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The Effect of Curing Light Intensity on Free Volume Size in Some Dental Composites

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A – research concept and design; **B** – collection and/or assembly of data; **C** – data analysis and interpretation; **D** – writing the article; **E** – critical revision of the article; **F** – final approval of the article

Abstract

Background. Dental composite resins – reinforced polymers – are types of synthetic resins that are used in dentistry as restorative material or adhesives. The effect of curing-light intensity on free volume sizes of 4 commercial dental composites has been studied by means of the well-known positron annihilation lifetime spectroscopy technique.
Objectives. The aim of the study was to compare the photosensitivity of 4 commercial dimethacrylate-based dental composites.
Material and Methods. Positron lifetime spectra were collected using a slow-fast coincidence lifetime spectrometer with a time resolution of 365 ps. The positron source was a ~20 μCi ^{22}Na beta emitter between two 7 μm thick stainless steel foils. The positron source was sandwiched between two identical samples under investigation. The 1st group of samples was polymerized by a 20-second photo-exposure, and the 2nd group of samples was irradiated by the blue curing light for 40 s. The positron annihilation lifetime spectrums were separated into components using the PAScual Positron Annihilation Spectroscopy data analysis program.
Results. The results showed that the lifetime component associated with free volumes differed in the different composites and depended on the irradiation time. The results indicated that the Coltene composite has higher photosensitivity than the other samples; the Denfil composite exhibited the lowest photosensitivity of the 4.
Conclusions. The appropriate light-curing intensity depends on the thickness of the composite, which in turn is proportional to the depth of the hole in the tooth undergoing repair **(Polim. Med. 2016, 46, 2, 129–133).**

Key words: free volumes, positron annihilation lifetime spectroscopy, dental composites, dimethacrylate resins.

Composite biomaterial is defined as a solid that contains 2 or more distinct constituent materials or phases when considered at a greater than atomic scale. Dental composite resins – reinforced polymers – are synthetic resins used as restorative material or adhesives in dentistry [1]. Resin composites have 4 main components: an organic polymer matrix, inorganic filler particle, a coupling agent and an initiator-accelerator system [1]. Today, a cross-linked matrix of dimethacrylate monomers is the organic polymer matrix in most commercial composites. Sakaguchi and Powers noted that "although these monomers can provide an optimum of optical, mechanical, and clinical properties, they are rather viscous and have to be mixed with low molecular-weight diluents monomers [1, 2]. The dispersed inorganic filler particles may consist of 1 or more inorganic materials such as finely ground quartz or glass, ceramics, micro-fine silica, or, more recently, nanoparticles" [1]. The coupling agent – a molecule with silane groups at one end and methacrylate groups at the other end – forms a link between organic and inorganic materials. Finally, the initiator-accelerator system is polymerization, which can be triggered by light- and chemical-curing [1–4]. However, depending on the material and structure, mechanical properties such as strength, resistance to temperature and antibacterial properties of the dental polymers are important [5]. The physical and chemical properties of polymeric materials, such as glass transition temperature, viscosity and toughness, are affected by the free volume holes – areas of zero electron-density – formed

during the polymerization process [6]. Local free volume holes occur due to irregular molecular packing in the materials. Positron annihilation lifetime spectroscopy (PALS), a non-destructive technique, measures the time interval between the arrival of a positron into a medium and its annihilation. The positron is a nuclear probe to investigate free volume in polymers [6–12]. As Mostafa et al. noted, "When a positron is injected into polymers, it interacts with molecules by an inelastic collision process leading to their ionization and excitation" [9]. This is the so-called thermalization process of the positron. A thermalized positron may be annihilated by an electron and emit two ~511 keV gamma rays [10]. In polymeric materials that have relatively open structure, there is a chance for a positron to form a bound state with an electron during the thermalization process. The bound state is called positronium (Ps) [13, 14]. The formation probability and lifetime of Ps are very sensitive to the electron density surrounding Ps. The Ps has two spin states, called para-positronium (p-Ps), and ortho-positronium (o-Ps), which are related to antiparallel or parallel spins of the positron and electron, respectively. In a vacuum, p-Ps decays into 2 gamma quanta with a mean lifetime of 0.125 ns, while o-Ps decays into 3 photons with a lifetime of 142 ns [10]. In molecular solids, the lifetime of o-Ps is reduced to a few nanoseconds, due to a competitive process called pick-off annihilation, in which the positron is annihilated by a foreign electron from surrounding atoms with an opposite spin direction. In polymeric materials, o-Ps localizes in the spaces between and/or at the end of polymer chains (the free volume holes) [15].

Experimentally, one expects to have 4 distinct lifetime components in a typical lifetime spectrum: free positron annihilation, p-Ps annihilation lifetime, o-Ps annihilation in polymers, and o-Ps annihilation in free volume holes [10–15]. Each lifetime component has an associated intensity, corresponding to the fraction of the annihilations taking place with the respective lifetime [10–15]. O-Ps annihilation in free volumes provides information about the size and the density of the free volume holes. A similar analysis is presented by Kleczewska et al [5]. The results showed that together, the PALS technique and scanning electron microscope (SEM) analysis are a useful experimental method for determining the morphology of dental composites. Analyzing the time and intensity of o-Ps annihilation made it possible to differentiate composites that had been pre-selected on the basis of their different mechanical and tribiological properties. Analyzing the information provided by PALS on the size and concentration of free volumes in polymer matrix and in polymer-filler interphase, crosslink density could be estimated and the quality of polymer-filler interactions could be compared [5].

In 2011 Pfeifer et al. reported that adding up to 40 mol% triethylene glycol dimethacrylate (TEGDMA) to bisphenol A diglycidyl dimethacrylate (BisGMA) increases the volumetric shrinkage of the resin. When this composition (BisGMA/TEGDMA 60–40 mol%) is light-cured for increasing periods of time (from 10 to 600 s), free volume decreases and volumetric shrinkage increases in a linear relationship with conversion [17].

In 2014 a study was done by Filipecki et al. to determine the dimensions of free volume holes in Dipol acrylic dental material by means of the PALS technique. Their study indicated that the long-lifetime components are related to the o-Ps trapped by free volume gaps in the research material. The research, repeated after 2 years, showed that the emergence of free volume holes is related to the degradation of primary holes, which may be associated with the aging process of the materials (stored at room temperature and in a dry place) [18].

The present study was conducted to compare the photosensitivity of the 4 commercial dental composites most commonly used in Iran. All 4 are dimethacrylate-based composites.

Material and Methods

In this research, 4 kinds of commercial dental composites were investigated. All 4 of the composites utilize bisphenolglycidyl methacrylate (Bis-GMA) monomer. Bis-GMA has a very high viscosity at room temperature, due to the hydrogen bonding interactions that occur between the hydrogen groups on the monomer molecules. Therefore, Bis-GMA must be diluted with a more fluid resin, such as triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA), ethoxylated bisphenol-A dimethacrylate (BisEMA) or decandiol dimethacrylate (DDMA). Fillers based on silicas or silicates comprise the denser polymeric regions of the samples [19]. The labeling of the samples as well as their technical details are shown in Table 1. All of the samples (2 mm thick) were irradiated for 20 s and 40 s by a tungsten halogen curing-light source, which provides a blue light 400–500 nm in wavelength with an intensity of ~500 mW/cm^2.

The source of the positron was a ^{22}Na radioisotope with activity of ~20 μCi surrounded by two 7 μm thick steel foils and positioned between two identical samples. The 1.28 MeV birth gamma ray and the 511 keV annihilation gamma ray can be detected by 2 fast plastic scintillator detectors. The time difference between the detection of these 2 gamma rays was designated as the positron lifetime and was recorded by a fast-slow positron lifetime spectroscopy setup. The time resolution of the fast-slow positron lifetime spectroscopy setup was about 365 ps, which was the full width at half maximum (FWHM) of the Gaussian distribution of the time difference between the detection of the two gamma rays of a Co60 radioisotope. The experimental run time for

Table 1. The samples used in this study

Label of sample	Sample	Manufacture	Matrix (wt%)	Filler (wt%)	Average filler particle size (μm)
1	Coltene	Coltene/ /Whaledent AG	(Bis-GMA+TEGDMA +Bis-EMA) (20)	Silicate glass (80)	0.6
2	Filtek Z250	3M-ESPE	(Bis-GMA+UDMA +Bis-EMA) (20)	Zirconia/Silica (80)	1.7
3	DenFil™	Vericom	(Bis-GMA+ TEGDMA) (20)	(Barium AliuminoSilicate- + Fumed Silica) (80)	< 1
					0.04
4	Heliomolar	Ivoclar/ Vivadent	(Bis-GMA+UDMA) (19) DDMA (3)	Silicon dioxide (78)	< 1

Table 2. Results of PALS analysis of the dental composites

Sample	Radiation time (s)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)
Coltene	20	0.368 ± 0.005	47.3 ± 2.7	1.092 ± 0.08	27.9 ± 4.6	2.362 ± 0.18	14.8 ± 7.3
	40	0.359 ± 0.007	48.3 ± 2.3	0.969 ± 0.16	20.6 ± 3.4	1.947 ± 0.14	21.1 ± 5.1
Filtek Z250	20	0.369 ± 0.005	55.9 ± 1.4	1.166 ± 0.23	16.7 ± 5.5	2.199 ± 0.25	17.4 ± 6.6
	40	0.356 ± 0.005	56.6 ± 1.5	1.139 ± 0.27	15.6 ± 6.1	2.161 ± 0.27	17.8 ± 7.3
Denfil	20	0.383 ± 0.008	44.5 ± 2.0	1.121 ± 0.16	28.4 ± 6.4	2.071 ± 0.27	17.1 ± 8.0
	40	0.391 ± 0.009	42.1 ± 2.1	1.130 ± 0.15	31.4 ± 7.1	2.064 ± 0.30	16.4 ± 8.8
Helimolar	20	0.361 ± 00.017	33.0 ± 1.9	1.069 ± 0.26	19.0 ± 7.3	1.965 ± 0.12	37.9 ± 8.8
	40	0.351 ± 00.014	35.8 ± 1.6	1.172 ± 0.38	18.7 ± 5.3	1.927 ± 0.20	35.4 ± 6.3

each sample was about 24 h in order to achieve ~3×10^6 counts. The resulting lifetime spectra were analyzed using the PAScual Positron Annihilation Spectroscopy data analysis program. Four lifetime components were fitted for every sample, as shown in Table 2. Positron annihilation inside the source capsule was assumed to be constant (τ_1 = 186 ps) in all spectra, with an annihilation intensity of I_1 = 10 percent. The other 3 lifetime components are associated with free positron annihilation (τ_2, I_2), o-Ps annihilation in bulk (τ_3, I_3) and o-Ps annihilation in free volumes (τ_4, I_4). The last component can be related to the mean radii of free volumes by using the Tao-Eldrup formula [20, 21]:

$$\tau_4 = 0.5 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1},$$

where $R_0 = R + \Delta R$ and $\Delta R = 0.166$ nm is the fitted empirical electron layer thickness. Variations in the free volume sizes in the different samples were investigated as well.

Results and Discussion

The positron lifetime components and their annihilation intensities extracted by the PAScual program are listed in Table 2. The free positron annihilation lifetime, τ_2, is almost the same for all samples but has different annihilation intensities in different composites. The differences between the annihilation intensities are due to the differences in molecular structure and consequently different chances for positron free annihilation. The positronium lifetime in the denser polymeric region of composites is τ_3, and it differs in different structures [5]. Filtek Z250 has the largest τ_3, which is consistent with its large average filler particle size (1.7 μm). The last component, τ_4, is related to o-Ps annihilation in free volume holes, and it varies from 1927 to 2362 ps; this corresponds to different hole sizes and is dependent on the light-curing time of the polymers. As the curing time increased, τ_4, and therefore free volume sizes, decreased. DenFil is a light-cured restorative hybrid composite resin designed for minimizing polymerization shrinkage by using a high load of inorganic fillers. DenFil has the least photosensitivity of the 4 composites in the study.

As Table 2 shows, the annihilation intensities of the Heliomolar samples (sample 4) are slightly different from the others. A greater proportion of Ps annihilation (I_3 and I_4) and therefore a lower value of I_2 suggests the existence of more open structures in the Heliomolar samples with more hole concentrations in the polymer matrix. This might be explained by the difference in the composite resins used as diluents in the polymer matrix: The DDMA in the Heliomolar matrix

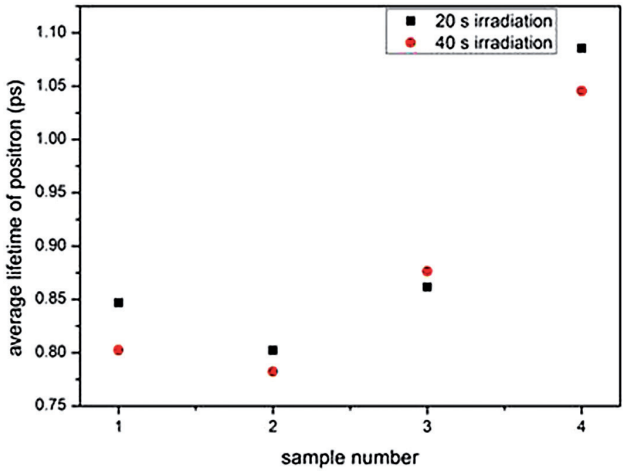

Fig. 1. The average o-Ps annihilation lifetime of the samples are plotted. The circles show 40 s irradiation times and the squares show 20 s irradiation times

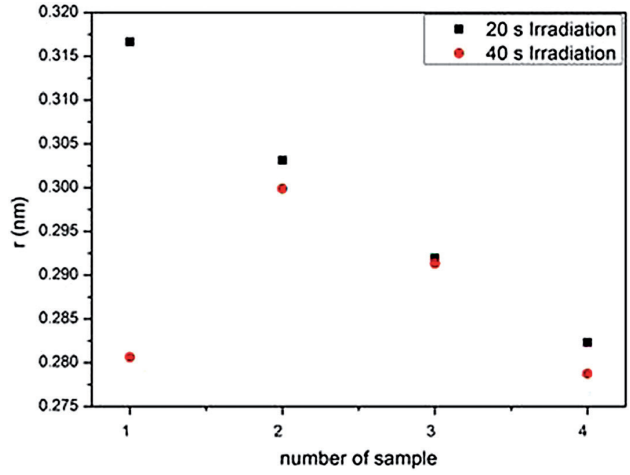

Fig. 2. The mean radii of the free volume holes of the samples were plotted using the Tao-Eldrup model. The circles show 40 s irradiation times and the squares show 20 s irradiation times

has a lower concentration of double bonds than the other matrix resins.

The average o-Ps annihilation lifetime is plotted in Figure 1. The more open structure of the Heliomolar samples can also be seen in Figure 1. The lowest average lifetime value in Figure 1 is associated with Filtek Z250 (sample 2), indicating its compact structure.

The mean radii of the free volume holes were calculated using the Tao-Eldrup model and are plotted in Figure 2. As noted earlier, the free volume size decreased as the curing time increased. Coltene polymer (sample 1) is more photosensitive than the other samples, while the least photosensitivity is observed in Denfil (sample 3). In clinical use, care has to be taken over the depth of cure with light-activated composites. Light is attenuated as it passes through the composite, which means that there is less light to activate polymerization deep within the material. Dentists are therefore advised to pay more attention to the irradiation time when they are using Coltene.

Conclusions

The positron annihilation lifetime spectroscopy method provides important information on the size and concentration of free volumes in polymers and can be used for dental composite analyses. The light-curing intensity significantly affects free volume size, and therefore affects the physical and biological properties of the composite. The appropriate light-curing intensity depends on the thickness of the composite, which in turn is proportional to the depth of the hole in the tooth undergoing repair.

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