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Investigation of PCM Microcapsules with Paraffin Filling by Positron Lifetime Spectroscopy

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Positron annihilation lifetime spectroscopy was applied to investigate the microcapsules composed of *n*-eicosane (filling material) and polysiloxane polymer (shell) in the range of temperatures 123–333 K. Pure components of microcapsules were also investigated as a base for interpretation of the measurement results. The temperature of phase transitions in microcapsules was determined. It showed the appearance of a rotary phase, which is not present in pure *n*-eicosane. In the considered material, two types of free volume have been identified. The sizes of free volumes able to accommodate Ps were estimated using standard models. On the basis of the *o*-Ps intensities, the content of polysiloxane in microcapsules was estimated as about 40%. Internal structure of the microcapsules (morphology) was observed by scanning electron microscopy.

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1. Introduction

Free positrons can either annihilate with electrons or create with them the positronium hydrogen-like atom (Ps), an unstable bound state of electron and positron. Its lifetime to the annihilation is influenced by several factors. Depending on the relative orientation of electron and positron spins, Ps can exist in two substates: singlet *para*-positronium (*p*-Ps, annihilating with emission of two photons) or triplet *ortho*-positronium (*o*-Ps, three-photon annihilation). The average lifetime of *p*-Ps is 125 ps, while *o*-Ps annihilate in vacuum with the lifetime of 142 ns. In the condensed medium, the *o*-Ps lifetime may be reduced to nanoseconds, due to the pick-off process (e^+ from triplet *o*-Ps state do not annihilate with its "own" e^-, but with e^- from the medium with opposite spin). As the lifetime of *o*-Ps depends on the size and shape of the free volumes present in the medium, Ps is considered to be a unique probe of subnanometric free volumes. One can also expect that the intensity of Ps is proportional to the number of free volumes in the medium. The positron annihilation lifetime (PAL) spectroscopy consists in determination of the average lifetimes (τ) and relative intensities (I) of free positrons and positronium. It allows to estimate the size and concentration of free volumes in which Ps is located.

The free (electron-less) volume in which Ps can be trapped represents a potential well assumed as stepwise one. The *o*-Ps decay constant $\lambda_{o-\mathrm{Ps}}$ is the product of the decay constant in the bulk ($\lambda_\mathrm{b} = 2\ \mathrm{ns}^{-1}$) and the probability P to find Ps outside of the potential well. The relation $\tau_{o-\mathrm{Ps}}$ vs. well radius R is described by the commonly accepted Tao–Eldrup model [1, 2]:

$$\lambda_{o-\mathrm{Ps}} = \frac{1}{\tau_{o-\mathrm{Ps}}} = 2\ \mathrm{ns}^{-1}\left(1-\frac{R}{R+\varDelta}+\frac{1}{2\pi}\sin\frac{2\pi R}{R+\varDelta}\right). \quad (1)$$

where $\varDelta$ is an empirical parameter, $\varDelta = 0.166$ nm.

In the literature, modifications of this model taking into account various void shapes [3], the size of object at the edge of detection [4], and population of excited states in the potential well [5] can be found.

To explain the *o*-Ps lifetimes in liquids, the "bubble model" is applied. The radius R of the bubble produced by Ps itself owing to its zero-point energy is determined by the minimum of total energy

$$\frac{\mathrm{d}}{\mathrm{d}R}\left[E_\mathrm{Ps}(R) + 4\pi R^2\sigma + \frac{4}{3}\pi R^3 p\right] = 0, \quad (2)$$

where $E_\mathrm{Ps}(R)$ is the energy of positronium; the second term in the equation corresponds to the surface tension energy (where σ is the surface tension), and the third term corresponds to the external pressure energy (at the atmospheric pressure p this term is by three orders of magnitude smaller than the second one, and therefore, in usual conditions can be neglected).

The object of this study were the phase change materials (PCM) in a form of microcapsules. In recent years, thermal and physical properties of PCM have been intensively studied by many techniques [6] because of their potential applications, e.g. in the textiles, construction materials, or in medicine. In the textile industry, microcapsules of micrometer diameter added to the fiber material of clothes improves its thermal protection parameters. The shell material of the microcapsules is responsible for their physical properties while the core material determines their thermal parameters. Depending on the manufacturing techniques and materials used it is possible to obtain the microcapsules of various morphologies: core-shell type, multicore or matrix.

The microcapsules investigated here have an alkane filling (*n*-eicosane) and polymer shell (polysiloxane). In principle, these compounds do not form chemical bonds, so the microcapsule properties should result from the properties of its building materials. The thermal properties of microcapsules are determined by the properties of *n*-alkanes which are saturated hydrocarbons C_nH_{2n+2}. Their melting temperature increases

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with the number of carbon atoms in the chain [7]. The odd-numbered n-alkanes with $n \leq 9$ and even-numbered with $n \leq 22$ exist in two phases: rigid and liquid. Alkanes with larger n show a waxy rotator phase (several K below the melting point). The n-eicosane ($n = 20$) as a function of increasing temperature shows only two phases: rigid crystalline and liquid one. However, recent studies on the crystallization of n-eicosane [8] indicate that at cooling a stable rotational phase, covering the range of 1 K only, may appear.

All n-alkanes in solid phase have a lamellar structure. The distance between the lamellae in even-numbered alkanes is smaller than in the odd-numbered ones (0.124 nm and 0.195 nm, respectively) and positronium locates in that gap. In the rotator phase some non-planar conformers appear [9]. The non-planar forms produce additional free volumes between the molecules inside the lamella also able to accomodate Ps atoms.

2. Samples

The microcapsule samples (MCP) were prepared in the Center of Molecular and Macromolecular Studies, Polish Academy of Science in Łódź. The manufacturing procedure was analogous to that described in the paper [10]. The microcapsules were more or less similar in shape to a sphere with an average grain size about 11 μm. The yield of microcapsules with the size in the range between 2 and 20 μm was 70%.

It was expected that the final product should have the form of core-shell structure, where the n-eicosane ($C_{20}H_{42}$, denoted here: C20) is the core, and the polysiloxane (PSX) builds the shell. The microcapsule properties should be related to the properties of materials they are made of, and therefore the pure substrates were also examined by the PALS technique. The n-eicosane with 99% purity was from Sigma-Aldrich. The siloxane spheres were provided by the microcapsule manufacturers.

3. Experimental

A convenient positron source used in our research was sodium ^{22}Na isotope decaying by positron emission to the excited state of neon, which after only 3.7 ps emits a gamma quantum of energy 1274 keV at the transition to the ground state of Ne. Registration of this quantum is considered the start signal (birth of positronium) for the lifetime measurements, and the quanta of energy 511 keV serve as a stop signal (e^+ annihilation). The signals are registered by two scintillation detectors with BaF_2 crystals and processed by the conventional fast-slow spectrometric system.

The ^{22}Na source with an activity of about 0.7 MBq is enclosed in an envelope of a thin (8 μm) Kapton film. The Kapton is thermally and mechanically resistant, positrons annihilate in it with a characteristic and easy to identify lifetime, so it is a convenient source packaging material. In all measurements the procedures were identical. Positron source was placed together with a sample in the measuring chamber at room temperature, then cooled to 123 K, and left at this temperature for 24 h. Finally, the temperature was raised in steps up to 333 K. The temperature of the chamber was regulated with an accuracy ±0.1 K using a combination of heating coil and liquid nitrogen cooling system, controlled by the Shimaden FP21 unit.

The spectra for MCP and PSX were collected during 1.4 h, and for C20 — during 1 h; the number of events accumulated during that time was about 2×10^6. The spectra were analyzed using the LT 9 programme [11] assuming the existence of three (for alkane) or four (for other samples) exponential components convoluted with the instrumental resolution curve. All parameters describing the spectrum τ_i, I_i were left free. The shortest lived component was ascribed to p-Ps (τ_1, I_1), the intermediate — to the annihilation of free positrons (τ_2, I_2), and the 3rd and possibly 4th longest one with mean lifetimes over 1 ns ($\tau_{3,4}, I_{3,4}$) corresponded to the decay of o-Ps. The correction for positron annihilation in kapton envelope was also applied ($\tau_S = 0.374$ ns, $I_S = 10\%$). The spectrometer time resolution was better than 260 ps.

The morphology of microcapsules was observed using a high resolution scanning electron-ion microscope Quanta 3D FEG form FEI company.

4. Results and discussion

The phases of n-eicosane are easily recognized by the PALS technique. The o-Ps lifetime in the rigid crystalline phase of even-numbered n-alkanes phase is about 1.2 ns. In liquid phase, near the melting point, the lifetime is independent of the hydrocarbon chain length, and is equal to 3.15 ns. The stepwise change of o-Ps lifetime (followed by the change of intensity) means alkane melting; in C20 it occurs at 37.5 °C (310.5 K).

Interesting changes of o-Ps intensity I_{3_C20} as a function of time at very low temperature (123 K) are shown in Fig. 1. The o-Ps lifetime does not change in time but the I_{3_C20} rises with time constant $\theta = 8.3$ h. This growth of intensity is typical for pure alkanes, it was also observed in other compounds [12,13]. It can be explained as the result of electron trapping [14]. High energy positrons lose their energy in the process of ionization and produce electrons, which can be trapped in the medium structure. With time elapse, the number of accumulated electrons rises, the next positrons emitted from the source may create additional Ps with those trapped electrons. The intensity I_{3_C20} increases with temperature until reaching the saturation value. As a function of temperature the I_{3_C20} above 240 K begins to decrease, which we ascribe to thermal emptying of electron traps. Just before the melting point the I_{3_C20} is small, 20% only, and increases stepwise at n-eicosane melting temperature.

The PALS spectra of polymer used as the capsule shell were also measured. In the PSX spectra one can distinguish two o-Ps lifetimes ($\tau_{3\_PSX} = 1$ ns and $\tau_{4\_PSX} = 2$ ns, at 123 K) attributed to two different sizes of free volume. Only one of them, τ_4, changes with temperature almost linearly to 3.6 ns at 333 K. At 123 K, the lifetimes and intensities are stable in time. In this polymer the electron trapping effect does not appear. The ratio $\frac{I_{3\_\mathrm{PSX}}}{I_{4\_\mathrm{PSX}}}$ for pure polymer at two selected temperatures 220 K and 325 K is 2.6 and 3, respectively.

Comparing the results obtained by the PALS technique for C20 and PSX we conclude that in the low temperature range the *o*-Ps lifetimes in alkane and in polysiloxane are almost identical. Also in the range of high temperatures (above 313 K) the lifetime in alkane and the longer of two lifetimes in polymer are quite similar.

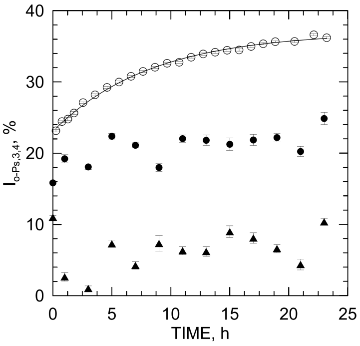

Fig. 1. The *o*-Ps intensities as a function of time at 123 K. Empty circles — *n*-eicosane, dots and triangles — intensities of long-lived and short-lived *o*-Ps component in microcapsules, relatively. The curve fitted to the *n*-eicosane data is: $I_3 = I_{30} + I_{3\mathrm{tr}}\left(1 - \mathrm{e}^{-\frac{t}{\theta}}\right)$.

In the PALS measurements for microcapsules we observe two *o*-Ps components. At the temperature 123 K the intensities of both *o*-Ps components are stable in time (Fig. 1). In the pure *n*-eicosane an increase of intensity was observed (see Fig. 1), while in MCP the *o*-Ps intensities are stable. It means that the electron trapping does not appear when the C20 is enclosed within the microcapsule. There can be two reasons of this behaviour:

1. The presence of impurities in the sample (it results in reduction or total lack of effect [15]);
2. The crystal structure of *n*-eicosane in microcapsule is different than that of macroscopic sample size (the electron traps are not created).

The PALS parameters in MCP change as a function of increasing temperature. The shorter of two *o*-Ps lifetimes (τ_3) has the value similar to the one found in *n*-eicosane (τ_{3_C20}) or to the shorter of two lifetimes in polymer (τ_{3_PSX}). The longest lifetime (τ_4) has the value like in polymer (τ_{4_PSX}). Both lifetimes vary smoothly with temperature. Based on the measured lifetimes of *o*-Ps we can determine the size of free volume using the Tao–Eldrup model, and the result of these calculations is shown in Fig. 2. The intensity of longer-lived *o*-Ps component I_4 is small below 310 K, and at 311 K it grows to 24%, while the intensity of short-lived component I_3 decreases. The intensity I_4 increases again at 315 K. Some changes of intensity I_3 at low temperature are seen, but the nature of these changes requires further investigation and will not be discussed here.

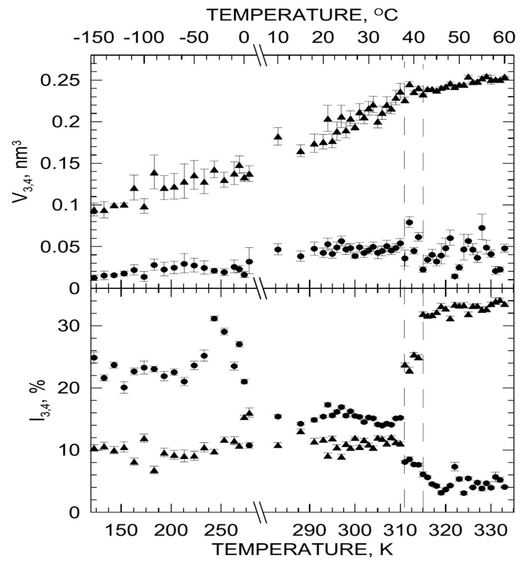

Fig. 2. The *o*-Ps intensities and free volume sizes as a function of temperature in microcapsules. Dashed vertical lines show the points of phase transitions. The temperature scale was extended above 273 K.

The *n*-eicosane melts at 310.5 K and we expected the same melting temperature in microcapsules. However, the change of intensity I_4 in two steps indicates that the melting point of the microcapsules is shifted to 315 K, and preceded by a formation of the rotational phase covering the range of 4 K. The existence of the rotator phase was a surprise, but it confirms our earlier conclusion about structural modifications of alkane core.

As it was mentioned earlier, the *o*-Ps lifetimes in C20 and in the PSX are hard to distinguish; at both low and high temperatures two of them overlap. This means that two types of the free volume belong in fact to three sources (Fig. 3). At low temperature (between 123 K and 263 K) the smaller free volume in microcapsules come from the alkane and smaller volumes in polymer, and the larger one can be assigned to the polymer only (Fig. 3a). Similarly, above 315 K (Fig. 3b) the larger of free volume in PSX and the free volume in molten C20 (determined using the bubble model) form the component seen as large free volume in MCP; we assign the smaller one to polymer only.

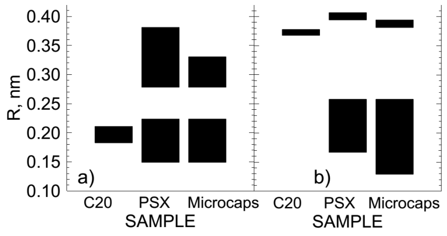

Fig. 3. The radii R of free volumes determined for *n*-eicosane (C20), polysiloxane (PSX) and microcapsules (Microcaps) in two ranges of temperature: (a) 123–263 K and (b) 325–333 K.

Superposition of the components indicates that in microcapsules two types of free volumes of varying sizes are present; this reflects also in intensities. At low temperature range, the intensities are: $I_3 = I_{3\_C20} + I_{3\_\mathrm{PSX}}$ and $I_4 = I_{4\_\mathrm{PSX}}$, while in the high temperature range (above 312 K) the I_{3_C20} should be added to I_4 value. If we take the I_3 and I_4 values for microcapsules and assume the ratio $\frac{I_{3\_\mathrm{PSX}}}{I_{4\_\mathrm{PSX}}}$ as found in the PALS measurements for pure PSX at two selected temperatures: 220 K and 325 K, we obtain the mass fractions of microcapsule components. At these selected temperatures the mass fraction of polymer was estimated as $38\% \pm 2\%$ and $42\% \pm 2\%$, respectively, consistent within the limits of error.

Taking into account the size of the microcapsules (average diameter is 11 μm), and assuming their spherical shape, we can estimate the thickness of MCP shell. This thickness was found equal to 0.7 μm, and is seems to us rather large. In similar commercially available microcapsules (with core-shell construction, diameter 23 μm, also with *n*-eicosane filling) the polymer shell constitutes 20% of mass only. Thus, we suspected that our microcapsules can have a different core-shell morphology.

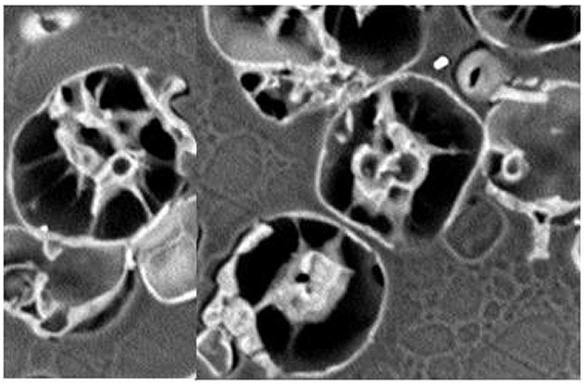

Fig. 4. Microcapsule morphology — SEM image with magnification 5000. Figure width 30 μm.

This supposition was checked by the scanning electron microscopy (SEM). To have a close look into the microcapsule interior, the samples were embedded in a resin. The resulting sample was cut with a knife, and a photo was taken (Fig. 4). In this picture a skeletal structure inside the microcapsules can be seen, which confirms our assumption. The thickness of microcapsules shell is relatively small, and a significant part of polymer mass builds the internal skeleton.

5. Conclusions

The PALS technique can be successfully applied to study the phase change materials (e.g. microcapsules). The PALS results obtained for both microcapsules and for materials they are made of are quite similar. However, some meaningful differences are observed:

In microcapsules:

— there is no electron trapping effect at low temperature;

— melting is preceded by a formation of the rotational phase in the range of 4 K;

— the melting point is shifted to higher temperature by 4.5 K.

Basing on the PALS results, we can:

— estimate the percentage content of components building the microcapsules (here ≈40% belongs to the polymer);

— notice the morphology of the microcapsules being different from that declared by the manufacturer.

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References

[1] S.J. Tao, *J. Chem. Phys.* **56**, 5499 (1972).

[2] M. Eldrup, D. Lightbody, J.N. Sherwood, *Chem. Phys.* **63**, 51 (1981).

[3] B. Jasińska, A.E. Kozioł, T. Goworek, *J. Radioanal. Chem.* **210**, 617 (1996).

[4] B. Zgardzińska, *Acta Phys. Pol. A* **125**, 700 (2014).

[5] T. Goworek, K. Ciesielski, B. Jasińska, J. Wawryszczuk, *Chem. Phys. Lett.* **272**, 91 (1997).

[6] K. Pielichowska, K. Pielichowski, *Prog. Mater. Sci.* **65**, 67 (2014).

[7] M. Maroncelli, H.L. Strauss, R.G. Snyder, *J. Chem. Phys.* **82**, 2811 (1985).

[8] A. Genovese, G. Amarasinghe, M. Glewis, D. Mainwaring, R.A. Shanks, *Thermochim. Acta* **443**, 235 (2006).

[9] M. Maroncelli, S.P. Qi, H.L. Strauss, R.G. Snyder, *J. Am. Chem. Soc.* **104**, 6237 (1982).

[10] W. Fortuniak, S. Slomkowski, J. Chojnowski, J. Kurjata, A. Tracz, U. Mizerska, *Colloid Polym. Sci.* **291**, 725 (2013).

[11] J. Kansy, *Nucl. Instrum. Methods Phys. Res. A* **374**, 235 (1996).

[12] A. Ekstrom, R. Suenram, J.E. Willard, *J. Phys. Chem.* **74**, 1888 (1970).

[13] Y. Ito, T. Hirade, E. Hamada, T. Suzuki, Y. Ito, *Acta Phys. Pol. A* **95**, 533 (1999).

[14] M. Pietrow, B. Zgardzińska, *Acta Phys. Pol. A* **110**, 641 (2006).

[15] B. Zgardzińska, T. Goworek, *Chem. Phys. Lett.* **547**, 35 (2012).