Positronics in contemporary nanocomposites science and engineering:

the case of polymer-filler dimethacrylate-based dental restoratives

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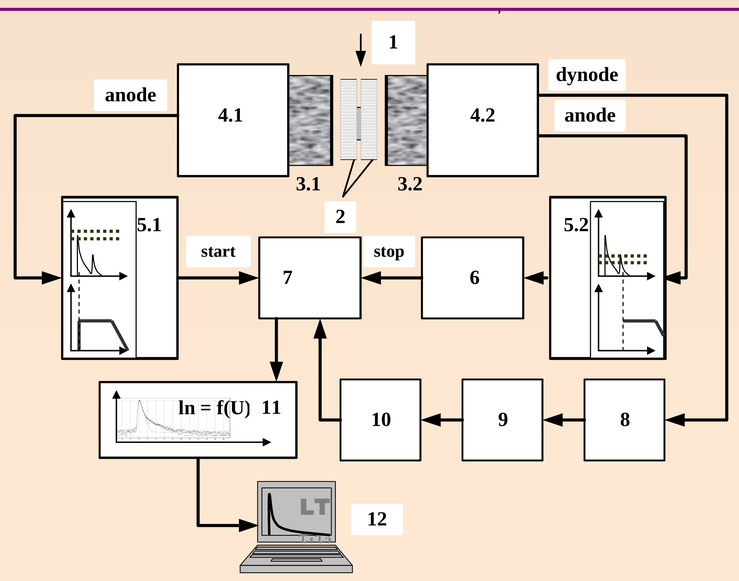
Abstract:

Possibilities of annihilating positrons in lifetime measuring mode is analyzed in application to commercially available dimethacrylate-based dental restorative composites, these being Charisma® (Heraeus Kulzer GmbH, Germany), Dipol® (Oksomat-AN Ltd, Ukraine) and ESTA-3 (Kiev, Ukraine). These composites are based on monomer consisted of bisphenol A-diglycidyl dimethacrylate (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA) modified by multisized filler particles (highly dispersive phase of silica glass). The positron annihilation lifetime spectra were treated with different algorithms described in details elsewhere [1,2]. In respect to data parameterized within constraint-free x3-term analysis, the annihilation processes in these nanocomposites are identified as conversion from "purely" positron trapping to positronium (Ps) decaying, where o-Ps component is caused entirely by free-volume holes in the polymer matrix, and positron-trapping component is defined preferentially by interfacial free-volume holes between filler particles and surrounding polymer matrix. Most adequate model-independent estimation of polymerization volumetric shrinkage in the studied nanocomposites can be performed in terms of average positron lifetime. Meaningful phenomenological description of photoinduced o-Ps transferring in positron-trapping sites, can be developed at the basis of semi-empirical model exploring a so-called x3-x2-CDA (x3-x2-coupling decomposition algorithm) [2].

1. Shpotyuk Olha, Ingram Adam, Shpotyuk Oleh // Nanoscale Res. Lett.-2016.-**11**.-P. 528-1-6.
2. Shpotyuk Olha, Ingram Adam, Shpotyuk Oleh, Bezvushko Elvira // Polim. Med.-2017.-**47**.-91-100.

EXPERIMENTAL: Positron Annihilation Lifetime (PAL) Spectroscopy



Block-scheme of conventional sample-source "sandwich" arrangement for PAL measurements using the ORTEC apparatus:

1 – foil-covered ^{22}Na source,
2 – two identical samples,
3.1 and 3.2 – scintillators of γ-quanta,
4.1 and 4.2 – photomultipliers,
5.1 and 5.2 – constant fraction discriminators,
6 – delay line,
7 – time-pulse height converter,
8 – preamplifier,
9 – amplifier,
10 – single channel analyzer,
11 – multichannel analyzer,
12 – personal computer.

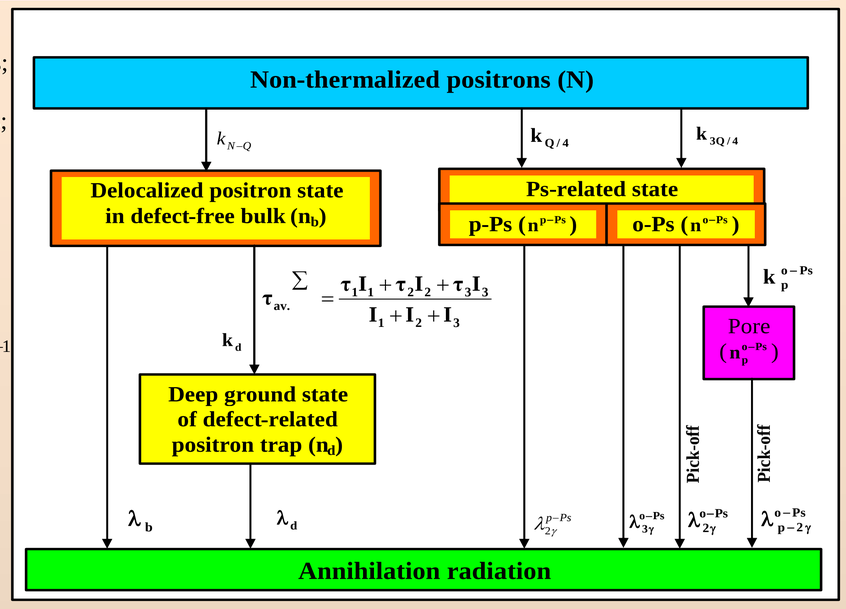
Mixed positron trapping and o-Ps decaying within three-state model

$n^{p\text{-}Ps}$ – number of p-Ps at time **t;**
$_{2\gamma}\lambda^{p\text{-}Ps}$ – 2γ-quanta annihilation rate of p-Ps;
$n^{o\text{-}Ps}$ – number of o-Ps at time **t**
$_{3\gamma}\lambda^{o\text{-}Ps}$ – 3γ-quanta annihilation rate of o-Ps;
$_{2\gamma}\lambda^{o\text{-}Ps}$ – annihilation rate of pick-off o-Ps;
$_{p}n^{o\text{-}Ps}$ – number of pores within o-Ps is formed;
$_{p\text{-}2\gamma}\lambda^{o\text{-}Ps}$ – o-Ps annihilation rate in pick-off process through pores;
$_{p}k^{o\text{-}Ps}$ – positron trapping rate of pore.

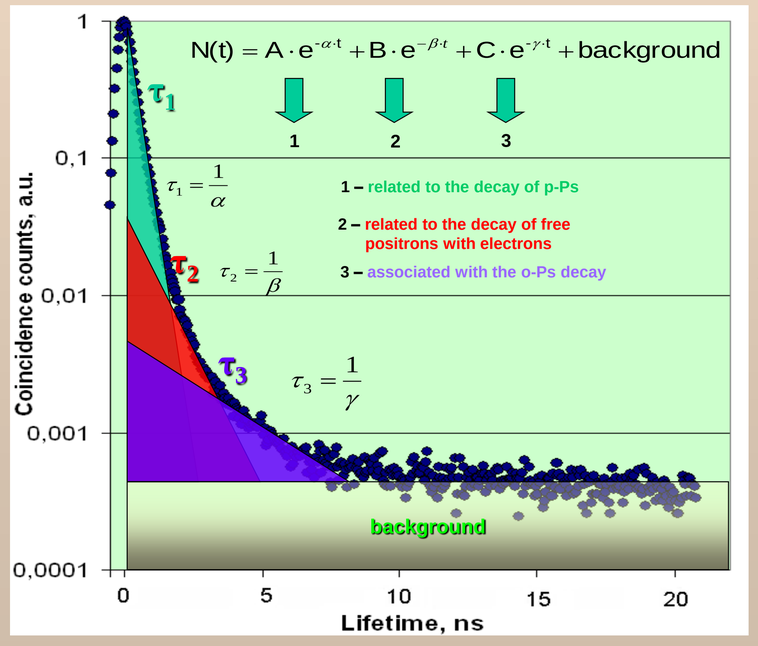
$$\tau_3 = [1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin(\frac{2\pi R}{R+\Delta R})]^{-1}$$

$$V_f = \frac{4\pi R^3}{3}$$

R – pore radius;
ΔR≈0.166nm – fitted empirical electron layer thickness;
V_f – free volume size.



MATHEMATICAL TREATMENT of PAL data:



τ_{av}	**Mean positron lifetime: cumulative defect environment prevailing in sample**
τ_b	**Lifetime τ_b: associated with positron trapping in defect-free bulk**
k_d	**Positron trapping rate in defects**
τ_2-τ_b	**Size measure of extended defects where positrons are trapped**
τ_2/τ_b	**Represents the nature of defects**

PAL spectra parameters for DRC ESTA-3 within unconstrained x3-term fitting

DRC	[FIT-1]	PAL spectra fitting parameters					$\tau_{av.}$, ns
		τ_1, ns	τ_2, ns	τ_3, ns	I_2, a.u.	I_3, a.u.	
ESTA-3 – 0	0.01	0.202	0.501	2.030	0.43	0.075	**0.468**
ESTA-3 – 60	0.01	0.211	0.529	1.768	0.39	0.080	**0.460**
Changes, abs.		+0.009	+0.028	-0.262	-0.04	+0.005	**-0.008**
Changes, %		**+4.5**	**+5.6**	**-12.9**	**-9.3**	**+6.7**	**-1.7**

PAL spectra parameters for DRC Charisma and Dipol within unconstrained x3-term fitting

DRC	[FIT-1]	PAL spectra fitting parameters					$\tau_{av.}$, ns
		τ_1, ns	τ_2, ns	τ_3, ns	I_2, a.u.	I_3, a.u.	
Charisma-0	0.020	0.179	0.447	1.946	0.540	0.092	**0.486**
Charisma-60	0.008	0.158	0.415	1.560	0.560	0.110	**0.458**
Changes, abs.		-0.021	-0.032	-0.386	+0.020	+0.018	**-0.028**
Changes, %		-11.7	-7.2	-19.8	+3.7	+19.6	**-5.8**
Dipol-0	0.038	0.178	0.444	1.978	0.510	0.085	**0.466**
Dipol-60	0.034	0.155	0.403	1.601	0.560	0.103	**0.442**
Changes, abs.		-0.023	-0.041	-0.377	+0.050	+0.018	**-0.024**
Changes, %		-12.9	-9.2	-19.1	+11.7	+21.2	**-5.1**
RC (abs), %		0.91	0.78	1.02	1.80	1.00	**1.17**
RC (%), %		**0.91**	**0.78**	**1.04**	**0.32**	**0.92**	**1.14**

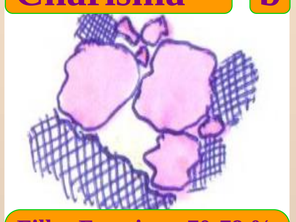
PAL trapping modes for light-cured DRC Charisma® (weight filler loading fraction WFLF = ~78 %), Dipol® (WFLF = ~72 %) and ESTA-3® (WFLF = ~79.5 %) within **x3-x2-CDA:**

DRC (volumetric shrinkage)	$\Delta\tau_{av.}/\tau_{av.}$	I component		II component		Positron Trapping modes				
	%	τ_n, ns	I_n, a.u.	τ_{int}, ns	I_{int}, a.u.	τ_{av}, ns	τ_b^{NP}, ns	κ_d, ns^{-1}	$\tau_{int} - \tau_b^{NP}$, a.u	τ_{int}/τ_b^{NP}, a.u
Charisma (2.9 %)	**-5.8**	0.409	-0.027	**0.656**	-0.086	0.597	0.573	0.70	0.083	1.14
Dipol (2.2 %)	**-5.1**	0.542	-0.018	**0.768**	-0.056	0.713	0.698	0.41	0.070	1.10
ESTA (1.5 %)	**-1.7**	0.149	-0.083	**0.342**	-0.069	0.236	0.200	1.72	0.142	1.71

ESTA-3® **a**

Filler Fraction ~80 %
Dense $\tau_b \rightarrow$ 0.2 ns
Small $\tau_{int} \rightarrow$ 0.3-0.4 ns

Charisma® **b**



Filler Fraction ~70-78 %
Loose $\tau_b \rightarrow$ 0.5-0.8 ns
Large $\tau_{int} \rightarrow$ 0.7-0.9 ns

Dipol® **c**

Filler Fraction ~70-78 %
Loose $\tau_b \rightarrow$ 0.5-0.8 ns
Large $\tau_{int} \rightarrow$ 0.7-0.9 ns

d

Filler Fraction < 70 %
Very loose $\tau_b \rightarrow$ ~1 ns
Large $\tau_{int} \rightarrow$ ~1 ns

Schematic illustration of inner structural channels inhibiting electron-positron annihilation in photopolymerized DRC due to positron traps in different environment (filler particles are reddish-color depicted, polymer matrix is cross-dashed):
(a) – e^+-trap in preferential environment of inorganic filler particles (high monolithization)
(b) – e^+-trap in mixed filler-polymer environment at lower filler content (medium monolithization)
(c) – e^+-trap in mixed filler-polymer environment at higher filler content (medium monolithization)
(d) – e^+-trap in preferential environment of polymer matrix (low monolithization)

Conclusions:

The annihilation process in the studied dental restorative (DR) nanocomposites is identified as mixed positron-Ps trapping, where o-Ps decaying is caused entirely by free-volume holes in the polymer matrix, and second component is defined mainly by interfacial free-volume holes between filler particles and surrounding polymer. The most adequate model-independent estimation of photopolymerization volumetric shrinkage in DR nanocomposites can be done using the averaged positron annihilation lifetime (the centrum mass of a whole positron annihilation spectrum). Partially-constrained x4-term analysis of the PAL spectra is less efficient giving greater scatter of variance with an additional artifact of fixed shortest lifetime allowing unresolved mixing in the second component. Meaningful phenomenological description of transformations in o-Ps-decaying and positron-trapping sites under light curing, which occurs more efficient in Charisma® than in Dipol® or ESTA nanocomposites, can be developed at the basis of semiempirical model exploring x3-x2-CDA (x3-x2-coupling decomposition algorithm).