Investigation of PCM microcapsules at various temperatures and pressures by PALS method

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Abstract. The positron annihilation lifetime spectroscopy (PALS) was used to investigate the properties of Phase Change Material (PCM): the Micronal® DS 5001 X microcapsules. The microcapsules are composed of a polymer capsule shell and a paraffin core. Two groups of free volumes were observed: those producing the long-lived component can be ascribed to the polymer, the other to the mixed alkanes. Both o-Ps components show the known effect of the intensity rise with positron irradiation time. At temperatures below -3°C we have observed the short lifetime as for alkane rigid phase, then the rotator-like phase preceded liquid phase. This form of temperature dependence of PAL spectra is discussed. There was no destructive effect of temperature. The PALS results were compared with those obtained by scanning electron microscopy.

1. Introduction
The lifetime of ortho-Ps substate depends on the size of free volume (void) where the o-Ps is trapped, thus Ps is considered as a convenient probe of medium structure.

Phase Change Materials (PCM) are able to absorb, accumulate and release a large amount of energy in the range of the phase transition temperature. The PCM in the form of microcapsules of core-shell morphology were the subject of this study. The shell material of microcapsules (polymer) determines their physical properties (e.g. strength, toxicity, reactivity), while the core material (paraffin) the thermal ones (e.g. operating temperature, capacity of accumulation and release of energy). When the environment temperature increases, the filler material absorbs the energy until the core becomes molten. When the temperature falls, the filler material solidifies, releasing back the energy to the environment.

The microcapsules Micronal® DS 5001 X (MPCM) were obtained from the producer and distributor the BASF Chemical Company. Their manufacturing process is described in [1]. The manufacturer declares the melting temperature 26°C. They are a kind of prefabricated material for building industry; for example they are added to the building materials: paints, plasters, fillings or cement mortar and can replace the air conditioning systems.

The filling material is usually alkane or their mixture. The pure hydrocarbons as well as the mixtures of alkanes were successfully investigated as a function of temperature or pressure by the PALS technique [2-5]. At low temperatures (usually below 200 K) in pure n-alkanes and some of their mixtures, the o-Ps intensity increases with time by several percent with time constant $\theta$ of several hours, while the o-Ps lifetime (1.1 ÷ 1.2 ns) does not change. The growth of intensity is associated with trapping the post-ionization electrons. The stepwise change of intensity and lifetime (as a function of $T$ or $p$) appears at the phase transition points.
The existing data about alkanes allow to single-out the share of them in the complex structure of microcapsule. It was particularly interesting to find out how the spatial limitation (encapsulation) affects the properties of the filling material (the formation of crystalline structures, phase transitions points, other effects typical for pure alkanes, e.g. low-temperature e- trapping).

2. Experimental
Positron annihilation lifetime spectra (PALS) were measured using two standard fast-slow spectrometers with different chambers: one to measure spectra as a function of temperature (T) and the other as a function of pressure (p). The chamber for f(T) measurements gives the opportunity to carry out the measurements in the range of 120 – 500 K. The other chamber was connected to the Unipress U11 gas compressor which allows to achieve the pressures from 0 to 500 MPa. The resolution time (FWHM) was about 260 ps and 240 ps, respectively. The 22Na positron sources of activity 0.80 MBq in the Kapton envelopes were used (8·10⁵ coincidences were collected during 1 h). The spectra were processed by the LT 9 programme [6]. The PAL spectra were assumed to consist of four exponential components convoluted with the instrumental resolution curve and random coincidence background. Two shortest-lived components were ascribed to the para-positronium (p-Ps) and to the annihilation of free positrons (e+). The remaining longest-lived ones belonged to the decay of ortho-positronium (o-Ps) in free volumes of different sizes. The correction for positron absorption in the Kapton foil was also applied. The structure of microcapsules was observed using a high resolution scanning electron microscope Quanta 3D FEG form FEI company. For our investigations the MPCM with grain size in the range 180-250 µm were selected.

3. Results and discussion
In the microcapsules two o-Ps components with different lifetimes exist. In the Figure 1, the growth of o-Ps intensities at 123 K in time is shown; the lifetimes, 1.1 and 1.7 ns were stable in time. This means that in the microcapsules electron trapping effect is still present, like in the previously described alkanes. The time constant of this process for the longer-lived o-Ps component is 9.6 h, while for the shorter-lived one is 4 h. The maximal increase of intensities is in both cases similar (4.6 and 4.8 %) and the scale of that rise was greatly reduced compared to neat alkanes. We suppose that the trapping effect can occur if the crystal structure of the filler material is the same as of macroscopic samples of the alkanes.

As one can see in the Figure 2, the lifetime of shorter-lived o-Ps component τ₄ is practically independent on temperature. The intensity I₄ decreases initially by 4%, then the rate of change slows, and above 269 K I₄ stabilizes at a relatively low value ~ 6%. The changes in the longer-lived component (τ₃, I₃) as a function of temperature are more pronounced. The lifetime τ₃ increases almost linearly up to 2.4 ns, and at 269 K the first stepwise change is visible. Above 298 K, the τ₃ stabilizes at the value of 2.95 ns. The intensity I₃ reaches a maximum at 143 K, but above this temperature the excess electrons are already throne out of the traps, that leads to the reduction of intensity down to 13%. Two steps of I₃ are seen, at 269 K and at 298 K. Such a dependence of τ₃, I₃ on temperature suggests that the 4th component should be attributed to the filling material of the microcapsules. The intensity I₄, significantly higher than I₃, suggests that in the mass composition of the microcapsules the filling is predominant. Stepwise changes of the τ₄ and I₄ allow us to specify the phase transitions points in MPCM, estimated as 269 K and 298 K. Above 298 K, the filling material is liquid. Below 269 K it should be in the rigid crystal phase. Between these two points we see the rotator phase. The o-Ps lifetime in liquid alkanes and their mixtures a few K above the melting point is about 3.15 ns, and is reduced to about 2.9 ns, it can be the result of the ortho-parapara conversion in non-degassed samples. The o-Ps lifetime τ₄ in MPCM is 2.95 ns – just like in the alkanes in the air, but after degasing the τ₄ increases to 3.1 ns (Fig.2), which confirms that the 4th component corresponds to the paraffin filling.

Melting point of 298 K is quite close to that of n-octadecane (301 K), however, in so short-chain even-numbered alkane the rotator phase does not appear, moreover, in pure alkanes the lifetime in rigid phase is 1.2 ns only. Increased lifetime in MPCM suggests that they are filled with a mixture of
alkanes, the longer of them is *n*-octadecane (because the mp. in mixture is an average of mp. of their components). Among several mixtures of alkanes investigated by us analogous behaviour was found in the mixture of 50% C_{16}H_{34} + 50% C_{18}H_{38}. As one can see in the Figure 2 (stars) the o-Ps lifetime in the mixture is similar to that measured in MPCM (except the liquid phase, because the mixture was degassed and the microcapsules were not). In the mixture the rotator phase appears and the phase transition points are roughly reproduced (deviations may be due to small difference in the percentage composition of the mixture).

In the MPCM, the intensity is smaller than in alkane mixture, because we have here two different kinds of free volumes. Comparing the intensities in the liquid, both MPCM and mixed alkanes, we observe the reduction to about 75% of that for pure mixture. Thus, one can expect that the polymer content on the capsule is about 25%. In the literature [7] one can find the information that the shell material is about 24% of microcapsule mass, well consistent with our estimate. Average size of our microcapsules is about 5 μm, thus the respective shell wall thickness should be 0.226 μm. It can be easily verified in the SEM images; the shell thickness of selected microcapsule with the diameter 4.75 μm is estimated as 0.225 μm.

After cooling the MPCM the measurements as a function of temperature were repeated on the same sample and found fully reproducible - there was no destructive effect of temperature, which is confirmed by SEM pictures.

The phase change (for example from liquid to rigid crystal) can be realized by decreasing the temperature or increasing the pressure. Microcapsules were investigated as a function of increasing pressure at constant temperature 293 K, when the MPCM were in the rotator phase. The increase of pressure by 1 MPa corresponds in alkanes to a decrease in temperature of about 0.22 K. Thus it was expected to observe the transition to the rigid phase at p \( \approx 80 \) MPa. The results illustrated in Figure 3 show that even small pressure significantly influences the PAL spectra parameters. At zero pressure o-Ps lifetimes are identical as in temperature measurements, but already above 6 MPa they are shorter than in the measurements as a function of T. Below 20 MPa the intensity \( I_3 \) increases - such an effect is rather unexpected. The lifetime shortening can be easily explained as the transition to rigid phase, the increase of intensity suggests microcapsules crushing, which leads to the relative increase of the share of o-Ps annihilating in polymer. We have verified this hypothesis by performing a SEM photograph of microcapsules treated with high pressure (Fig. 4). The grain capsules are deformed, some of the grains

**Figure 1.** (up) Increase of o-Ps intensities (\( I_3 \) – triangles, \( I_4 \) – dots) with time at 123 K.

**Figure 2.** (right) Temperature dependence of o-Ps lifetimes and intensities in MPCM (\( \tau_3 \), \( I_3 \) – triangles, \( \tau_4 \), \( I_4 \) – dots) and alkane mixture (stars). Open circle – \( \tau_4 \) in degased MPCM.
has been broken, split into smaller fragments. As can be seen in the Figure 4 the microcapsules were squeezed but on the grain boundary region only. Inside the grain deformed microcapsules were observed.

4. Conclusions

Positronium is a useful probe in the research of microcapsules. Using the PALS technique we can state that in microcapsules the electron trapping effect occurs, suggesting that the crystalline structure formed inside the microcapsules is the same as the lamellar structure of pure paraffins. The phase transitions points in MPCM were determined, and the presence of additional phase (rotator) has been found. Comparing the changes of PAL spectra in MPCM and mixtures allows to determine the composition of the microcapsules. The filling material was identified as a mixture of \( n \)-hexadecane and \( n \)-octadecane in equal proportions. The percentage weight of the core was estimated as 75%. The devastating effect of pressure was found. The SEM images confirmed the conclusions from the PALS measurements.

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