of these materials is of extreme relevance given that the free volume structure of these materials is a decisive factor in their performance and suitability and it is in order to meet this need that this work has emerged from.

2 Objectives and work plan

As stated before, the general goal of the thesis is to optimise a PALS technique based spectrometer, present at GREI's facilities and with it analyse a range of radiation processed polymer-based and hybrid materials, used for biomedical applications and for the consolidation of stone-based materials. These materials constitute two fundamental lines of the research group regarding research in advanced materials. Therefore, two main objectives are set up, that regard:

- The optimisation of a PALS spectrometer at the facility, by revising and improving the fast coincidence electronic system. This process will be backed up by the acquisition of experimental PALS spectra with the apparatus, for reference materials with well known behaviour, such as pure copper, silicon, cadmium and/or Polytetrafluoroethylene, or PTFE (high-purity commercial Teflon);

The optimisation will be achieved through the fine tuning of the associated nuclear electronics modules, such as Constant-Fraction Differential Discriminators (CFDD), Fast Coincidence Units, Time-

to-Amplitude Converters (TAC) and Multi Channel Analysers (MCA), for acquiring whether energy or timing signals. The fine tuning of the experimental setup will then be confirmed or improved through the comparison of the results obtained from the acquired spectra of the reference materials with literature data. This will happen only after a careful selection of the materials' parameters to analyse and include on the available software for data reduction, taking as reference the MLT10 Program code [4].

- The evaluation of spectral fitting models applied to macromolecular materials, such as radiation processed polymer-based and hybrid materials, in order to analyse important morphological and structural characteristics of these types of materials regarding their applications.

3 Work schedule

In order to accomplish the objectives that were set out to achieve, the required tasks and the associated time periods in which they are to be carried out, are presented below.

TABLE 1: Tasks and associated completion months

Task/Month	1	2	3	4	5	6
Familiarise with the principles of operation of PALS system: acquire energy spectra of ^{60}Co and ^{22}Na sources; spectra time calibration						
Acquire PALS spectra for reference materials, with careful choice of parameters to include on the software for data reduction						
Revise and improve the fast coincidence electronic system for PALS. Repeat and compare new obtained spectra with the ones obtained in Task 2						
Application on the characterisation of macromolecular materials						
Thesis writing and scientific work dissemination						

4 Background

Given the scope of the work, some background must be given for a better understanding of the physical processes of positron annihilation in solids, that constitute the basis of the PALS technique. As well as that, an insight into the instrumentation and procedures surrounding a measurement using a PALS spectrometer is also required. In addition, a description of the methods and tools of analysis of the positron lifetime spectra and the information regarding the free volume structure that can be extracted from them is also provided.

4.1 Positrons in solids

When injected into a solid, an energetic positron will lose energy until it reaches thermal equilibrium with the medium, by processes that are dependent on its energy. For the highest kinetic energy of positrons, being $E_{\text{kin}} < 20$ MeV, the main mechanism for energy loss is the ionisation of the core electrons of the medium's atoms. After losing some energy, positrons will mainly cause electron-hole excitations, which are excitations of an electron up to the conduction band, creating a hole in the valence band. Finally, at even lower energies, of a fraction of eV, the scattering of phonons dominates. It is at this point that a thermal equilibrium is achieved and the positrons begin to diffuse through the material, undergoing a three dimensional random walk through the lattice, interacting with its surroundings. While most of the

positron penetration into a solid occurs during thermalisation, there is also a minor contribution from the diffusion process [2, 5].

At thermal energies, positrons have a much higher probability to annihilate with both a valence electron of an atom and a free electron. In the annihilation process, the particles collide, disappear and electromagnetic energy, in the form of gamma photons, is created as a result. In the centre-of-mass frame, the photons' total energy is given by $E = 2m_0c^2 = 1022$ keV, where m_0 is the rest mass of the electron (or positron). In a homogeneous material, free of defects, all positrons injected in the material annihilate with the free electrons at the same rate, which is characteristic of the material as it is proportional to the effective electron density sampled by positron [5]. This annihilation almost always yields two γ -rays of equal energy, meaning each has an energy $E = m_0c^2 = 511$ keV, travelling in opposite directions, in accordance with the conservation of energy and momentum. One- γ and three- γ annihilations are also possible, but rather rare, given that the one- γ annihilation is only possible in the presence of a third body, in order to absorb the recoil momentum and that the three- γ annihilation has pin-averaged cross section of only 0.27% of that for the two- γ one [6, 7]. In materials with defects, such as vacancies, vacancy clusters, voids, dislocations, and others, other annihilation processes are possible. On the other hand, the annihilation is also dependent on the type of material where it takes place as it depends on the material's electron density. The extreme cases of annihilation processes in defected materials, with high or low electron density, will be examined in the following sections.

4.1.1 Materials with a high electron density

In materials such as metals and semi-conductors, there is a high density of free electrons in the conduction band, which favours electron-positron annihilation. Nonetheless, in materials with lattice imperfections, both atoms and electrons are missing or their density is locally reduced at these flaws. Then, due to the combined effects of a reduction in the Coulomb repulsion by the positively-charged ion cores and the redistribution of electrons, which causes a negative electrostatic potential at these defects, positrons see these locations as strongly attractive centres in the material. Therefore, a localised positron state at one of these defects has a lower energy than the state of the free positron. The transition from this free state to a localised one is called positron trapping [2, 5, 6]. At these sites, the local electron density is lower, thus it's expected that the positron resides there for a longer period of time, given that it has increased difficulty in finding an electron to annihilate itself with. In fact, the larger the defect size, the longer the positron can live in it and vice-versa. Consequently, regardless of the defect size, the trapped positrons have a longer lifetime than free positrons [8]. Therefore, in these materials, apart from the annihilation of free positrons, there is also a fraction of the injected positrons which annihilate from a trapped state. Hence, the existence of positron trapping provides valuable information about the material in question. On one hand, the concentration of defects in the material can be deduced from the ratio of trapped to free positrons. Additionally, characteristic annihilation parameters of the trapped positrons, such as the annihilation rate (the inverse of the positron lifetime) reflect the local nature of the defect as they can reveal their size and internal electronic structure [6].

4.1.2 Materials with a low electron density

On the other side of materials' structural organisation, we have materials with a low electron density, such as polymers and insulators. Due to a low density of electrons, once positrons are thermalised the processes of free positron annihilation and positron trapping can still occur, but they are rarer. In addition, a fraction of the injected positrons, typically 10-50%, will form positronium atoms, before they have a chance to annihilate with an electron [7, 9]. Positronium, or Ps, is created when a positron captures a host electron and an unstable bound state of the positron-electron pair is formed, as an analogue of the hydrogen atom, but with the proton replaced by a positron [5, 7]. Ps can be formed by two distinct processes, described by the Ore model and spur model of Ps formation [9]. The Ore model or Ore gap model describes Ps formation by a positron which hasn't yet completely thermalised and, given its excess of kinetic energy, is capable of capturing an electron from a surrounding molecule [10]. This process is most probable when the positron energy lies within a gap where no other electronic energy transfer process is possible. In

fact, Ps formation under these circumstances can only take place if the kinetic energy of the positron is greater than $E_i - E_{Ps}$, where E_i the ionisation energy of the medium and E_{Ps} is the binding energy of the positronium, which in vacuum is 6.8 eV, but may be smaller in the medium [6]. The spur model states that at the end of the positron process of slowing-down, when its kinetic energy is only a few hundred eV, it creates a track, or spur, of electrons and ions, resultant from the last ionisation collisions. It goes on to say that a positronium can be formed when, through electrostatic attraction, a positron captures an electron in its own spur, competing against other processes, such as electron-ion recombination, diffusion of electrons and the positron out of the spur and annihilation [6, 11].

Regardless of the process, once created, the positronium in the ground state can exist as a singlet state, also called para-positronium, or p-Ps, which corresponds to 1/4 of the Ps atoms formed, where the spins of the electron and positron are in opposite directions (relative spin state equals 0). Or it can exist as a triplet state, also called ortho-positronium, or o-Ps, which corresponds to 3/4 of the Ps atoms formed, where the spins of the electron and positron are in the same direction (relative spin state equals 1). The p-Ps state, which has a mean lifetime of 125 ps in vacuum, can only annihilate into an even number of photons. Nevertheless, it decays primarily by emitting two back-to-back γ -rays of 511 keV, being this the only decay mode with a significative branching ratio. The o-Ps state, with a longer characteristic lifetime of 142 ns in vacuum, can only decay into an odd number of photons. However, as in the previous case, only one decay mode is significant, that is the decay into three γ -rays [6, 12]. Given the much larger lifetime of o-Ps, this state will play the key role in providing the relevant information concerning the material's structure, so this will be the focus of the rest of the section.

In these materials, o-Ps is attracted to areas of lower nuclear and electron charge density, such as voids, vacancies, pores and free volumes. Once there, the o-Ps will move through the void, lose energy, by deflecting off the walls and interact with the surrounding molecularly bound electrons. If it finds an electron with opposite spin to that of the positron, a singlet type interaction, a so-called "pick-off" annihilation, will occur. This is the process by which the positron in the o-Ps does not annihilate with its bound electron, but instead with the found electron with opposite spin, in a 2 γ -ray emission process [9, 13]. If the material's pores are closed, then o-Ps atoms will be trapped there and will bounce around in the walls. It is estimated that an o-Ps atom can undergo 10^6 wall collisions before annihilation, still, the o-Ps lifetime is reduced to about 1 ns, compared to its characteristic lifetime in vacuum of 142 ns [9]. With each bounce, there is a probability to annihilate with a molecular electron, until eventually "pick-off" annihilation occurs. This probability is strongly dependent on the void size, given that in smaller pores, more Ps-wall collisions will take place, which results in a faster "pick-off" annihilation. Hence, the lifetime of the Ps atoms is directly related with the size of the voids, then from a distribution of void sizes, an o-Ps lifetime distribution will emerge. However, in the case of the voids in the material being interconnected, o-Ps, being light and mobile, will diffuse within the porous network, over great distances, that can even surpass the material thickness. In some cases, it may even happen that the o-Ps can diffuse out of the material and into the surrounding vacuum, where it will annihilate into its most significant branching ratio of 3 γ -rays, in the vacuum lifetime of 142 ns. This is an indicator that we are in the presence of a material with interconnected pores. Despite that the process of "pick-off" annihilation can also occur for the p-Ps atoms, it is not as relevant, because they tend to self-annihilate before they have a chance to be attracted to such voids [9, 14].

4.1.3 Annihilation processes

As already stated in the beginning of the report, the lifetime of different positron-electron annihilation processes in matter, dependent on the positron state, is crucial for the analysis carried out through the PALS technique. In fact, as seen in the previous sections, the lifetime of the different positron or positronium states is related to the characteristics of defects or voids present in matter. Therefore, the lifetime determination through PALS allows us to probe the size and concentration of free volumes in the material.

As already explained before, during one of the phases of the work, high-purity materials, such as metals (copper and cadmium), semi-conductors (silicon) and insulators (PTFE) will be analysed. For these reference materials, their characteristic structure and morphology are well known, thus, the values for the positron lifetime components in them can be estimated. It is with these expected values, that the

results obtained from the spectra acquired during the work will be compared in order to confirm the optimisation of the setup performed.

The possible annihilation processes, discussed in the two previous sections, are summarised in *Table 2*, together with their characteristic time scales [5]. From the presented processes, all can take place in materials with a low electron density. However, only the top two can occur in materials with a high electron density, as all positrons in these materials annihilate before they have a chance to form a Ps atom. Furthermore, as can be seen, the trapped positron 2γ self-annihilation and the p-Ps and o-Ps 2γ pick-off annihilation processes do not have a well-defined characteristic time scale, given that the lifetime of positrons that annihilate through these processes is dependent on the morphology and structure of the respective free volumes where they take place.

TABLE 2: Characteristic time scales of the different positron annihilation processes in matter

Positron state	Type of process	Characteristic time scale
Free e^+	2γ self-annihilation	0.1-0.4 ns
Trapped e^+	2γ self-annihilation	0.2-0.5 ns
p-Ps	2γ self-annihilation	125 ps
	2γ pick-off annihilation	> 1 ns
o-Ps	3γ self-annihilation	142 ns
	2γ pick-off annihilation	> 1 ns

4.2 PALS technique

Besides PALS, there are several spectroscopic methods used to characterise defects or pores in a range of materials based on the principle of positron annihilation. In all of them, the γ -rays resultant from the positron or positronium annihilation are detected, however, they differ on the method of detection, as well as the photons' characteristics of interest and subsequent analysis. The remaining positron annihilation based techniques are Doppler-broadening spectroscopy (DBS), angular correlation of annihilation radiation (ACAR), Ps time-of-flight (Ps-TOF) and 3γ annihilation spectroscopy ($3\gamma/2\gamma$). Despite all being extremely useful in characterising certain aspects of the material's porosity, the most widely employed are PALS and $3\gamma/2\gamma$ [9].

PALS is performed in the time domain. In fact, it measures the lifetime of individual positrons as the time interval between the implantation of a positron into the material being tested and the detection of any γ -ray resultant from its annihilation through one of the possible processes. Subsequently, after a reasonable number of detected events (10^5 to 10^6), a lifetime spectrum is obtained, that contains several lifetime components associated with different annihilation processes and with the existence of defects or voids in the material. This is due to the fact that each annihilation process has its own characteristic time signature and the fact that trapped positron or Ps atoms in defects and voids will reside there for different time periods. It's with the decomposition of the acquired spectrum into individual lifetime components and corresponding intensities that is possible to extract information regarding the size, concentration and nature of the free volumes in the probed material [3, 9].

Therefore, in order to perform an analysis of the free volume structure of solids based on the PALS technique three aspects are essential: a source of positrons; an experimental setup, where the time of each event can be detected; and an analysis method and software that enable the decomposition of the acquired spectra in individual time components and the correlation of these results with the intended information regarding the free volume structure of the material under study. All these necessary resources will be further analysed in the following sections, with an emphasis on the ones that will be employed during this work.

4.2.1 Positrons source

There are two ways of implanting the positrons into the sample to be analysed. These consist of using a positron emitting radioactive source, that suffers β^+ decay or using a linear accelerator to produce positron beams. Despite being a more straightforward technique, the use of a positron emitting source

is unsuitable for probing thin films, given the high energies and broad energy range of the positrons. Linear accelerators on the other hand, enable this study by delivering a focused mono-energetic positron beam onto the sample. Additionally, they enable a deep-defect analysis of materials, by varying the implantation energy of the incident positrons [2, 9].

In this work, a ^{22}Na radioactive source will be used as the positron source, due to the fact that it is easy to handle and substitute and the fact that it has a suitable half-life for the intended studies. This radioisotope has a half-life of 2.6 years and it decays to either the 1.274 MeV excited state of ^{22}Ne or the ground state of the latter. This last decay occurs through β^+ decay and has only a 0.1% branching ratio. Therefore, the relevant decay is to the excited state of ^{22}Ne . This can happen either by β^+ decay, with a branching ratio of 90.4%, where positrons are emitted with a continuous energy spectrum ranging from zero to an end-point energy of 545 keV, or by electron capture, with a branching ratio of 9.5%. The half-life of the excited state of ^{22}Ne is only about 3 picoseconds, resulting in a prompt emission of a 1.274 MeV γ -ray, as the isotope transitions to its ground state. Given the extremely short lifetime of this excited state, both positron and 1.274 MeV γ -ray emissions can be considered as simultaneous [2, 5, 8].

As the positrons leave the source in all directions, with possible annihilations in any material they cross, it is extremely important to assure that the ^{22}Na source is completely encapsulated by the material to be studied. Otherwise, the results obtained will have an undesirable contribution from the positron annihilations in adjacent materials or from the air gap between the source and the sample. Two disks of the sample to be analysed are then placed on either side of the source, in close contact with the latter. The sample disks must be thick enough to ensure that the positrons completely stop and annihilate within the material, without preventing the 511 keV γ -rays created as a result of the annihilation processes from being completely attenuated before they reach the detector. A thickness of around 1.5 to 2 times the range of the 550 keV positrons in the material (tabulated for a range materials) fulfils both requirements [8].

4.2.2 The experimental setup

The optimisation of the setup, achieved by the fine tuning of the electronic modules is one of the most important aspects of the work to be developed. Hence, a brief description of the experimental setup, with a focus on the referred electronic modules is essential to better understand the scope of the project.

The experimental setup comprises a set of analog electronic modules with two scintillation detectors. The radioactive source is positioned between two fast scintillators, where the detection of the implantation of a positron into the material and its annihilation are performed. This means that a start and stop signal must be detected, with the time difference between the two giving the positron lifetime. Given the almost simultaneous emission of the positron from the radioactive source and the 1.274 MeV γ -ray from the de-excitation of the ^{22}Ne radionuclide, the detection of this γ -ray is taken as the start signal. The stop signal, on the other hand, is considered as the detection of a 511 keV γ -ray resultant from a 2 γ -ray positron annihilation process in the material. These detectors are assembled together with a photomultiplier each, that convert the flash of light resultant from the detection of a photon by the respective scintillator into an analog, electronic pulse [2, 3, 8].

The electronic modules comprise: two Constant-Fraction Differential Discriminators (CFDD), each connected to the base of one photomultiplier; a Fast Coincidence Unit; a Time-to-Amplitude Converter (TAC); and a Multi Channel Analyser (MCA) [1].

The CFDDs are used to mark the exact arrival time of the pulses from the photomultipliers, by the generation of a fast signal. Apart from that, CFDDs also select the range of energies that will be accepted to generate the timing pulses. In that sense, one of the CFDDs is used to mark the start signal, by accepting only the 1.274 MeV γ -rays and the other is prepared to accept only 511 keV photons and therefore generate the stop signal. The resultant signals are then led to the start and stop inputs of the TAC and to the Fast Coincidence Unit. This latter produces a gate signal for the TAC only when it detects a coincidence event of photons with proper energies (a start and stop signal within a proper time interval of each other). The TAC converts the time difference between the two signals into an analog pulse, whose amplitude is proportional to the time delay. This analog signal is later digitised by the MCA, which stores the event in a histogram as one count in the channel corresponding to the signal amplitude. During a run of data acquisition, multiple events are then stored in this histogram that represents the number of

annihilation events of the implanted positrons versus lifetime and constitutes the positron annihilation lifetime spectrum [3, 5, 8].

4.2.3 Lifetime spectrum analysis

As stated before, a PALS spectrum is a lifetime spectrum that corresponds to a combination of several exponentially decaying lifetime components, corresponding to different annihilation processes, dependent on the positron state, summarised in *Table 2*. From the spectrum resultant from a PALS measurement using a radioactive source as the positrons source, several characteristics of the free volume structure can be extracted. In materials with a high electron density, the decomposition of the spectrum into its different lifetime components provides information regarding the defect sizes, the defect size distribution and the defect concentration within the material. In the case of materials with a low electron density, given the occurrence of other annihilation processes, additional information can also be retrieved. In fact, from the analysis of a lifetime spectrum, the pore sizes, pore size distribution, pore concentration and pore interconnection length can be determined.

Size For the case of both defect and pore size determination in materials with high and low electron density, respectively, some theoretical models that relate the lifetime of positrons or positroniums in these free volumes and their sizes have been developed. These models are briefly reviewed in *Section 5.1*. Hence, based on these models, the determination of the lifetime associated with one of the spectrum's components related to annihilations in free volumes yields an average free volume size [9]. PALS is sensitive to all free volumes greater than a few angstroms [14].

Size distribution In materials with free volumes of varying sizes, the trapped positrons and/or positroniums will experience distinct lifetimes in different free volumes. Therefore, a lifetime distribution is produced in the spectrum. A typical porous material requires two to six discrete lifetimes to account for the range of free volumes in the material [9]. Then, from the singular relationship between free volume size and positron(ium) lifetime, a PALS continuum lifetime distribution can be easily transformed into a free volume size distribution [14]. Furthermore, in the case of low electron density materials, a measured free volume size distribution also reflects a free volume shape distribution. This is due to the fact that the "pick-off" lifetime of o-Ps is slightly dependent on the voids' geometry for voids of the same volume [15].

Concentration The relative intensity of a given lifetime component is directly correlated with the number of positrons which have annihilated through the corresponding process. Therefore, a comparison of the relative intensities of the different lifetime components, and thus annihilation processes, can give an insight into the concentration of defects or pores in the material. This is due to the fact that a higher concentration of these free volumes will yield a larger number of positrons annihilated in them through process which take place inside them, such as trapped positron 2γ self-annihilation and the p-Ps and o-Ps 2γ pick-off annihilation and vice-versa [3, 15, 16].

Interconnection length As already stated before, in *Section 4.1.2*, the diffusion of o-Ps atoms out of the material is an indicator of interconnected voids in the material. In the case of fully interconnected voids, Ps can diffuse through the film, up to 1000 nm thick, and annihilate in vacuum with its telltale signature of a long 142 ns lifetime. For partially interconnected voids, the Ps diffusion length is much smaller, which results in a slightly more short-lived Ps lifetime components. Then, the long lifetime components of the lifetime spectrum correspond to the mean free path that Ps atoms travel in void volumes throughout the film thickness, giving information regarding the voids interconnection length [9, 14].

Analysis software

The analysis of the lifetime spectra acquired during a data acquisition run will be performed with the MLT10 Program code, one of the most popular software for positron lifetime spectra analysis.

The ideal spectrum of positron lifetimes is a sum of exponential decay functions, described by:

$$y(t) = \sum_{i=1}^n \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

where $y(t)$ is the counting rate as a function of time, τ_i and I_i are the mean lifetime and intensity of the i^{th} component, respectively, and n is the number of exponential decay components, associated with the different states which the positrons can annihilate from [8].

The experimentally obtained spectrum differs from this analytical description given that it also has contributions from a flat background function that accumulates under the spectrum and from the finite time resolution function of the detectors and electronics. The background accounts for the contributions from the material that encapsulates the radioactive source, the air between the samples and the detectors and any contributions from the non-local experimental environment. This function can be considered as a constant that is added up in *Equation 1*. The time resolution function of the time spectrometer is its response to prompt coincidences. It is a peak in the time spectrum that has approximately the shape of a Gaussian function, with a typical full width at half maximum from 180 to 250 ps, depending on the tuning of the time spectrometer. Therefore, the measured spectrum will be described by a function that constitutes the sum of the background function with *Equation 1*, convoluted with the time resolution function [2, 5, 8].

The referred software is then used to deconvolute the lifetime spectrum into a few discrete exponential components, by implementing least-square fits of the convolution function, described above, to the recorded spectrum. From this analysis, both the lifetimes and intensities of the various spectrum components can be extracted. Apart from that, MLT10 has an important feature, which is the simultaneous analysis of a set of experimental spectra, in one computational procedure. This process allows to determine common values for certain parameters which are constant for all the spectra analysed. These include the ones related to the positron source contribution and to the spectrometer time resolution. Such procedure, by reducing the number of degrees of freedom, produces far more reliable and unequivocal values for these common parameters than if the analysis was performed for each spectrum individually [2, 17, 18]. Finally, the program provides information regarding the free volume structure of the analysed material. In fact, from the determination of the various lifetime components and respective intensities, the program presents us the necessary parameters that enable a complete characterisation of the material's free volumes with regard to their size, size distribution, concentration and interconnection length.

5 State of the art

The PALS technique and the physical phenomena that rule its principle of operation are already relatively well studied topics, with applications in many fields. However, this is still a subject that currently drives new developments and is employed in new exciting applications. Hence, we now focus on some new theoretical models that correlate the lifetime of positrons or Ps atoms in matter and the size of the free volume they annihilated in. In addition, an overview will be provided of the more recent applications and uses of this powerful analytical tool. Finally, we briefly describe the materials that will be analysed during this work, as well as their applications.

5.1 Theoretical models for pore size determination

The models that relate the annihilation rate or lifetime of positrons or positroniums in free volumes and the size and geometry of said volumes are at the base of the PALS technique. Different models were developed to relate these two quantities in a simplified manner, in different media. We now focus on the theoretical models concerned with the self-annihilation of positrons trapped in the solid's defects and the pick-off annihilation of the Ps atoms in voids.

For the trapped positrons self-annihilation, the currently accepted model is the two-state trapping model [19, 20, 21], which advocates that the positron can only exist in one of two states in the material, the bulk state or the defect-trapped state. First, it defines a total trapping rate of the positron from the bulk state to the defect-trapped state, which is proportional to the defect concentration in the material, by a constant, specific for each kind of defect. Therefore, the defect concentration to which the positrons are sensitive to can be estimated by the experimental determination of the ratio of trapped to free positrons, which is related to the trapping rate. The model then correlates this quantity and another measurable one,

the trapped positrons lifetime, in both bulk and defect-trapped states with characteristic shape parameters. This correlation allows the nature of defects to be deduced, such as size and geometry. In fact, the difference between the lifetime of the trapped positrons and that of the free ones is directly related to the size of the positron traps and the ratio between the two can be ascribed to the nature of these defects [5, 7, 22].

For the pick-off annihilation of the Ps atoms in voids, the original method for void size estimation was the quantum mechanical Tao-Eldrup model [23, 24], that is only valid for very small voids, with a diameter inferior to 1 nm. The model regards the Ps atom in the void as a localised particle in a ground state of a spherical, infinite potential well. Ps can then only undergo pick-off annihilation when there is a superposition of its wave function with the bulk one, which occurs when the Ps is within a short distance of the void surface. Consistent with the model's assumptions, it's then possible to arrive at an expression for the annihilation rate that relates it with the radius of the spherical void [9, 25, 16]. Given the size limitations of this model, a new one was developed, the extended Tao-Eldrup model [26], that allows the calculation of the annihilation rate for voids larger than 1 nm. It does so by assuming that when the void diameter approaches the thermal De Broglie wavelength of the Ps atom, the Ps will also occupy excited states, that possess different superimposition probabilities. A rectangular void geometry is assumed, where the Ps atom will randomly occupy all the states with a probability governed by the Maxwell-Boltzmann distribution [9, 25, 16]. Therefore, for a given temperature, a correlation between the annihilation rate and the geometry and size of the void is established.

In the cases where the Ps mean free path between collision is much larger than the De Broglie Ps wavelength, which means for void sizes of several tens nm, a classical model [27] can also be applied. This model relates the annihilation rate with the pick-off annihilation probability per collision with the cavity wall, determined by experiments, the thermal velocity and the mean free path between collisions. This latter is related to the void's shape and dimension through $l = 4V/S$, where V/S is the ratio of volume to surface area and is thereby a measure of void size that is independent of its geometry. Besides, the Ps lifetime depends only on the mean free path and not on the detailed void geometry. This model, however, is not suitable for small pores [9, 14, 25]. A new classical model, the modified classical model [25], removes the constraint for the smaller mean free length region, by taking into account the effect of the size of the Ps atom. By setting the value of an adjustable parameter, this model then smoothly merges with the Tao-Eldrup model, where the radius of the spherical void is transformed in a mean free path by the relation $l = 4V/S$. The mean free path value for which the two models intersect defines a piecewise annihilation rate and a model for every void's size is achieved. Finally, it is worth mentioning another model for the calculation of ortho-Ps lifetimes in insulators, using a novel path-integral Monte Carlo computation model, formulated to tackle some unaddressed issues in the Tao-Eldrup model, namely asymmetric open-volume regions and changes in the void surface chemistry [28]. One of the ways it does this is by considering the Ps atom as a two-component system consisting of an electron and a positron as opposed to considering it as a single quantum mechanical particle, as in previous models.

5.2 Applications of PALS

As already discussed, the PALS technique is a powerful tool in probing the characteristics and behaviour of free volumes of materials, which have a major impact on their physical, chemical and mechanical properties. Given its tremendous potential it has been applied to the analysis and characterisation of a wide range of materials. More recently, one of the most intensively studied materials are polymers, both from an experimental and a theoretical point of view.

In polymers, as with other materials, the concentration, dimension and length of voids has a major influence on their performance and suitableness. Besides that, PALS allows the estimation of the spacing between polymeric chains and assess the existence of cross-linking effects, which is the creation of a bond that links one polymer chain to another and that is directly correlated to the physical and chemical properties of the material. In that sense, the detection of the glass transition and physical aging in a polyester is reviewed in [29]. As well as that, the mechanical and structural peculiarities of two new groups of cellulose esters were evaluated in [15], where PALS has been applied to the determination of the number density of free volume holes and their average size. In particular, it was found an inverse

linear relationship between the hardness of the materials and the number density of free volume holes in them. In another study [22], PALS was applied to the characterisation of the free-volume structure of polyvinylpyrrolidone, a polymer employed in the pharmaceutical industry for the production of many drugs, which is especially appropriate for this application due to its characteristic free-volume entities.

Nevertheless PALS has also been applied to other materials. For instance, porous silicon nanoparticles, which can be used as containers for the delivery of diagnostic markers or drugs for therapy of cancer tumours. One of their properties that makes them suitable for such an application is their large pore volume. In a recent study [16], the pore size distribution of porous silicon nanoparticles was determined to assess if the samples were suitable for such an application. In another study, PALS was applied to the determination of the type and concentration of defects in two FeAl alloy samples, produced at different temperatures, to investigate the influence of the aging process and the thermal treatment on these properties, extremely relevant for the material's mechanical performance [30].

5.3 Polymer-based and hybrid materials

As it has become obvious, the PALS technique has a number of applications in the complete characterisation of the porous structure of different solids. Therefore, apart from the applications of a positron(ium) annihilation spectrometer to the study of the materials that were reviewed in the last section, the PALS technique has the potential to also be applied to the characterisation of the materials that will be studied during this work. These are polymer-based and hybrid materials, synthesised by the research group through irradiation methods, to be used in biomedical applications, such as human tissue repair or in the consolidation of stone-based materials for the conservation of cultural heritage artefacts. In these materials, the porous structure is of major relevance as it can influence some important aspects that determine whether or not said materials are suitable for their intended final application. Some of these types of materials recently developed by the research group and candidates to be analysed during this work are reported below. The importance of the porous structure in these materials is also evidenced.

One of these materials were LDPE based copolymeric films obtained by manipulation of the molecular structure of polymeric based materials by gamma irradiation for the development of new materials, whose properties are promising for use in medical implant devices. [31]. In order to make these materials suitable for bio-applications, one of the aspects that have to be improved is the bio-interaction ability, which includes cell adhesion and proliferation, which is strongly related to the porous structure. In the referred study, the 3D porous network, dependent on the radiation dose received by the samples and extremely important in the hydration/dehydration kinetics of the films, was analysed. Another set of these materials, prepared in different irradiation conditions, was analysed in [32]. In this case, the films were intended to be used as catalyst membranes in catalytic membrane reactors, applied in fine-chemical and environmental applications, for the production of medical active molecules, food additives and biofuels. For this purpose, the membranes have to be highly stable, a condition that requires a homogeneous porous distribution. Other materials developed were PVA supported catalytic membranes obtained by γ -irradiation [33], where they were probed in order to assess their viability to be used in pervaporation membrane reactors, for the production of biodiesel. In addition, chitosan-based matrices were prepared by γ -irradiation to be used as scaffolds, supports that are used as a template at a body injury to guide cell growth and regeneration, thereby assisting the body in growing new and functional tissue [34]. One of the requirements that a material has to satisfy in order to be used as a scaffold is to have a suitable porosity for cell in-growth, which means a three-dimensional interconnected porous architecture where cells could easily attach and proliferate. This study demonstrates how γ -irradiation processing of chitosan-based matrices can be a useful method of modelling a material to have, among others, this one fundamental property required to be used in tissue regeneration.

So far, we have seen examples of polymeric materials. However, hybrid materials have also been extensively developed by GREI due to their potential in innumerable fields, in particular, the biomedical one. In fact, hybrid materials resultant from the mixture of three different composites, prepared by γ -irradiation, have been studied, with a particular focus on their micro and nanostructures [35, 36]. These structures are concerned with the porosity of the material and consequently have an influence in the design of these materials for biomedical applications. For instance, in bone cement or when cellular

anchoring processes are required, to keep the cells together and the structural cohesion of tissues, given that the porosity in these types of materials facilitates tissue and vessels ingrowths.

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