

Digital Age-Momentum Correlation Spectroscopy Development and Application to Polymer Microstructure

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***Keywords :** positron annihilation age-momentum, correlation, flash ADC, Digital setup

1. Introduction

The behavior of positrons and positronium was utilized to investigate electronic structures and chemical environments with high precision. Among the positron annihilation spectroscopy techniques, positron annihilation lifetime spectroscopy (PALS) and Doppler broadening spectroscopy (DBS) have been widely applied to the analysis of microstructural features in materials. The age-momentum correlation (AMOC) technique was developed based on these methods to allow simultaneous measurement of positron lifetime and momentum distribution [1]. Through this approach, different positron states can be effectively distinguished. Through this method, structural characteristics such as open and closed pores in porous materials, crystal structures, and positronium formation and annihilation mechanisms were clarified.

Recent advancements in digital data acquisition systems marked a turning point [2]. These developments help overcome the limitations of analog-based measurement systems, including noise, reduced resolution, and low data efficiency. In digital systems, entire pulse waveforms can be stored. Various signal processing algorithms can then be applied offline, resulting in significantly enhanced analytical performance. In response to this trend, the transition of the AMOC system to a digital format has also been increasingly demanded.

In the present study, a digital-based AMOC system was developed and applied to the analysis of representative polymer samples. Through this application, microscopic information on positron-electron interactions was obtained.

2. Materials and Methods

Polyethylene terephthalate (PET) and low-density polyethylene (LDPE) were chosen as model polymers for the experimental analysis. Both samples were purchased from Goodfellow and were cut into pieces (10 mm × 10 mm) without any additional chemical pretreatment. The thickness of each sample was approximately 2 mm. A pure silicon (Si) sample (10 mm × 10 mm × 1 mm) was also used for comparative analysis.

A positron source was prepared using ²²NaCl and a polyimide film (10 mm × 20 mm × 7.6 μm). A small amount of ²²NaCl aqueous solution (activity: 3.7 MBq) was dropped onto a polyimide film and allowed to dry naturally. The film was then folded in half to encapsulate the source. Adhesives were not used due to their potential to distort the positron annihilation spectrum [3].

For high-precision digital processing of positron annihilation signals, an FADC500 module (NOTICE, Daejeon, Korea) was used. This device supported four-channel simultaneous input and provided a sampling rate of 500 MS/s with a 12-bit analog-to-digital conversion resolution. The maximum analog input voltage was 2.5 V, and the bandwidth was 250 MHz. The trigger processing rate reached approximately 40 MHz.

A total of three detectors were used, consisting of two CeBr₃ detectors (cylindrical type; 25 mm × 25 mm) and one high-purity germanium (HPGe) detector (Ortec p-type coaxial detector, USA). All detectors were connected to the FADC500. The three detectors were linearly aligned with respect to the source to maximize the coincidence detection probability by utilizing the back-to-back emission characteristic of annihilation gamma rays (Fig. 1).

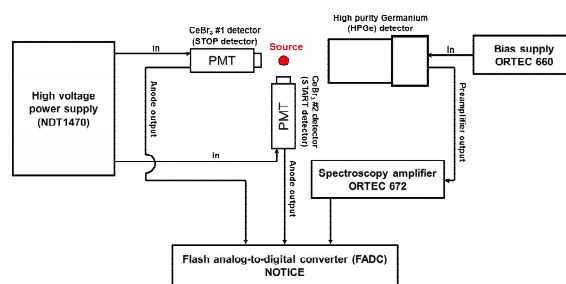


Fig. 1. Schematic diagram of the age-momentum correlation (AMOC) system.

Data analysis was performed by digitizing the input analog pulses in real time and storing them in memory, followed by offline processing. Timing information was extracted using a digital constant fraction discriminator. The energy information was obtained through digital CR-RCⁿ filtering (applicable to CeBr₃ detectors only). To quantify the annihilation probability with low-momentum electrons over time, the S(t) function (the

ratio of counts in the central region of the annihilation line to those in the total energy region) was applied by utilizing both energy shift (ΔE) and age (τ). The positron lifetime (= age) distribution was fitted using a multicomponent exponential function with the *PALSfit3* program. The free volume analysis was conducted based on the Tao–Eldrup model.

3. Results and Discussion

Fig. 2 shows the normalized positron lifetime spectra measured for PET, LDPE, and pure Si samples. Since Si does not possess free volume, only a single lifetime component was observed. In contrast, longer lifetime components were detected in PET and LDPE, indicating the presence of free volume and active positronium formation within the polymers. In particular, the difference in the long-lived components (> 1.5 ns) between PET and LDPE was interpreted as reflecting the distinct free-volume structures of the two polymers. The results of the positron lifetime analysis for PET, LDPE, and pure Si are summarized in Table 1.

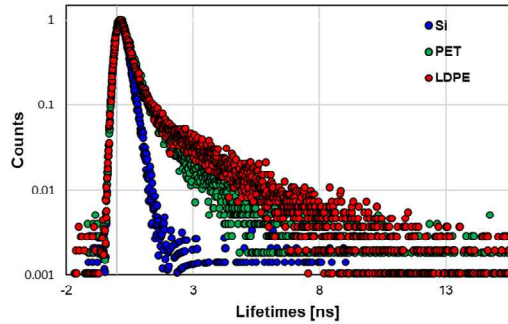


Fig. 2. Positron lifetime spectra measured for PET, LDPE, and pure Si samples.

Table 1. Positron lifetime analysis of PET, LDPE, and pure Si samples. Each sample was quantitatively analyzed based on lifetime components (τ_1 , τ_2 , τ_3) and their corresponding intensities (I_1 , I_2 , I_3), free volume radius (R), free volume fraction (FFV_R)

	PET	LDPE	Pure Si
τ_1 [ns]	0.09 ± 0.04	0.14 ± 0.03	0.24 ± 0.01
τ_2 [ns]	0.38 ± 0.02	0.38 ± 0.03	-
τ_3 [ns]	1.70 ± 0.05	2.51 ± 0.05	-
I_1 [%]	11.7 ± 2.6	19.5 ± 5.3	100
I_2 [%]	64.7 ± 2.1	48.4 ± 5.0	-
I_3 [%]	23.6 ± 0.9	32.1 ± 0.6	-
R [Å]	2.56 ± 0.05	3.28 ± 0.04	-
FFV _R [%]	2.97 ± 0.30	8.51 ± 0.44	-

Fig. 3 shows the analysis results of the line-shape parameter $S(t)$. Both PET and LDPE exhibited time-dependent variations during the initial slowing-down region. In the lifetime region after 1 ns, LDPE consistently showed higher $S(t)$ values than PET. This difference was attributed to variations in the chemical

environment surrounding the free-volume cavities. In PET, oxygen atoms account for approximately 18.2% of all atoms. The valence electrons of these oxygen atoms possess relatively higher momentum compared with those of carbon or hydrogen. Thus, annihilation with oxygen electrons produces a larger Doppler shift, resulting in a lower $S(t)$ value. This lower $S(t)$ value indicates that oxygen atoms are located near the free-volume boundaries and demonstrates that the electronic structure of surrounding atoms influences the pick-off annihilation process. As a result, the difference in $S(t)$ curves between PET and LDPE reflects quantitative differences in valence electron distribution and local electronic environments at the free-volume boundaries. This difference provides important insight into the microstructural characteristics of polymers.

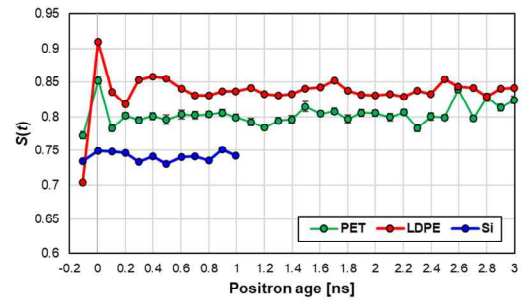


Fig. 3. Comparison of time-resolved S -parameter, distributions measured for PET (red dashed line), LDPE (blue dashed line), and pure Si (black dashed line).

4. Conclusions

In this study, a digital AMOC system was independently developed to acquire positron lifetime and momentum data simultaneously. The established system was shown to expand both the interpretability and analytical dimensionality of positron annihilation characteristics in polymer materials. The expansion of interpretability and analytical dimensionality represents a significant improvement over conventional techniques. The applicability of the system to a wide range of polymer materials was demonstrated.

Acknowledgement

This work was supported by the Korea government (MSIT) (1711078081)

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