Indentation Size Effect in Autopolymerized and Microwave Post Treated Poly(methyl methacrylate) Denture Reline Resins

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Abstract: Various hardness test methods have been used to determine the polymer materials resistance to local plastic deformation in scientific community. The most commonly used method is Vickers microindentation. However, it is of crucial importance to fully understand the influence of the indentation load, since its value influences the obtained result. In this paper, two commercial PMMA dental reline resins in untreated and microwave treated condition have been tested. Vickers microindentation with different loads has been used to assess the materials microhardness: 30, 50, 70, 200, 300 and 500 gf. One way ANOVA statistical analysis followed by Tukey's test was used to determine the statistical differences between various groups. Finally, three models that quantitatively describe load-dependence of the measured Vickers hardness values were used: Meyer's law, PSR and modified PSR model. It was found that the optimal load for determining PMMA dental reline resins in both untreated and microwave treated conditions is 300 gf. This value may be regarded as loading independent hardness, or H_{LIH}. At lower loads, a more or less pronounced indentation size effect was noticed, while at higher loads, forked crack development leads to an unreliable indentation diagonal measurement and therefore an unreliable microhardness result. The most adequate load-dependence model was found to be modified PSR, that takes into consideration the surface stresses induced by specimen preparation by grinding.

Keywords: Vickers microhardness; indentation size effect; poly(methyl methacrylate); microwave irradiation

1 Introduction

Microhardness has been widely used as an indicator of the materials mechanical properties, crucial for determining the materials performance. The most common hardness tests comprise of indentation techniques, which provide both materials resistance to local plastic deformation and a correlation to flexural and compressive strengths [1]. Although Vickers hardness is considered as the most widely used method for testing of denture materials of acrylic type, other methods have been used in scientific community. The Knoop hardness has been successfully used as an alternative to Vickers test, with an advantage of a less likely cracking in brittle materials. However, this method penetrates less into the specimen surface and thus, it is more sensitive to surface texture. Furthermore, the successful and accurate Knoop test indentations require larger specimens to be used [1]. Other researchers even used methods that are predominantly oriented towards hardness testing of metallic materials. Azzarri et.al. [2] used Rockwell P method (1/4 inch steel ball indenter and a load of 150 kgf), while Idol and Lehman [3] reported the application of Brinell hardness test on acrylic and other polymer materials.

For testing of acrylic resins, the lack of an agreement on the test method and testing parameters such as load prevents straightforward comparison of the results obtained in different studies. Another problem in obtaining comparable results is the Indentation size effect (ISE) which represents a phenomenon that may be briefly described as an indentation-depth-dependent hardness [4]. By the application of different loads, different hardness values are obtained, usually a lower indentation depth results in an increased hardness [5]. The ISE was observed in ceramic, metallic and polymer materials. While well understood and investigated for metals, which is not the case with polymers [6]. In metals, the ISE effect may be related to plastic deformation and dislocation movement and the notion of geometrically necessary dislocations increasing flow stress and hardness values [7, 8]. At indentation depths smaller than 0.2 μm, the roughness of the surface and other surface effects may influence the deformation mechanisms and hardness obtained [9, 10]. However, the ISE effect observed in polymers cannot be explained by dislocation theory. In turn, different theories developed to explain the ISE effect in polymers. Some researchers attributed the ISE to structural differences in depth [11, 12], while others linked ISE to the elastic strain and elastic deformation energy that is proportionally higher in polymers compared to plastic strain and deformation energy in metals [13, 14], related to polymer nematic-like molecular structure. In this model, polymer chains possess finite stiffness, which can be considered as a system consisting of interacting rodlike segments [15].

The aim of this study was to determine the ISE in Poly(methyl methacrylate) (PMMA), which are the most widely used types of materials for providing better retention of removable protheses in cases of alveolar resorption, as well as for

denture reparation in case of crack or fracture. Denture reline resins have a lower mechanical properties compared to denture resins, since the components (powder and liquid) are manually mixed together for a limited period of time, when polymerization process is started. Such material possesses a higher amount of monomer, which acts as empty space, or a microvoid, which, under load may propagate and cause fracture. Furthermore, the ISE of microwave treated dental reline resins, which is a common method for improving mechanical properties by decreasing the amount of monomer, were tested [16, 17].

2   Materials and Methods

Two autopolymerizing denture materials; Simgal-R (Galenika, Serbia) and Akrilat-R (ADA Dental Products/Dentaurum, Serbia/Germany) were tested in this study. Materials consisted of powder and liquid, which, when mixed, the polymerization process is initiated. Simgal-R and Akrilat-R powder consist of PMMA, benzoyl peroxide and inorganic pigments, while the liquid component contains the methylmetacrylate monomer and tertiary amine. Samples were prepared as advised by the manufacturer, with powder to liquid ratio of 2:1 in weight and subsequently cast in elastomer molds (Wirosil, Bego, Germany). After polymerization, a set of SiC papers (150, 400 and 1200 grit) were used to get the desired shape, dimensions and surface quality of the samples. Samples were of the cylindrical shape, 2 mm thick and 25 mm diameter. Two samples of each material were tested: control sample and a sample microwave after-treated with a power of 550 W during 4 min. Microwave aftertreatment was conducted in a microwave device with a turntable and output power of 800 W (Elin MW8020MG, Austria).

Microhardness measurements were made with two Vickers microhardness testing machines, used in two loading ranges: low (Zwick Z323, Germany) and high (Reichert Me-F, Austria). Low loads applied were 30, 50 and 70 gf, while high loads were 200, 300 and 500 gf. Vickers hardness number (VHN) was determined as an average of five indentations. VHN microhardness values were obtained by using a common formula:

$$HV = 1.8544 F/d^2 \tag{1}$$

Where 1.8544 is a constant geometrical factor for the Vickers pyramid, F is load [kgf] and d is indentation average diagonal [mm]. The data was compared by one way analysis of variance (ANOVA) followed by Tukey's test with the significance value set at 0.05.

3   Results

The results obtained by Vickers microhardness testing, as well as standard deviations and ANOVA statistical analysis are shown in Tables 1 and 2. Only the results obtained with 30, 50, 70, 200 and 300 gf are shown, due to forked crack development at the indentation tip that occurs when a load of 500 gf or more is applied for all tested materials, Fig. 1.

Figure 1

Vickers microhardness indentations obtained by the application of different loadings, from left to right: 500 gf, 300 gf, 200 gf and 70 gf. Indentation with 500 g load results in a cracking at indentation edge

In Table 1, mean microhardness results and standard deviations are shown. It can be seen that, as indentation load is increased, Vickers microhardness values decrease. This trend is obvious for both tested materials, Simgal-R and Akrilat-R. Furthermore, the same trend can be detected for microwave treated samples, but their microhardness values were higher, when the load independent hardness (H_{LIH}) is reached at applying 300 g load. By applying ANOVA one-way analysis, it can be seen that for untreated samples made of Simgal-R, all results obtained with 30, 50, 70 and 200 gf load are significantly different from the result obtained with 300 gf load. However, treated Simgal-R microhardness obtained with 70 and 200 g are not significantly different from the result obtained with 300 gf. Vickers microhardness testing of untreated and treated Akrilat-R revealed that the application of 70 and 200 gf load does not result in a significantly different results compared to the results obtained with 300 gf load. On the other hand, for values obtained with 500 gf load, all values have shown a statistically significant difference compared to the value obtained with 300 gf.

Table 1

Mean microhardness values and standard deviations given in parantheses

Load [gf]	Simgal-R untreated	Simgal-R treated	Akrilat-R untreated	Akrilat-R treated
30	22.25 (0.60)	22.18 (0.38)	22.25 (0.36)	26.81 (0.46)
50	21.95 (0.34)	20.92 (0.33)	21.22 (0.60)	24.50 (0.73)
70	19.66 (0.47)	19.96 (0.36)	20.28 (0.63)	23.22 (0.84)
200	18.16 (0.65)	19.88 (0.18)	18.92 (0.20)	21.51 (0.92)
300	17.27*(0.39)	19.70*(0.22)	18.21*(0.29)	20.43*(0.56)
500	20.65 (0.65)	22.38 (0.61)	22.54 (0.58)	23.85 (0.53)

∗ Values than may be considered as load independant hardness (H_{LIH})

Table 2

Statistical difference in relation to the result obtained with a load of 300 g of tested materials in relation to indentation load

Load [gf]	Simgal-R untreated	Simgal-R treated	Akrilat-R untreated	Akrilat-R treated
30	P<0.05	P<0.05	P<0.05	P<0.05
50	P<0.05	P<0.05	P<0.05	P<0.05
70	P<0.05	NS*	P<0.05	P<0.05
200	P<0.05	NS*	NS*	NS*
300	-	-	-	-
500	P<0.05	P<0.05	P<0.05	P<0.05

* No significance

For more convenience, indentation size effect is shown in Figs. 2 and 3 in the form of a diagram. A trend showing the drop of microhardness by applying a higher indentation load is shown. Furthermore, Simgal-R test results have shown that at relatively low loads, results of actually softer material (untreated Simgal R) may show higher microhardness compared to an actually harder material (treated Simgal-R), where $H_{(LIH\text{-}untreated\ Simgal)} < H_{(LIH\text{-}treated\ Simgal)}$.
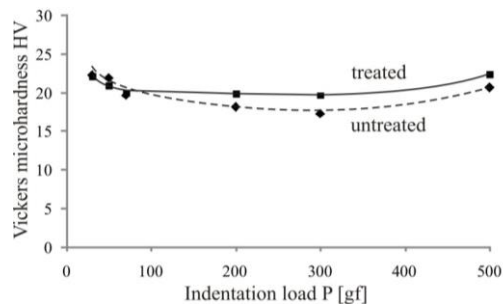

Figure 2

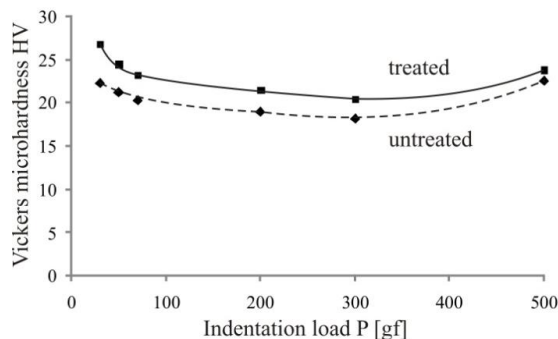Vickers microhardness in relation to indentation load for Simgal-R in untreated and treated condition

Figure 3

Vickers microhardness in relation to indentation load for Akrilat-R in untreated and treated condition

4   Discussion

Vickers hardness and microhardness consists of forcing a diamond pyramidal indenter into the prepared surface of the material being tested. After indenter removal, indentation diagonals are being measured by application of light microscope. Hardness value is calculated, basically as dividing indentation force by indentation area obtained from the indentation diagonals. In this study, four materials (PMMA denture reline resins) were tested, all of them showing an ISE, as well as the cracking phenomenon that occurs at higher indentation loads near the indentation edge.

By increasing indentation load, the apparent hardness of the material decreases, asymptotically reaching an apparently constant value. This value is the materials true hardness, or load independent hardness, H_{LIH}. Only this value may be used to assess and compare microhardnesses of two tested materials. If hardness obtained with a lower indentation load is used, relations between the obtained results may be misleading, or even worse, quite opposite to the relations between true hardness values (H_{LIH}). A typical example are the results obtained for Simgal-R in untreated and microwave treated conditions, where H_{LIH} of the treated sample is higher than that of the untreated, while at lower indentation loads of 30 and 50 gf, the apparent hardness of the untreated sample is higher compared to the treated one. This may be explained by the samples inhomogeneous structure, obtained after manual mixing and subsequent polymerization that resulted in 6.5% of unconverted monomer [16]. After microwave post – treatment, unconverted monomer in Simgal-R slightly decreased to 4.8% [16], which may have left sufficient degree of inhomogenity that influenced the microhardness results obtained with a low indentation loads. In this respect, polymer microhardness testing may be related to the hardness testing of cast iron, where Brinell method is applied. This method comprises of the indentation of a steel ball having a sufficiently large diameter of 5 or 10 mm to eliminate the influence of the low-hardness graphite present in the structure which is randomly distributed. By applying such a large indenter, a mean hardness is obtained, since a sufficient number of graphite particles is present in the indentation.

Another limiting factor is the cracking of the relatively brittle polymer such as PMMA when 500 gf or more indentation load is applied. Cracking occurs at indentation edge in form of forked cracks that limit the length of the diagonal, resulting in a considerable diagonal length difference. This effect influences the reliability of the obtained results, which, limits the indentation load to less than 500 gf.

When ISE and cracking effects are taken into consideration, Vickers microhardness optimal load for PMMA testing is 300 gf, the highest that does not lead to cracking in the specimen. Lower loads compared to 300 gf may in some experiments result in statistically insignificant difference compared to the results obtained with 300 gf, however, loads under 200 gf should be avoided.

The load-dependence of the measured Vickers hardness values can also be described quantitatively through the application of the classical Meyer's law:

$$P=Ad^n \tag{2}$$

where P is the indentation load and d is the resulting indentation size, that is, diagonal. The parameter A and n are values that can be derived directly from the curve fitting of the experimental data [18]. The Meyer's law parameters determined by the regression analyses are summarized in Table 3 and presented in Fig. 4, with 500 gf loading results omitted. The ISE is commonly related to the deviation of the n-value from two. For virtually all materials the power law exponent n is experimentally observed to be between 1 and 2, which indicated that lower indentation test loads result in higher apparent microhardness. ISE is more pronounced in specimens having the power law exponent n closer to 1 and vice versa. The results of n-exponent presented in Table 3 indicate that the most significant ISE is obtained in the case of untreated Simgal-R specimen ($n=1.796$), while the most non-significant ISE was obtained in the case of treated Simgal-R specimen ($n=1.914$). The correlation factors R^2 are consistent at 0.999 for all tested specimens.

Table 3

Regression analysis resuts of the experimental data according to Mayer's law

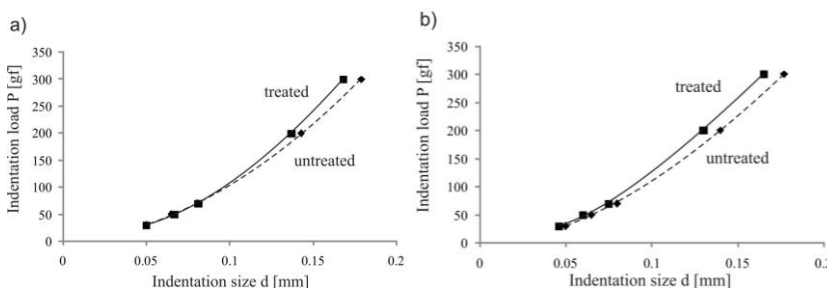|	A	$\log A$	n	Correlation factor (R^2)
Simgal-R untreated	8964.0	3.952	1.796	0.999
Simgal-R treated	6579.1	3.818	1.914	0.999
Akrilat-R untreated	7815.2	3.893	1.820	0.999
Akrilat-R treated	7080.1	3.850	1.805	0.999

Figure 4

Correlation between P and d according to Meyer's law (full line treated, dashed line untreated specimens): a) Simgal-R; b) Akrilat-R

An alternative analysis of ISE to the Meyer's law is proportional specimen resistance (PSR) model based on the following equation:

$$P=a_1 d+a_2 d^2 \tag{3}$$

S. Balos *et al.*
Indentation Size Effect in Autopolymerized and Microwave Post Treated
Poly(methyl methacrylate) Denture Reline Resins

where a_1 and a_2 are experimental constants. Eq. (2) describes the observed ISE by testing linearity between P/d and d. The results are summarized in Table 4 and Fig. 5. From Fig. 5 it is evident that in each system the data points show linearity with correlation factor (R^2) between 0.996 and 0.998.
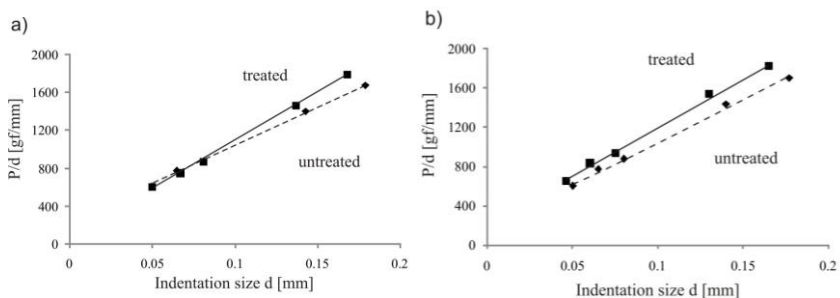

Figure 5

Correlation between P/d and d according to PSR model (full line treated, dashed line untreated specimens): a) Simgal-R; b) Akrilat-R

Table 4

Regression analysis resuts of the experimental data according to PSR model

	a_1	a_2	Correlation factor (R^2)
Simgal-R untreated	67.89	10172.31	0.998
Simgal-R treated	205.41	8264.21	0.998
Akrilat-R untreated	215.62	9868.14	0.996
Akrilat-R treated	189.60	8631.22	0.997

The modified PSR model proposed by Gong and Li [18] may be mathematically described as:

$$P=P_0+a_1d+a_2d^2 \tag{4}$$

where P_0 is experimental constant, while a_1 and a_2 have the same physical meaning as in the Eq. (3). This model was proposed by Gong and Li, who found that the surface of the specimen is not in stress free state, but rather exposed to the stress induced by, in this case, grinding, necessary for conducting microhardness test. The fit values of all parameters included in Eq. (4) are given in Table 5, while their graphical representation is presented in Fig. 6. The regression analysis returns correlation coefficients between 0.999 and 1. From Table 5, it can be seen that parameters P_0 and a_1 may have positive or negative values. In accordance to the work by Gong and co-workers [18], this phenomenon may be reasonably explained by the porosity of the materials examined. Indeed, the materials used were mixed manually, by a technician [19], where some porosity is very difficult to avoid, partially due to the limited amount of time before polymerization commences.

Table 5

Regression analysis resuts of the experimental data according to modified PSR model

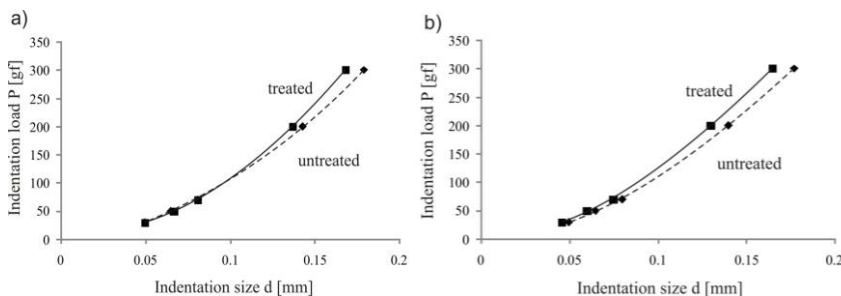|	P_0	a_1	a_2	Correlation factor (R^2)
Simgal-R untreated	8.45	-128.71	11108.11	1
Simgal-R treated	-5.54	330.40	7700.24	0.999
Akrilat-R untreated	-14.32	563.09	8178.31	0.999
Akrilat-R treated	-14.91	525.92	7107.10	0.999

Figure 6

Correlation between P and d according to modified PSR model (full line treated, dashed line untreated specimens): a) Simgal-R; b) Akrilat-R

Conclusion

In accordance to the presented results, some conclusions can be drawn:

- For testing of PMMA denture reline resins, untreated or microwave treated, optimal load is 300 gf.

- The loads lower than 300 gf result in an inconsistent statistical significance that may or may not give an adequate result. Loads lower than 200 gf are inadequate. Loads lower than 200 gf are inadequate, since the diagonal of the indentation is not sufficient to avoid materials imperfections such as unconverted monomer, which may influence the obtained result.

- At loads higher than 300 gf where forked cracks occur, the result can be regarded as unreliable and should be avoided.

- Before microhardness testing, a careful optimization of indentation load is needed to reveal the materials true hardness, or load independent hardness H_{LIH}. To determine this, conducting a pre-experiment is needed.

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