Study of PMMA Biopolymer Properties Treated by Microwave Energy

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The aim of this study was to test the hypothesis that microwave post-polymerization treatment influences the rise of hardness, flexural strength, impact strength and fracture toughness of autopolimerizing poly(methyl-methacrylate) by the decrease in residual monomer content. Specimens produced from a commercial acrylic denture reline resin were polymerized according to manufacturers instructions. Control group was left untreated, while other five were post irradiated in a microwave oven with different power and time settings, keeping the irradiation energy constant. Each group of samples was tested for mentioned mechanical properties. Enthalpies of polymerization were tested by differential scanning calorimetry (DSC), while the amount of residual monomer was determined using fourier transform infra-red spectroscopy (FTIR). Microwave post-irradiation resulted in increase of all tested mechanical properties. The highest mecanical properties were obtained with maximum irradiation power, which was confirmed by the results of ANOVA statistical analysis. It has been found that residual monomer content strongly influences the benefits in all tested mechanical properties, increasing biocompatibility. These results have been confirmed by the results of Scanning electron microscope (SEM) fracture surface analisys.

Keywords: PMMA biopolymer, microwave post – irradiation, mechanical properties, residual monomer

Poly(methyl-methacrylate) (PMMA) has been used traditionally as a shatterproof replacement for glass. The main reason for this is its transparency, which results in a broad array of applications, some of which are aircraft canopies, protective goggles, automobile running lights, as well as construction panels, etc. However, PMMA has also been known as a biocompatible material, the most notable application being as a denture base material. A special type of this biopolymer, autopolymerizing PMMA denture reline resin, has been widely used to provide better retention of removable protheses in cases of alveolar resorption, as well as for denture reparation in case of crack or fracture [1]. On the other hand, mechanical strength of autopolymerizing PMMA is lower than that of heat-polymerized PMMA used for base denture [2], the main reason being higher unconverted monomer content in autopolymerizing resin, as reported by various authors [3,4]. Unconverted monomer acts as empty space, not unlike a microvoid, representing an initial crack causing stress concentration, weakening the material. Residual monomer content might be decreased by heat post-teatment, which can be achieved by immersion in hot water, in a similar way as with heat-polymerized denture base resins [5], as well as by microwave post-irradiation [6]. The influence of different power and time setings on flexural strength has been investigated [7], as well the influence on flexural and impact strength [8-11].

The purpose of this work is to investigate the effect of microwave irradiation parameters such as power and time on a broader array of mechanical propeties such as hardness, flexural strength, impact strength and fracture toughness on an autopolymerizing PMMA denture reline resin. The hypothesis is that microwave irradiation post - treatment causes the decrease in unconverted monomer, which acts as a microvoid. This might cause the decrease not only the hardness and flexural strength, but also impact strenght and fracture toughness, by causing crack initiation and developement.

The present work was carried out as a part of a continuing programme at the University of Novi Sad, to study the influence of microstructure, composition, and mechanical properties of polymer materials.

Experimental part

The material used in this study was a commercial acrylic denture reline resin (Simgal, Galenika, Belgrade, Serbia). It was supplied separately in powder and liquid, the first consisting of the polymer, benzoyl peroxide and inorganic pigments, while the second, the methylmetacrylate monomer and the tertiary amine. Benzoyl peroxide and tertiary amine initiate the radical polymerization process. Samples were prepared according to manufacturers intructions, with powder : liquid ratio of 2:1 in weight. Samples were cast in elastomer molds (Wirosil, Bego, Bremen, Germany).

After resin polymerization, with duration of 15 min, a set of silicone grit papers (150, 400 and 1200-grit) was used to get the desired shape and dimensions of the samples. The dimensions were verified by a Feinmesszeugfabrik (Suhl, Germany) micrometer, accurate to 0.01 mm at three locations. 30 specimens were used for each testing.

Samples were divided in six groups, of which the first was untreated, while the rest were irradiated in a microwave oven with a turntable (Elin MW8020MG with 800 W output power) at a frequency of 2450 MHz. Specimens were placed on the turntable and exposed to microwave irradiation directly. Power and time settings were: 150 W for 15 min (designated as 150/15), 250 W for 9 min (250/9), 350 W for 6.5 min (350/7), 450 W for 5 min (450/5) and 550 W for 4 min (550/4). The energy of microwave irradiation was kept constant at 135 KJ.

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Hardness measurement was performed on Vickers hardness instrument (Zwick Z323, Ulm, Germany), using 300 g (1.96 N) load, on 20x20x4 mm specimens. The hardness of each specimen was measured on five areas (5 mm from each specimen edge and in the center), resulting in 150 measurements for each set of specimens.

Flexural strength and fracture toughness were tested using a mechanical tensile testing machine (Toyoseiki AT-L-118B, Tokyo, Japan). Crosshead speed was kept constant at 50 mm/min for both tests. Flexural strength test was performed using 3-point bending test, with the distance between the supports of 40 mm. Specimens dimensions were 6x2.5x50 mm. Fracture toughness was performed by using 4-point bending test, with the distance between the supports of 20/40 mm, over and under the test bar, respectively. Specimen dimensions were 3x4x45 mm, with a notch cut at the longitudinal center of the beam. A preliminary U – notch was cut using SiC disc, while the final V-notch was cut manually with a commercial razor at the middle of the V-notch. Preliminary notch serves only as a guide for the following manual V-notching, which represents an initial crack. The depth of the V-notch was cca 1 mm. The measurement of the V-notch depth was performed on Leitz light microscope at a magnification of 100x. This method for determining fracture toughness is identical to SEVNB (single edge V-notch beam) described in [12]. Although this method is used for advanced ceramic materials, initial crack formed with a commercial razor can be also applied to brittle polymers [13 - 16] such as PMMA.

Impact strength was determined using the standard Charpy method (Zwick D-7900, Ulm, Germany), with instrument capacity of 15 J and 160 ° angle. Specimen dimensions were 6x4x50 mm, without notch, due to the brittle nature of PMMA.

All mechanical property values were statisticaly analyzed using a one-way analysis of variance (ANOVA), with the significance value of $P<0.05$.

Differential Scaning Calorimetry (DSC) analysis was performed on TA Instruments Q20 device. The analysis has been performed from 20 to 200°C. The scope was to detremine enthalpies of polymerization, which is proportional to residual monomer in the material. For a quantitative determination of residual monomer, Fourier Transform Infrared Specrtoscopy (FTIR) was used. In this analysis, carbonyl group (C=C), representing residual monomer of each specimen was detected on a Thermo Nicolet Nexus 670 FTIR spectrometer (Thermo Electron Corporation, Madison, WI, USA), equipped with a deuterated triglycine sulphate (DTGS) detector. Each spectrum was obtained by co-addition of 32 scans at 4-cm^{-1} resolution. All spectra were recorded at room temperature using standard instrument settings.

Fracture surfaces were examined by JEOL JSM-6460LV (JEOL Ltd., Tokyo, Japan) scanning electron microscope (SEM), operating at 20 kV. The specimens were coated with gold, using Balltec SCD-005 coating device.

Results and discussions

Hardness, flexural strength fracture toughness and impact strength results, their standard deviations and one-way analysis of variables (ANOVA) are shown in tables 1-4. It can be seen that all mechanical properties were improved after microwave irradiation process. However, although irradiation energy was kept constant, the effects of power settings on mechanical properties were diferrent. For more convinience, mechanical properties of treated and untreated samples is presented by charts, figure 1-4.

The highest hardness value was obtained for specimens 550/4, being 14 % higher than that of the untreated ones. The smallest hardness standard deviations were for specimens 350/4 and 450/5, table 1. Flexural strength values for irradiated samples had been similar, the only exception being 450/5, which performed an increase of 46 %. Other specimens shown an increase of 21 – 26 % over the untreated samples. Standard deviations were, similarly to impact strength, generally higher for treated samples, the only exception of 350/7, table 2. The highest fracture toughness value was for the sample 350/7, 23 % higher than the untreated sample, while standard deviations were similar for all tested specimens, table 3. The highest impact strength reached 69% increase over the untreated samples, but standard deviation of treated samples was also considerably increased, table 4. Furthermore, ANOVA statistical analysis has shown that only flexural strength of specimens 250/9 and fracture toughness of specimens 150/15 are not significantly higher than the values obtained with untreated specimens (tables 1 – 4).

DSC curves are shown in figure 5. It can be seen that polymerization peaks become less pronounced as microwave iradiation power decreases, regardless of time.

Table 1
HARDNESS, STANDARD DEVIATION AND P-VALUE OF ONE-WAY ANOVA SATISTICAL ANALYSIS

Specimen group	Hardness HV0.3 [daNmm^{-2}]	Standard deviation [daNmm^{-2}]	P-value
0	17.27	0.49	
150/15	18.67	0.46	0.04300
250/9	18.83	0.39	0.02400
350/7	18.80	0.22	0.01570
450/5	19.50	0.24	0.00455
550/4	19.70	0.65	0.01340

All P-values show significant difference between non-treated and treated samples (P<0.05).

Table 2
FLEXURAL STRENGTH, STANDARD DEVIATION AND P-VALUE OF ONE-WAY ANOVA SATISTICAL ANALYSIS

Specimen group	Flexural strength [MPa]	Standard deviation [MPa]	P-value
0	56.22	6.45	
150/15	70.22	8.40	0.03770
250/9	68.88	9.78	0.08520
350/7	70.84	5.91	0.02750
450/5	82.33	10.97	0.00763
550/5	73.29	8.95	0.03650

All P-values show significant difference between non-treated and treated samples, except for 250/9 (P<0.05).

Table 3
FRACTURE TOUGHNESS, STANDARD DEVIATION AND P-VALUE OF ONE-WAY ANOVA SATISTICAL ANALYSIS

Specimen group	Fracture toughness [MPam$^{-1/2}$]	Standard deviation [MPam$^{-1/2}$]	P-value
0	1.016	0.100	
150/15	1.081	0.070	0.32100
250/9	1.244	0.135	0.02670
350/7	1.250	0.122	0.01810
450/5	1.184	0.055	0.01910
550/4	1.218	0.090	0.01740

All P-values show significant difference between non-treated and treated samples, except for 150/15 (P<0.05).

Table 4
IMPACT STRENGTH, STANDARD DEVIATION AND P-VALUE OF ONE-WAY ANOVA SATISTICAL ANALYSIS

Specimen group	Impact strength [Jcm^{-2}]	Standard deviation [Jcm^{-2}]	P-value
0	0.340	0.019	
150/15	0.439	0.041	0.04300
250/9	0.438	0.041	0.02400
350/7	0.467	0.041	0.01570
450/5	0.525	0.075	0.00455
550/4	0.574	0.081	0.01340

All P-values show significant difference between non-treated and treated samples (P<0.05).

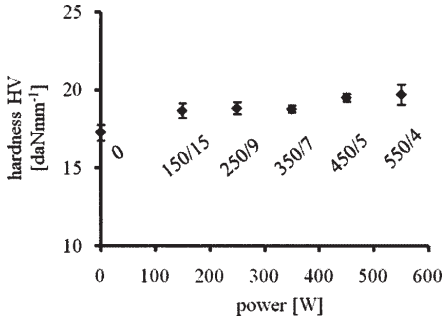

Fig. 1. Hardness of untreated and treated samples in relation to microwave irradiation power.

This is proved by enthalpies of polymerization, which are shown in table 5. They clearly indicate that the amount of monomer decreases.

FTIR analysis, shown that by applying microwave energy after polymerization process, carbonyl peaks become lower, indicating the decrease in residual methyl – methacrylate monomer content, figure 6, table 5.

If enthalpy of polymerization is plotted against methyl – methacrylate monomer content, a linear trendline may be

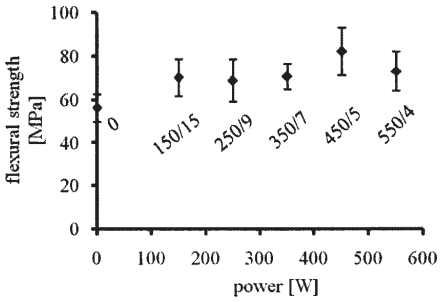

Fig. 2. Flexural strength of untreated and treated samples in relation to microwave irradiation power.

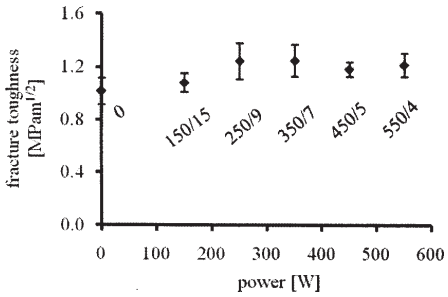

Fig. 3. Impact strength of untreated and treated samples in relation to microwave irradiation power

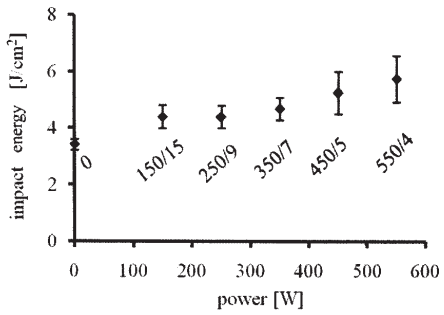

Fig. 4. Fracture toughness of untreated and treated samples in relation to microwave irradiation power

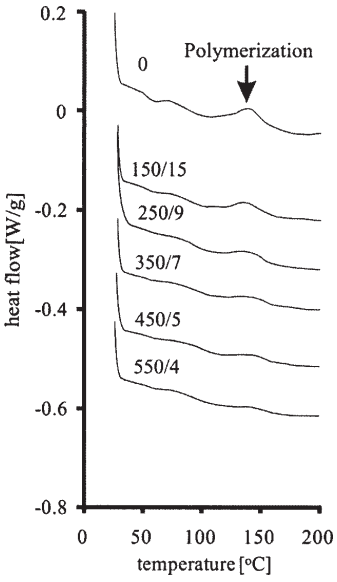

Fig. 5. DSC curves showing polymerization peaks for various microwave irradiation parameters.

devised, with a correlation coefficient of R^2=0.978, figure 7.

This decrease in residual monomer content is inversely proportional to increase in all tested mechanical properties: hardness, flexural strength, impact strength and fracture toughness. That indicates that a lower residual monomer

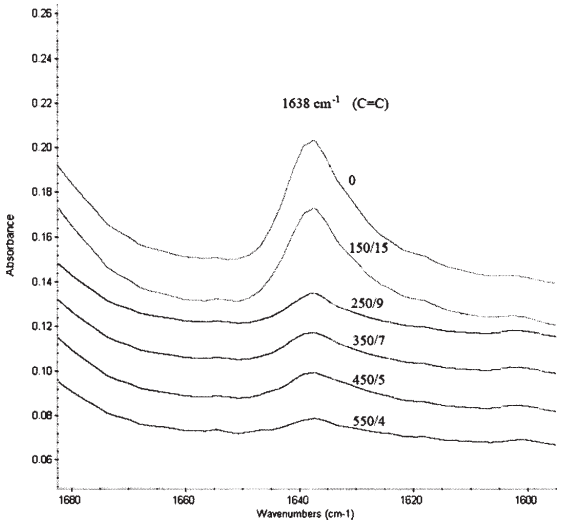

Fig. 6. FTIR peaks of carbonyl groups (C=C) representing methyl methacrylate monomer

Table 5
METHYL METHACRYLATE MONOMER OBTAINED USING FTIR SPECTROSCOPY.

Specimen group	Enthalpy of polymerization [J/g]	Methyl methacrylate monomer [weight %]
0	4.212	6.5
150/15	3.073	5.4
250/9	2.733	5.4
350/7	2.657	5.3
450/5	1.884	4.8
550/4	0.888	3.7

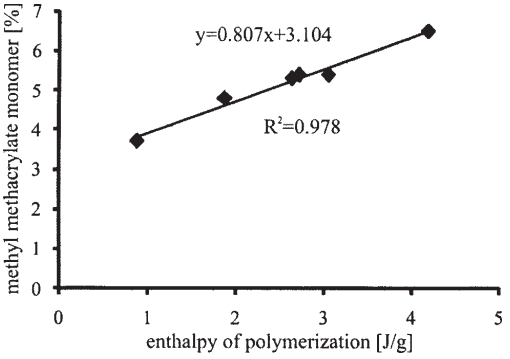

Fig.7. Enthalpy of polymerization and methyl – methacrylate monomer content graph

content has a crucial importance for increasing mechanical properties. This means that initial hypothesis might be true.

SEM micrographs of fracture surfaces show that poly(methyl methacrylate) biopolymer in untreated and treated condition behave in brittle manner, as some river marks are present on fracture surfaces, figures 8 and 9, similar to those found on the fracture surfaces of a typical brittle ceramic material [13]. From the micrographs, it can be seen that the river marks are more pronounced in

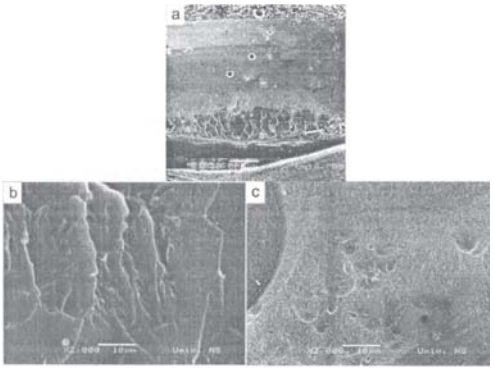

Fig. 8. Fracture surface of untreated sample after fracture toughness testing: a) river marks present near the notch, b) river marks detail, c) surface structure

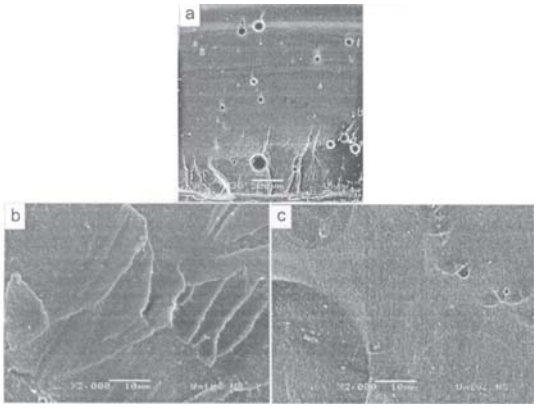

Fig. 9. Fracture surface of treated sample after fracture toughness testing: a) river marks present near the notch, b) river marks detail, c) surface structure

untreated samples, indicating a more crack-sensitive nature of these specimens, which is in accordance with mechanical properties obtained.

The subject was treated also by other authors [18].

Conclusions

According to the results presented in this work, some conclusions can be drawn.

Microwave irradiation after polymerization of acrylic denture reline resin proved to be beneficial for increasing hardness, flexural strength, fracture toughness and impact strength.

Power and time are highly influential parameters, even when the energy of irradiation is kept constant. Higher irradiation power (450, 550 W) is desirable for achieving higher hardnes, flexural strength and impact strength, while medium irradiation power (250, 350 W) gives higher fracture toughness.

Residual monomer of PMMA is a very important parameter that increase hardness, flexural strength, fracture toughness and impact strength, where it is inversely proportional to the increase in mechanical properties.

Microwave irradiation is a quick and very convinient method from the point of view of availability, for increasing the quality and durability of denture reline resins and repaired dentures in general.

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Manuscript received: 13.12.2010