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COINCIDENCE DOPPLER BROADENING POSITRON ANNIHILATION SPECTROSCOPY STUDIES OF POLYURETHANE MEMBRANES

F. CONSTANTIN[a*], C. BARNA[a], E. BARNA[b], M. STRATICIUC[a], I. BURDUCEA[a]

[a]*"Horia Hulubei" National Institute for Physics and Nuclear Engineering, P.O.B. MG-6, RO-077125, Romania*

[b]*Bucharest University, Faculty of Physics, PO BOX MG - 11, Bucharest RO-077125, Romania*

Several polyurethane membranes deposited by electrospinning, with and without silver nanostructures, have been irradiated with gamma-rays with doses ranging between 25 kGy and 100 kGy and the behavior of the free volumes generated by gamma irradiation in these polyurethane membranes was investigated by Coincidence Doppler Broadening Positron Annihilation Spectroscopy. The studies of the wing component revealed the existence of two thresholds in gamma-ray irradiation doses.

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1. Introduction

The concept of free volume in polymeric materials was introduced more than fifty years ago [1-3]. It was based on the idea that the molecular motion in bulk state depends on the presence of holes or places where there are vacancies or voids. For polymers, this concept explains a lot of their mechanical, thermal and relaxation properties. More than one free volume (or hole) is required for a polymer chain movement. In polymers, the local free volume holes or cavities of atomic and molecular dimensions arise due to the irregular packing of the chains in the amorphous state (static) and molecular relaxation of the polymer chains and terminal ends (dynamic and transient state). Due to the presence of these holes, the density of the polymer samples is about 10% less than the density of the corresponding crystalline state.

A number of techniques are being employed to examine the free volume properties of polymers. The most powerful approach is to monitor the physical and chemical changes at molecular level by means of atomic probes, such as Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and by molecular spectroscopic methods, such as Fourier Transform Infrared (FTIR) and Raman spectroscopy, Nuclear Magnetic Resonance (NMR) and Electron Spin Resonance (ESR). Along with the above-mentioned techniques, Positron Annihilation Spectroscopy can reveal useful information about the electronic and defect properties of materials. Being a non-destructive technique, it looks as the ideal way of probing defects at atomic and molecular levels [4].

Coincidence Doppler Broadening Spectroscopy (CDBS) has the advantage - over single detector spectroscopy - that a lower background is present in the region of high longitudinal momentum of the annihilation pair electron-positron. These annihilations correspond to fast electrons, making CDBS method suitable for probing the chemical sensitivity in open (free) volumes trapping sites [5-7].

*Corresponding author: fconst@ifin.nipne.ro

This article is focused on the study with CDBS of the effects induced by gamma irradiation of polymeric membranes, namely polyurethane fibers with and without silver nanostructures. This study was triggered by the fact that there is an increased interest in medical applications of polyurethane doped with silver membranes which can serve as antiseptic bandages for skin burns, taken into account the well-known antimicrobial effect of silver ions. However, an eventual gamma-ray irradiation for sterilization purposes of such polyurethane membranes could lead to a loss of their mechanical properties, such as elasticity.

2. Experimental

The investigated polyurethane samples were prepared by electro spinning [8]. This method uses an electrical charge to draw very fine fibers (typically in the micro- or nanometer diameter range) from a liquid. The process is non-invasive and does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution. This makes this process particularly suited for the production of fibers using large and complex molecules.

The thickness of the resulting polymer membranes was around 100 μm. Some of the polyurethane samples have been implanted during the manufacture with silver nanostructures of about 10 nm in diameter. Figure 1 presents a Scanning Electron Microscope (SEM) image of the electrospun polyurethane fibers with silver nanostructures.

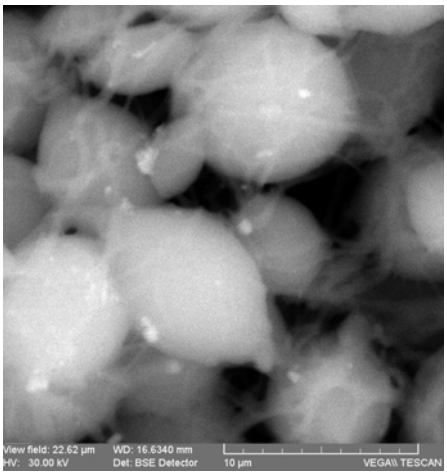

Fig. 1. SEM image of the polyurethane fibers with silver nanostructures (10000× magnification).

The polyurethane membranes have been irradiated with gamma-rays from a ^{60}Co source in a multipurpose gamma irradiator based on a SVST ^{60}Co 100 kCi source [9], with doses ranging from 25 kGy to 100 kGy. Following the gamma-ray irradiation, free volumes were generated in the membranes and the corresponding modifications were studied by CDBS. Fig. 2 presents a SEM image of a polymer sample irradiated with 100 kGy gamma-ray dose.

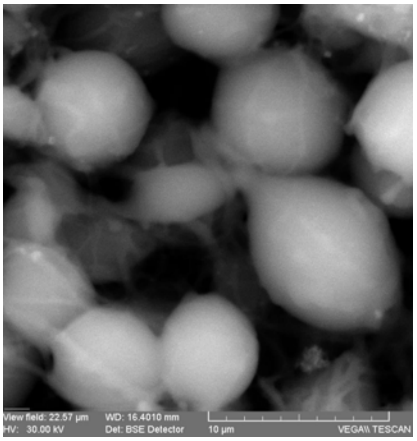

Fig. 2. SEM image of the polyurethane fibers with silver nanostructures after 100 kGy gamma irradiation, (10000× magnification).

The experimental setup used in this study is typical for CDBS measurements [10, 11, 12. Two HPGe detectors operate in a back-to-back geometry and they measure the energy of both annihilation gamma-rays. Between the detectors lies the sandwich made out of samples and the positron source. The resolution of the HPGe detectors is about 1.2 keV at 511 keV, permitting the study of the Doppler broadening.

The positron source was a droplet of ^{22}Na wrapped in a 5 micrometers thickness mylar envelope; the activity of the positron source was 2 μCi. Each of the two identical polyurethane samples were put on a tungsten disc, the positron source being pressed in-between them.

The data acquisition system is based on a CAEN VME ADC, an USB communication bridge and a PC [13]. The software was custom designed in order to acquire, store and examine the data.

3. Method

The first approach for polymers studies with Positron Annihilation Spectroscopy used the shape factor in order to describe the behavior of the free volumes [14, 15].

Since the background in the region of the wings is drastically reduced in CDBS method, then an accurate study of the wing factor by means of relative comparison between the axial momentum densities becomes possible.

In our case, the thickness of the polymeric membrane is large enough to thermalize and annihilate all emitted positrons. Since the spectrum of ^{22}Na source covers a broad energy domain and the emerging positrons have large thermalization ranges, we can conclude that our CDBS measurements are volume-oriented.

For each investigated polyurethane sample, the function ρ, equal to the longitudinal momentum density versus the longitudinal momentum was calculated.

One of the samples - characterized by the corresponding $\rho_{reference}$ function - was taken as a reference, and a new function called Δ was defined as:

$$\Delta = \frac{\rho - \rho_{reference}}{\rho_{reference}}$$

The software developed by us permits the extraction of the Δ function from every pair of samples; the energy calibration of both detectors was necessary for the calculation of the longitudinal momentum.

Figure 3 represents a screenshot of the application software; the first two pictures on the left of the main windows represent the ρ functions for two polyurethane samples plotted along the second diagonal of the bi-dimensional coincidence spectra; the first one is for the reference

sample. The picture on the right part of the window is the Δ function superimposed on the two ρ functions; the vertical scale is magnified to allow a better visualization of the bumps of wing contribution. As it can be seen from this figure, the un-normalized Δ function is able to sense minor changes in the wing factor. The behavior of the free volumes is related to the small bumps appearing symmetrically around the 0 value of the longitudinal momentum.

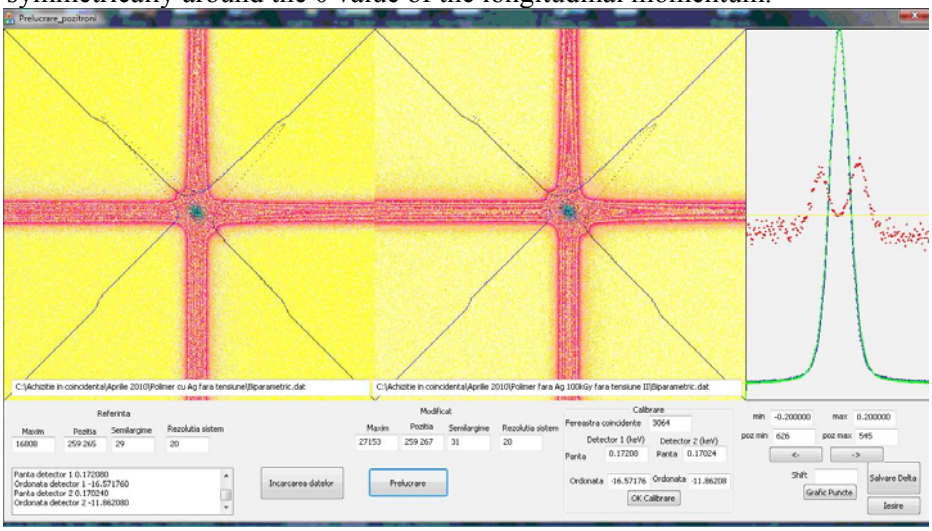

Fig. 3. Longitudinal momentum distribution for two samples and the extraction of the non-scaled Δ function.

4. Results and discussions

Before presenting the obtained results, two assumptions that we made must be emphasized:

a. The regular chemical structure of the polyurethane is responsible for the momentum distribution of the electrons that can annihilate with the positrons, therefore the main contribution to the positron annihilation is due to this regular chemical structure of polyurethane;

b. Half of the polyurethane samples contain silver nanostructures with 10 nm diameter; such a nanostructure contains tens of silver atoms, which behave like bulk silver with conduction bands and implicitly with slow conduction electrons. At the same time, the silver content is only a few ppm, so that the chemical composition of the polyurethane is not drastically affected by the presence of silver nanoparticles.

Taking into account these two assumptions, we selected as a reference the non-irradiated polyurethane doped with silver nanostructures, i. e. the sample that contains the highest concentration of slow electrons available for annihilation.

Fig. 4 presents the evolution of Δ function for different samples, namely: non-irradiated polyurethane without silver nanostructures; polyurethane irradiated at 25 kGy; polyurethane irradiated at 50 kGy; polyurethane irradiated at 100 kGy and polyurethane with silver nanostructures irradiated at 100 kGy.

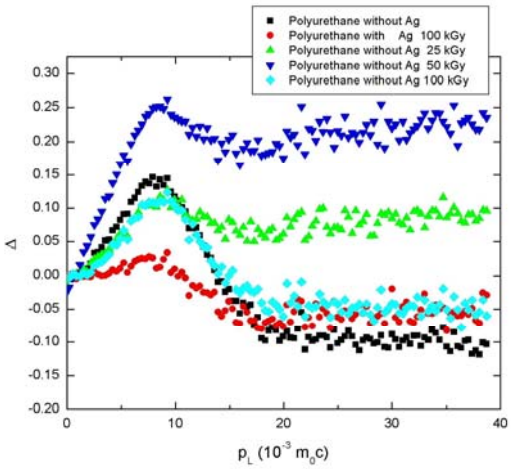

Fig. 4. Momentum density relative to the non-irradiated polyurethane sample with silver nanostructures.

For all samples, Δ function reveal a maximum for the same value of the longitudinal momentum at 8×10^{-3} m_0c; this maximum represents the contribution to the annihilation of the electrons originating from the free volumes of the polymer having a high momentum.

There is a difference between the polyurethane with and without silver nanostructures; as it was previously discussed, the small amount of silver nanostructures does not modify the density and dimension of the free volumes. It means that the silver nanostructures positioned in the free volumes act like positrons traps, providing slow electrons for annihilation. This is the reason for which the polyurethane sample with silver nanostructures was chosen as a reference.

The behavior of polyurethane sample without silver irradiated at 25 kGy was not very different from the one of the non-irradiated sample; this low gamma-ray dose was insufficient to generate enough free volumes.

The situation changed for the polyurethane without silver nanostructures irradiated at 50 kGy. A spectacular jump of the Δ function peak - compared to the non-irradiated sample - took place, showing a considerable increase of the number of free volumes; the additional 25 kGy irradiation indicating that an irradiation threshold was passed. Both samples irradiated at 25 kGy and 50 kGy show peaks at 8×10^{-3} m_0c longitudinal momentum, but in the case of 50 kGy irradiation, the tail towards greater momentum values is higher.

Spectacular is also the behavior of the sample without silver nanoparticles irradiated at 100 kGy; the peak at 8×10^{-3} m_0c did not increase with the irradiation dose, its height being lower than for the sample irradiated at 50 kGy. Moreover, the tail towards greater longitudinal momentum disappears. The explanation for this behavior might be related to the fact that at a 100 kGy dose, another irradiation threshold is passed. In this case, the free volumes became larger, as they join together, while the density of free volumes decreased. According to the Heisenberg principle, free volumes larger in size mean a larger uncertainty in position and a smaller one in momentum. This behavior can be seen also in the SEM pictures presented in Figure 1 and 2: the image of the irradiated polyurethane sample shows larger dark regions compared to the image of the non-irradiated polyurethane.

The same polyurethane sample with nanostructures was irradiated also with gamma-rays at 100 kGy. This sample showed the smallest peak at 8×10^{-3} m_0c longitudinal momentum. The gamma irradiation induced multiple free volumes with larger dimensions, but the number of nanostructures remained the same. A net increase of free volumes without silver emerged in the sample and consequently the number of annihilation events with fast electrons increased.

5. Conclusions

CDBS using wing parameter method of polyurethane samples with and without nanostructures irradiated with different doses of gamma-rays turned out to be a sensitive and

accurate way to describe the modifications induced in polymers by gamma-irradiation. In our studies, it was confirmed that the main contribution to the positron annihilation was due to the regular chemical structure of polyurethane. The presence of silver nanostructures was shown to contribute to the increase in the number of recombinations with slow electrons originating from the conduction bands.

Regarding the apparition of free volumes as a consequence of the gamma irradiation, two irradiation thresholds, corresponding to 50 kGy and 100 kGy gamma-ray doses, were found. The first threshold is caused by the increased number of free volumes of regular size, while the second one is due to the increase not number, but in size of the free volumes.

Acknowledgements

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