Nanostructure of Amber Observed by Positronium Probes

R. Idczak[a,*], M. Sachanbiński[b], J. Chojcan[a] and R. Konieczny[a]
[a]Institute of Experimental Physics, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland
[b]College of Handicraft and Management, pl. św. Macieja 21, 50-244 Wrocław, Poland

(Received November 9, 2014; in final form May 6, 2015)

The nanostructure of several non-crystalline amber samples of different origin was investigated with positronium atoms. It was found that the volumes of the pores observed by positronium atoms are relatively small, not greater than about 0.25 nm^3 for all studied samples. Moreover, the obtained data show that the nano-porous structure of amber may be associated with its age.

DOI: 10.12693/APhysPolA.128.64
PACS: 78.70.Bj, 91.60.Np, 81.05.Lg

1. Introduction

The term "amber" is mostly regarded as a collective term for a very complex organic polymer/copolymer materials formed from plants resins via a fossilization process by crosslinking of the original organic resin by free radical polymerization [1–3]. Moreover, the chemical composition and structure of the amber changes with time owing to the aging or fossilization process. Due to natural beauty, physical and chemical properties as well as presence of ancient plants and insects trapped inside the amber, this type of materials is widely used in jewellery, pharmaceuticals, oil varnish, archaeology, geology, and glass physics [3]. Thanks to that they are intensively studied with various techniques in order to classifying them with respect to their age and geographic origin. These questions become more and more important since false amber pieces appear on the market in increasing amounts. Such ambers are produced from ground amber scraps or even synthetic resins, often with interesting inclusions of a recent plants and small animals [2]. One of the characteristic features of amber is its relatively high nano-porosity which can be investigated by several techniques among which a family of positron annihilation methods belongs to really effective tools [4, 5]. The positron methods are usually very fruitful even in the case of complex, porous substances because some of these components in a positron annihilation spectrum which can be relatively easily extracted from the whole spectrum measured, are determined mainly by the size and concentration of the empty spaces occupied by positronium atoms (Ps — the electron–positron bound state) before their decay. In particular these really useful spectrum components are the long-lived *ortho*-Ps ones in the positron annihilation lifetime spectra. The mean lifetime of the long-lived component is determined by the size of the positronium traps whereas the intensity of the component is related to the concentration of the traps. From investigations concerning porous media [6, 7] one can conclude that positron annihilation lifetime spectroscopy (PALS) can be used to investigations of the pore sizes up to about 100 nm. Finally, it is worth noting that the one of the most important advantage of PALS is its non-destructive nature. In this paper PALS was applied to check if porous structure of amber observed with positronium atoms can be useful for the classification purposes.

2. Experimental and results

The measurement were carried out for eight dissimilar samples of ambers originating from Poland (succinite), Russia (succinite), Czech Republic (valchovite), Borneo and Dominican Republic. The age of valchovite is 90–80 Ma (million years), succinite — 50–40 Ma, Dominican amber — about 20 Ma and amber from Borneo — about 17 Ma [5, 8–10].

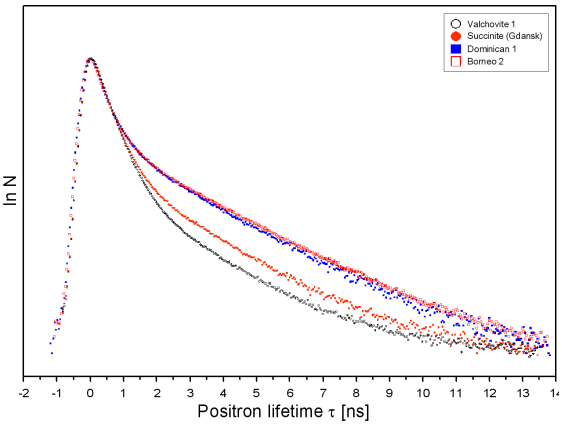

Fig. 1. Positron annihilation lifetime spectra for ambers.

The room temperature PALS spectra were collected by means of a conventional fast-timing apparatus with plastic scintillators, constant fraction differential discriminators (Ortec 583 Model), a time-to-pulse-height converter (Ortec 457 Model) and a multichannel analyser data buffer (Ortec 919 Model). The full width at half

*corresponding author; e-mail: ridczak@ifd.uni.wroc.pl

maximum (FWHM) of the time resolution function of the spectrometer is about 310 ps. As the source of positrons the ^{22}Na isotope of the activity of the order of 10^4 Bq was used. It was sandwiched between two pieces of the same studied material. Spectra were recorded in the time range 0–45 ns making use of 860 channels of the multichannel analyser. The total number of counts for one lifetime spectrum was at least 4×10^6. Some of the measured spectra are shown in Fig. 1.

The obtained positron lifetime data were analysed with the LT computer program [11], in terms of two three-component models. The first one is a set of free discrete components with different mean lifetimes τ and intensities I. The second one assumes (1) the intensity ratio of annihilating *para*- and *ortho*-positronium of 1:3, (2) lifetime of annihilating *para*-positronium, τ_1, of 125 ps, (3) the presence of the log–normal distribution for both, the mean lifetimes τ_2 corresponding to free annihilation of positrons and the mean lifetimes τ_3 related to annihilation of *ortho*-positrons by "pick off". In the analysed spectrum this corresponds to components with mean value $\langle\tau_2\rangle$ and dispersion value σ_2 as well as mean value $\langle\tau_3\rangle$ and dispersion value σ_3, respectively. The second spectrum model consists of the two components with dispersions because one could expect that the natural materials under investigation are not homogeneous ones as well as the atomic-scale empty spaces existing in them are of different sizes. The fitted parameters of the models are presented in Tables I and II.

TABLE I

The best-fit parameters of the model I (discrete three components).

Sample	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	R [nm]
valchovite 1	0.38310(87)	73.75(37)	1.7422(65)	8.238(70)	0.261(1)
valchovite 2	0.4052(32)	45.41(66)	1.7576(88)	9.08(14)	0.262(1)
succinite from Gdansk	0.3819(17)	65.62(62)	1.8267(45)	13.79(17)	0.268(1)
succinite from Kaliningrad	0.4313(44)	33.33(55)	1.8186(49)	18.39(21)	0.268(1)
Dominican amber 1	0.527(25)	22.3(1.4)	1.957(13)	27.03(78)	0.281(1)
Dominican amber 2	0.542(20)	21.6(1.1)	2.0059(74)	26.28(57)	0.285(1)
amber from Borneo 1	0.3942(19)	62.93(57)	1.9956(60)	17.20(20)	0.284(1)
amber from Borneo 2	0.4071(24)	47.18(43)	2.0793(34)	29.57(26)	0.292(1)

TABLE II

The best-fit parameters of the model II (one discrete and two complex components).

Sample	$\langle\tau_2\rangle$ [ns]	σ_2 [ns]	$\langle\tau_3\rangle$ [ns]	σ_3 [ns]	$I_1 + I_3$ [%]	$\langle R\rangle$ [nm]
valchovite 1	0.3544(16)	0.0635(50)	1.568(55)	0.565(56)	13.75(48)	0.241(6)
valchovite 2	0.3528(24)	0.0929(60)	1.709(59)	0.592(60)	16.00(55)	0.257(6)
succinite from Gdansk	0.3494(25)	0.0793(65)	1.756(46)	0.429(56)	20.10(50)	0.261(5)
succinite from Kaliningrad	0.3461(22)	0.0767(60)	1.823(22)	0.487(25)	30.22(31)	0.268(2)
Dominican amber 1	0.3516(71)	0.092(18)	1.856(40)	0.368(51)	42.02(77)	0.271(4)
Dominican amber 2	0.3528(56)	0.111(13)	1.914(35)	0.364(46)	40.33(63)	0.277(3)
amber from Borneo 1	0.3626(19)	0.0758(56)	1.932(29)	0.429(38)	24.72(32)	0.279(3)
amber from Borneo 2	0.3649(31)	0.1044(77)	2.045(20)	0.355(30)	40.87(55)	0.289(2)

On the basis of the Tao–Eldrup model, the relationship between the lifetime τ_3 of an *ortho*-positronium atom and the radius R of the spherical empty space trapping the atom before its decay could be described by the following formula [12, 13]:

$$\tau_3[\text{ns}] = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1}, \qquad (1)$$

where $R_0 = R + \Delta R$, and $\Delta R = 0.1656$ nm. The R and $\langle R\rangle$ values computed for the determined τ_3 (model I) and $\langle\tau_3\rangle$ (model II) ones with formula (1) are given in Tables I and II. In case of the spectra analysis, based on model II, the formula (1) was used also to calculate the normalised distributions $g(R)$, $y(V)$ of radius and volume of the empty spaces "seen" by positronium atoms in the studied materials [14]. It was done on the basis of the obtained log–normal distribution of τ_3 values, described by the $\langle\tau_3\rangle$ and σ_3 parameters. Results of the calculation are presented in Figs. 2 and 3 where the area under each distribution $g(R)$, $y(V)$ is the same. From the findings it follows that the concentration of nanopores as well as their radius (volume) decreases with the age of an amber

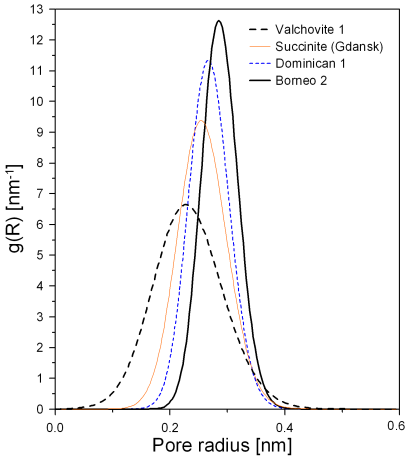

Fig. 2. Normalised radius distributions of empty spaces in samples of amber.

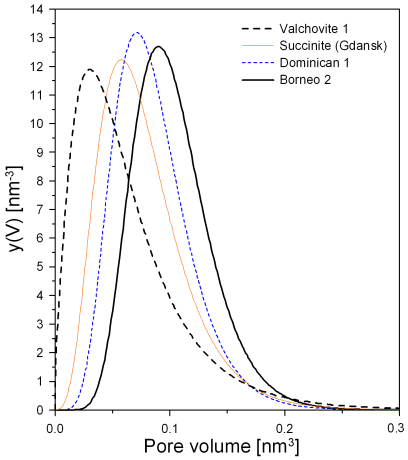

Fig. 3. Normalised volume distributions of empty spaces in samples of amber.

sample or porosity of the sample is related to the duration of the natural fossilization process going inside it. Such conclusion can be reached if it is noticed that studied valchovites are about twice older than succinites under consideration and about four times older than Dominican and Borneo ambers. Moravian valchovites were formed in Upper Cretaceous (90–80 Ma) whereas studied succinites were created in Late Eocene (50–40 Ma). The Dominican and Borneo ambers were formed during the late Early Miocene through early Middle Miocene (15–20 Ma).

3. Conclusions

The presented results provide a sufficient evidence that the non-destructive PALS is a very useful tool to the study of nanoporosity of ambers. It was found that the volumes of the pores observed by positronium atoms are relatively small, not greater than about 0.25 nm^3 for all studied samples. Moreover, the nanoporous structure of amber may be associated with its age. In particular, the concentration of nanopores as well as their radius (volume) determined by the PALS spectra analysis allow to distinguish between three groups of studied samples of amber — the oldest valchovites, two times younger succinites and the youngest Dominican and Borneo ambers. These observations speak in favour of the suggestion that the porous structure of the amber changes with time due to the aging or fossilization process [3, 9]. Taking the above into account it seems that PALS should be a good tool for age classification of ambers.

Acknowledgments

This work was supported by the University of Wrocław under the grant 1010/S/IFD.

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