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THERMALLY TREATED EFFECTS ON POLYMERS BASED ON ACRYLATE OLIGOMERS BY POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

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Positron annihilation lifetime spectroscopy has been applied to the study of free volume properties in polymers based on the acrylate oligomers. The measurements have been made on samples heated to a temperature of 483 K. The longest lifetime, in three-component analyses of the spectra was associated with the pick-off annihilation of *ortho*-positronium trapped in free volumes. After the thermal treatment changes in the *ortho*-positronium lifetimes and the relative intensity of the longest component were observed. These results are discussed on the basis of free volume model.

Key words: positron annihilation; polymers, organics.

There has been interest in acrylate oligomers-based polymers due to the possibility of applications in different branches, such as optoelectronics, holography and polygraphical material engineering [1–3]. Since the materials properties of amorphous polymers are frequently interpreted in terms of the free volume concept, it is advantageous to have a spectroscopic technique by means of which quantitative information on free volume can be generated. During recent years, it has been established that positron annihilation lifetime spectroscopy (PALS) is a useful method for such analysis. It gives a measure of positron and positronium annihilation times and is the technique most commonly applied to polymers.

Positrons injected in substances lose their energy through elastic collisions and finally annihilate with electrons through several processes. In the case of non-conductive molecular materials in addition to the annihilation of the positron, formation and annihilation of positronium (Ps) take place. Ps is the bound state of positron and electron having an atomic radius comparable to that of the hydrogen atom. It exists in two spin states. One is called *para*-positronium (*p*-Ps) in which the positron and electron spins are antiparallel. The other state is *ortho*-positronium (*o*-Ps), in which the particle spins are parallel. Positronium appears in the para or ortho spin state with a relative formation rate of 1:3. Annihilation of *p*-Ps occurs with a lifetime in the order of 125 ps, whereas *o*-Ps decays after approximately 140 ns. However, in the condensed matter, the positron in *o*-Ps predominantly annihilates, during a collision with atoms or molecules, with an electron other than its bound partner and possessing an opposite spin. This process,

called pick-off annihilation, reduces the o-Ps lifetime in polymers to a few nanoseconds. Ps cannot form in materials with high electron densities. The positronium formation probability and lifetime are extremely sensitive to the electron density surrounding Ps. The o-Ps localises in the space between and along polymer chains and at chain ends (free volume holes), and the lifetime gives indication on the mean radii of these holes [4, 5]. The original free volume theory for the positron annihilation in molecular substances was proposed by Brandt, Berko and Walker [6]. The free volume was defined as the cell volume minus the excluded volume, which was based on the Wigner-Seitz approximations. The free volume model expresses that Ps can only form in those free spaces of the lattice, having a size superior to some critical values. The electron pick-up depends on the overlap of the positron component of the Ps wave function with the lattice wave function. As the size of the free volume cavity increases, the local electron density, surrounding the o-Ps, decreases. Thus the o-Ps has a slower annihilation rate and longer lifetime. Tao and Eldrup et. al. [7, 8] derived the equation to correlate experimentally observed o-Ps lifetimes and free volume hole dimensions in polymers. They proposed a simple model in which the o-Ps particle resides in a spherical potential well, having an infinite potential barrier of radius R_0. It is assumed that an electron layer forming a thickness ΔR is present on the wall of the hole, which effective radius is consequently $R=R_0-\Delta R$ and that the lifetime of the o-Ps in the electron layer is the spin averaged Ps lifetime of 0,5 ns. Furthermore, a very successful semi-empirical equation has been established relating on the o-Ps lifetime to the size of the free volume hole in which it annihilates, thus τ_3 corresponds to a spherical space with a radius R, according to the following equation:

$$\tau_3(ns) = 0,5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}, \tag{1}$$

where ΔR=0,166 nm is the fitted empirical electron layer thickness. By fitting the above equation with the measured τ_3 values, R and free volume size as $V_f = (4\pi/3)R^3$ can be evaluated. The relative intensity of the longest component, I_3, is generally correlated to the density of the holes, which can be considered as a kind of trapping centres for Ps. A semi-empirical relation may be used to determine the fraction of free volume (f_V) in polymers as [4, 5]:

$$f_V = CV_f I_3, \tag{2}$$

where V_f is the free volume calculated from τ_3, using eq. (1) with a spherical approximation, I_3 (in %) is the intensity of long-lived component; C is an empirical parameter, which can be determined by calibrating with other physical parameters.

The studies of the changes occurring in the structure of materials after the thermal treatment are important for the material science. The aim of this paper is to investigate the changes induced by thermal treatment in the microscopic structure of a sample of acrylate oligomers-based polymers, using positron annihilation lifetime spectroscopy (PALS).

Positron lifetime studies were performed in the UV-cured composition based on the acrylate oligomers. The photocompositional mixtures identified as D-1, D-2, D-4, D-5-1, D-5-2 and D-5-2 were chosen for the further investigations. Mixture compositions are presented in table 1. Their molecular structures are given in fig. 1; isobutylbenzoin ether (signed as i-BEB) was used as a photoinitiator. The photodissociation of photoinitiator reaction is presented in fig. 2. R' and R" denote fee chemical radicals which are created

after a breaking of the photoinitiatior; R_1, R_2, R_3 and R_4 (fig. 1) denote the oligomer fragments which remain unchanged during photopolymerization. The number n of the identical oligomer fragments may usually vary from one to four.
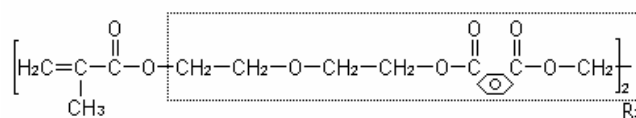
Table 1

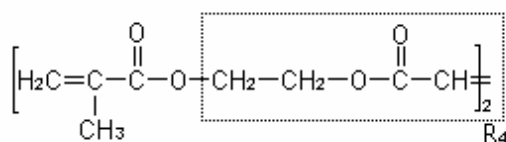Contents of the photocompositional mixtures in the investigated samples

Sample	% OKM-2	% MDF-2	% DMOEM	% TGM-3	% i-BEB
D-1	88,8	-	-	10,0	1,2
D-2	50,0	38,8	-	10,0	1,2
D-4	-	88,8	-	10,0	1,2
D-5-1	-	-	48,3	50,5	1,2
D-5-2	-	61,7	27,1	10,0	1,2
D-5-3	50,0	-	38,8	10,0	1,2
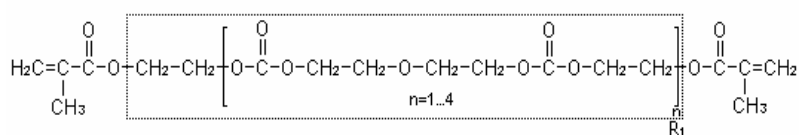
OKM-2

MDF-2

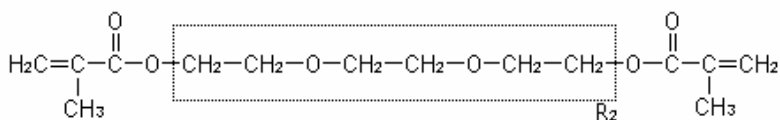**DMOEM**

TGM-3

Fig. 1. Chemical formulae of mixture content

The photochemical polymerization process takes place in the system due to the presence of the double C=C bonds at the ends of the chain. Under the influence of UV-irradiation the chemical bonds on the sides of oligomer constituents are broken. This leads to a "sewing" of single carbon bonds and occurrence of solid photopolymerized phase. All these components form a complex of a three-dimensional network.
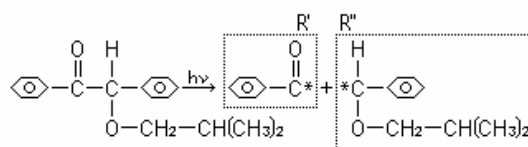
Fig. 2. Photodissociation reaction of photoinitiator

The photopolymerization was performed by an UV-hydrogen lamp (λ_{max}~350 nm). The UV fluence used to cure the polymers was 2,7 kJ/m^2 for 1 min. UV-curing process was carried out for 20 min. The details concerning sample preparation have already been reported [2, 3].

The DSC analysis shows absence of any heat effects at the temperature of about 423 K, it indicates the high thermal stability of investigated polymers. The heating to temperatures higher than 483 K caused destruction of the samples. It is interesting to compare free volume hole sizes before and after heating the samples up to about 483 K to investigate the effect of their previous thermal history on the free volume hole sizes.

As-prepared polymer samples were heated to a temperature of 483 K before the measurements in an air oven. The heated samples were cooling down (10,0 K/min) to the room temperature before the positron annihilation measurements. All the samples proved amorphous using X-ray analysis.

The measurements of positron lifetimes were curried out after cooling down the samples, with an ORTEC spectrometer of about 270 ps FWHM (Full Width at Half Maximum) resolution. A Na^{22} isotope with 7,4·10^5 Bq activity was used as the positron source. It was placed between two identical samples, forming a „sandwich" system.

The PAL spectra were measured at room temperature and analysed through the common "Microcomputer program for analysis of positron annihilation lifetime spectra LT" designed by Kansy [9] with a three-component model. The four-component analysis generally does not give better fitting for the variance value. Therefore, only three-component results are presented here. In polymers, the shortest lived component is usually attributed to *p*-Ps annihilation. In our case, because of the relatively poor time resolution and no constraints on lifetimes during computer analyses, it might contain not only *p*-Ps annihilation contribution but also contributions from the positron compounds. Therefore, during the fitting for the shortest lifetime, τ_1, it was fixed at 125 ps (the *p*-Ps lifetime). The intermediate lifetime ($\tau_2 \approx 0,36$ ns) is due to the free positrons annihilation with electrons in the bulk material. It shows some quite small variations after the heating. The results of the calculation of the mean values of positron lifetimes for the investigated samples showed the existence of a long-lived component in the positron annihilation lifetime spectra. According to the common interpretation we attribute the longest component τ_3, to the pick-off annihilation of *o*-Ps trapped by free volumes. In any given, sample all the free volume holes are not the same size. The LT results are the averaged values, but the real long-lived annihilation events have some

time-distribution around the averaged value. So, the concept of the average free volume size is used in practice.

As the o-Ps component is relevant to the free-volume properties, and it is markedly sensitive to the microstructure changes, in this paper, our main attention is paid to the τ_3 and I_3 . The lifetime parameters for the samples in the initial state, before thermal treatment, have already been reported [10–12]. The variations of o-Ps pick-off lifetime and its intensity for the investigated samples before and after thermal treatment are presented in table 2. The errors are the results of the mathematical analysis.

Table 2

Mean values of the lifetime, τ_3, and relative intensity, I_3, of the o-Ps

Sample		τ_3 [ns]	I_3 [%]
D-1	initial state	1,721±0,004	22,27±0,08
	thermally treated	1,698±0,007	20,54±0,11
D-2	initial state	1,675±0,004	21,40±0,07
	thermally treated	1,653±0,006	20,45±0,18
D-4	initial state	1,651±0,005	18,56±0,09
	thermally treated	1,631±0,009	13,55±0,22
D-5-1	initial state	1,591±0,006	3,08±0,08
	thermally treated	1,696±0,028	4,33±0,16
D-5-2	initial state	1,543±0,004	5,38±0,09
	thermally treated	1,557±0,009	8,64±0,10
D-5-3	initial state	1,783±0,030	4,85±0,18
	thermally treated	1,611±0,028	5,64±0,21

The average size of the free-volume holes V_f was calculated according to eq. 1. The values of the V_f and $V_f \cdot I_3 = f_V/C$ for the investigated polymers before and after the thermal treatment are shown in fig. 3 and in fig. 4, respectively. The errors bars are smaller than symbol plots.

As it can be seen in table 2, all the samples exhibit a change in o-Ps lifetimes, τ_3, as well as the relative intensity of o-Ps, I_3, which indicates that the thermal treatment changes the microstructure of the investigated polymers.

In the case of the samples D-1, D-2 and D-4, a decrease of τ_3 can be observed. It does not change significantly in the samples D-1, D-2 and D-4, a decrease of about 1%, taking into account the initial samples and the heated ones, can be detected. It follows that the free volume size values change nearly more than $2 \cdot 10^{-30}$ m^3. As it can be seen in table 2, the thermal treatment in these samples leads to decrease of the relative intensity of o-Ps, I_3. It suggests that the o-Ps formation probability slightly decreases after heating.

In the case of the sample D-5-3 a decrease of τ_3 can be observed too, but difference is much larger and additionally the relative intensity of o-Ps, I_3 slightly decreases after heating of this sample.

However, in the case of D-5-2 sample the difference of free volume size values before and after heating is in the range of the errors of the mathematical analysis. It seems that in the sample D-5-2, the thermal treatment does not change the microstructure. But simultaneously, the relative intensity of o-Ps, I_3 increases significantly, from 5,38 % for the initial state sample, to 8,64 % for the heated one (see table 2). Because the concentration of the free volume sites is proportional to the

intensity of o-Ps, we assumed that the concentration of free volumes in the sample D-5-2 is much larger after the thermal treatment.
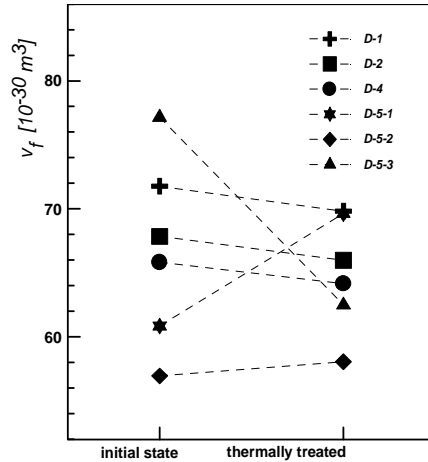

Fig. 3. Average free volume size, V_f for the investigated samples before and after thermally treatment. Lines are drawn as a guides for the eye
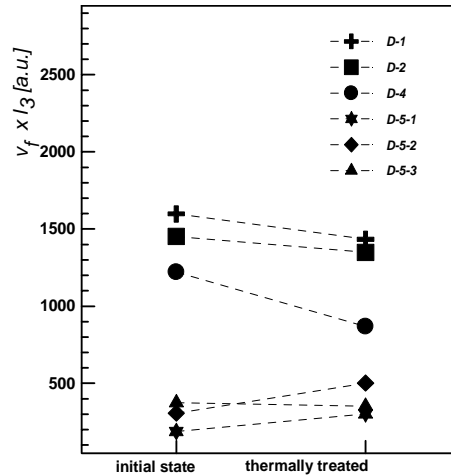

Fig. 4. The $V_f I_3 = f_V/C$ values for the investigated samples before and after thermally treatment. Lines are drawn as a guides for the eye

Absolutely different is behaviour of the sample D-5-1. As can be seen in table 2 only in D-5-1, thermally treatment leads to increase the o-Ps lifetime. It means that the mean free volume holes size increases after the heating only in D-5-1 (see fig. 3).

The fractional free volume is proportional to $V_f \cdot I_3$, because C in eq. 2 is constant. Hence, these results suggest that after the thermal treatment, the fractional free volume, slightly decreases in the samples D-1 and D-2, but significantly in the sample D-4, as it is presented in fig 4. Increasing of the fractional free volume is observed in the samples

D-5-1 and D-5-2. It is interesting that in spite of the largest decrease in free volume size value after heating, the fractional free volume in D-5-3 does not change.

The effect of the heating is such that either free volume size value or the fractional free volume change in the investigated polymers after the thermal treatment. In the samples marked as D-5-1, D-5-2 and D-5-3 (i.e. polymers based on the oligomer DMOEM) quite large variations are observed. Among of these three polymers D-5-2 sample indicates the least change and it seems to be result of the lowest presence of DMOEM in the composition of this sample.

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1. *Berlin A.A., Korolev G.V., Kefeli T.Ja., Sivergin Yu.M.* Akriłowyje oligomery i matieriały na ich osnowie. Chimija, Moskwa. 1983.
2. *Merwinskij R.I., Gudzowskaja L.A., Hranowskij W.A.* et al. Żurnał Naucznoj i Prikładnoj Fotografii. 1992. Vol. 37. 473 p.
3. *Merwinskij R.I., Gudzowskaja L.A., Roter W.E.* Chimija Wysokich Energij. 1994. Vol. 28. 182 p.
4. *Jean Y.C.* NATO Advanced Research Workshop. Advances with Positron Spectroscopy of Surfaces. 1993 Varenna, Italy, July 16-17.
5. *Pethrick R.A.* // Prog. Polym. Sci. 1997. Vol. 22. 1 p.
6. *Brandt W., Berko S., Walker W.W. //* Phys. Rev. 1960. Vol. 120. 1289 p.
7. *Tao S.J.* // J. Chem. Phys. 1972. Vol. 6. 5499 p.
8. *Eldrup M., Lighbody D., Sherwood J.N.* // J. Chem. Phys. 1981. Vol. 63. 51 p.
9. *Kansy J.* Nucl.Instr.and Meth. in Phys. Research. 1996. Vol. A374. 235 p.
10. *Hyla M., Filipecki J., Mandecki Z., Mervinskii R.I.* // J. Mat. Sci. Lett. 1997. Vol. 16. 1859 p.
11. *Hyla M., Filipecki J., Mandecki Z., Mervinskii R.I.* // J. Non-Cryst. Solids. 1998. Vol. 232–234. 446 p.
12. *Hyla M., Filipecki J., Mandecki Z.* et al. // J. Non-Cryst. Solids. 2001. Vol. 290. 20 p.

ЕФЕКТИ ТЕРМІЧНОЇ ОБРОБКИ В ПОЛІМЕРАХ НА ОСНОВІ ОЛІГОМЕРІВ АКРИЛАТУ, ВИВЧЕНІ МЕТОДОМ ПОЗИТРОННОЇ АНІГІЛЯЦІЙНОЇ СПЕКТРОСКОПІЇ

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Вивчено властивості вільного об'єму в полімерах на основі олігомерів акрилату методом позитронної анігіляційної спектроскопії. Дослідження проводили на зразках, нагрітих до температури 483 K. Під час аналізу спектрів довготривалий час життя третьої компоненти був пов'язаний з процесором pick-off анігіляції орто-позитронію, який захоплювався у вільному об'ємі. Після термічної

обробки були виявлені зміни в часі життя орто-позитронію та відносній інтенсивності довготривалої компоненти. Отримані результати проаналізовані на основі моделі вільного об'єму.

Ключові слова: позитронна анігіляція, полімери, органіка.

ЭФФЕКТЫ ТЕРМИЧЕСКОЙ ОБРАБОТКИ В ПОЛИМЕРАХ НА ОСНОВЕ ОЛИГОМЕРОВ АКРИЛАТА, ИЗУЧЕННЫЕ МЕТОДОМ ПОЗИТРОННОЙ АННИГИЛЯЦИОННОЙ СПЕКТРОСКОПИИ

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Изучены свойства свободного объема в полимерах на основе олигомеров акрилата методом позитронной аннигиляционной спектроскопии. Исследования проводили на образцах, нагретых до 483 К. Во время анализа спектров долговременное время жизни третьей компоненты было связано с процессором pick-off аннигиляции орто-позитрония, который захватывался в свободном объеме. После термической обработки были обнаружены изменения времени жизни орто-позитрония и относительной интенсивности долговременной компоненты. Полученные результаты проанализированы на основе модели свободного объема.

Ключевые слова: позитронная аннигиляция, полимеры, органика.