Flexural and Impact Strength of Microwave Treated Autopolymerized Poly(Methyl - Methacrylate)

SEBASTIAN BALOS[1]*, TATJANA BALOS[2], LEPOSAVA SIDJANIN[1], DUBRAVKA MARKOVIC[2], BRANKA PILIC[3], JELENA PAVLICEVIC[3]

[1] Faculty of Technical Sciences, Department of Production Engineering, Trg Dositeja Obradovica 6, 21000, Novi Sad, Serbia
[2] School of Medicine, Department of Dentistry, Hajduk Veljkova 3, 21000, Novi Sad, Serbia
[3] Faculty of Technology, Department of Material Engineering, Bulevar Cara Lazara 1, 21000, Novi Sad, Serbia

The aim of this study was to optimize microwave post-polymerization treatment parameters, power and irradiation time, in order to achieve the maximum applicable flexural and impact strength of autopolimerizing poly(methyl-methacrylate) denture reline resins. Specimens were produced from two types of commercial materials. Control group was left untreated, while the other twelve were post-irradiated in a microwave oven with different power and time settings: 500, 550, 600 and 650 W; and 3, 4 and 5 minutes. The amount of residual monomer was determined using DSC and FTIR. Furthermore, visual control has been conducted, in order to check if there any surface changes have appeared. Microwave post-irradiation resulted in increase of all tested mechanical properties, for all specimens. The highest mechanical 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. The fracture mode of all specimens in untreated and treated conditions was found to be mostly brittle. However, the highest power (650 W) and the longest irradiation time (5 min) resulted in unacceptable surface color and roughness modifications.

Keywords: biopolymers, microwave post – polymerization, mechancal properties, residual monomer

Poly(methyl-methacrylate) (PMMA) has been one of the most widely used polymer material, due to the combination of properties, involving transparency, aestetics, biocompatibility and, for many applications, adequate mechanical properties. One of the most notable applications have been denture bases. Today, 90% of all dentures are made from PMMA [1].

A special type of these biopolymer materials, autopolymerizing PMMA denture reline resins, have 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 [2, 13]. However, their mechanical properties are compromised if compared to heat-polymerized materials used for base denture [3]. The main reason is higher unconverted monomer, as reported by various authors [4, 5, 16]. Monomer acts as a microvoid, representing an initial crack causing stress concentration, which makes the material less resistant. There are two methods of decreasing residual monomer content: by heat post-teatment, which can be achieved by immersion in hot water, or by microwave post-irradiation [6-11].

The purpose of this work is to find the optimal parameters for achieveing the highest flexural and impact strength of a PMMA autopolymerizing dental resin. These mechanical properties were compared to residual monomer content. The residual monomer (methyl-methacrylate) over 5 %, quite common for an autopolymerizing PMMA dental resin may elicit irritation, inflammation, and an allergic response in oral mucosa, causing a lower biocompatibility [1, 14]. In addition, flexural and impact strength were compared to those of one of the most advanced and expensive PEMA dental repair materials. This material, having a different composition of two components (powder and liquid), does not contain methyl-methacrylate and therefore causes no negative effect on patient's mucosa [12].

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

Materials used in this study were two commercial autopolymerizing denture resins, known by their trade names Simgal-R (Simgal, Galenika, Belgrade, Serbia) and Akrilat-R (ADA Dental Products, Belgrade, Serbia in collaboration with Dentaurum, Ispringen, Germany). The reference PEMA material used was Ufi-Gel Hard C (Voco, Cuxhaven, Germany). All materials were supplied separately in powder and liquid. When these two components are mixed, the polymerization process is initiated. Simgal-R and Akrilat-R powder consists of the PMMA, benzoyl peroxide and inorganic pigments, while the liquid component contains the methylmetacrylate monomer and the tertiary amine. Benzoyl peroxide and tertiary amine produce free radicals, necessarry for the radical polymerization process. Ufi-Gel Hard C powder consists basically of PEMA, while the liquid contains 2-hydroxyethil-methacrylate (HEMA) and 1,6-hexanediol-dimethacrylate (1,6-HDMA). As such, Ufi-Gel hard C is methyl-methacrylate free, thus reduces the risk of an allergic reaction and irritation. Furthermore, there is no exothermic heat given off during polymerization so cuing can take place in patient's mouth, increasing the accuracy of fit of the repaired denture [12, 15].

Samples were prepared according to manufacturer's intructions, with powder - liquid ratio of 2:1 in weight. Samples were cast in elastomer molds (Wirosil, Bego,

---

* *email address: sebab@uns.ns.ac.yu; Tel.: +381214852339*

Bremen, Germany). After polymerization, a set of SiC papers (150, 400 and 1200 grit) were used to get the desired shape and dimensions of the samples. Dimensions were verified by a Feinmesszeugfabrik (Suhl, Germany) micrometer, accurate to 0.01 mm at three locations.

Samples were divided in 13 groups, of which the first was left untreated, while the rest were irradiated in a domestic microwave oven with a turntable (Elin MW8020MG with output power of 800 W) at a frequency of 2450 MHz. Specimens were placed on the turntable and exposed to microwave irradiation directly. Power settings were 500, 550, 600 and 650 W, while irradiation time settings were 3, 4 and 5 minutes (power of 500 W and treatment duration of 5 minutes was designated as 500/5). These settings were chosen according to previous results [9 - 11], where higher power and shorter irradiation has shown to be more beneficial than lower power and longer irradiation, at the consant irradiation energy.

Flexural strength was determined using a mechanical tensile testing machine (Toyoseiki AT-L-118B, Tokyo, Japan), with a crosshead speed of 50 mm/min. The test was performed using 3-point bending, with the distance between the supports of 40 mm. Specimens dimensions were 6x2.5x50 mm.

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 a notch.

The obtained results were statisticaly analyzed using an one-way analysis of variance (ANOVA), followed by Tukey's test with the significance value of $P<0.05$.

Differential Scaning Calorimetry (DSC) analysis was performed on TA Instruments Q20 device, to detremine glass transitions temperatures as well as enthalpy of polymerization. The analysis has been run from 20 to 200°C. Enthaply of polymerization was compared to the results obtained by Fourier Transform Infrared Specrtoscopy (FTIR). FTIR analysis was performed on a Thermo Nicolet Nexus 670 FTIR spectrometer (Thermo Electron Corporation, Madison, WI, USA), equipped with a deuterated triglycine sulphate (DTGS) detector. Carbonyl group (C=C), representing residual monomer of each specimen was detected. 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.

Visual examination of the treated specimens was performed in order to check if there occurred any surface changes, as the result of exposure to microwave irradiation. Fracture surfaces were examined by JEOL JSM-6460LV (JEOL Ltd., Tokyo, Japan) scanning electron microscope (SEM), operating at 25 kV. The specimens were coated with gold, using Balltec SCD-005 coating device.

Results and discussion

Flexural strength and impact strength obtained for Simgal-R, Akrilat-R, and Ufi-Gel Hard C are shown in tables 1 and 2, respectively. For more convinience, the results are presented by charts as well, figures 1-4.

From tables 1 and 2, and figures 1-4, it can be seen that as the power and time increase, flexural and impact strength increase too. Furthermore, statistical analysis ANOVA followed by Tukey test (tables 1 and 2), shown that statistically significant differences occur mostly on samples treated at higher power and time settings. It can be seen that, although both are PMMA, there are differences between mechanical properties of Simgal-R and Akrilat-R.

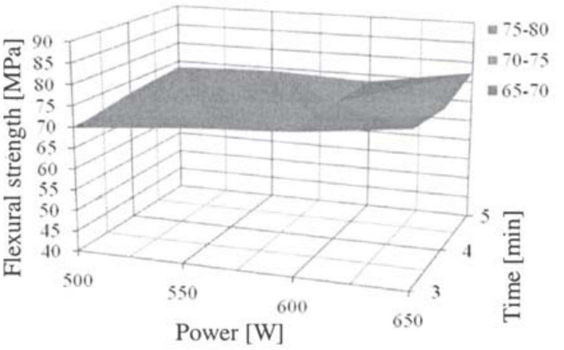

Fig. 1. Flexural strength in relation to power and time

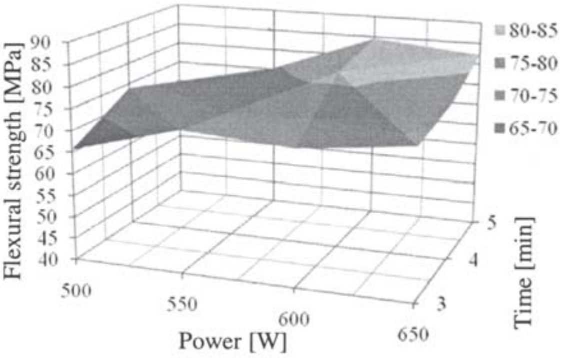

Fig. 2. Flexural strength in relation to power and time

Table 1
FLEXURAL STRENGTH AND P-VALUES

Material	Sample	Flexural strength σ_{SM} [MPa]	P
Simgal-R	0	58.68	
	500/3	69.72	0.02217
	500/4	72.15	0.00998
	500/5	73.45	0.00751
	550/3	71.93	0.00844
	550/4	73.29	0.03656
	550/5	74.26	0.00294
	600/3	73.31	0.01124
	600/4	73.84	0.00524
	600/5	73.26	0.00829
	650/3	76.21	0.00149
	650/4	74.37	0.00787
	650/5	77.39	0.00217
Akrilat-R	0	65.71	
	500/3	73.93	0.01310
	500/4	65.28	0.58153*
	500/5	72.51	0.07631*
	550/3	77.62	0.03558
	550/4	75.28	0.00255
	550/5	70.92	0.06215*
	600/3	82.54	0.00274
	600/4	83.24	0.00098
	600/5	73.93	0.05760*
	650/3	79.65	0.01056
	650/4	83.50	0.00251
	650/5	65.71	0.00259
Ufi-Gel Hard C	0	37.15	

**Values P>0.05 indicate that, the difference between untrated and treated samples is not significant (probability of 95 %).*

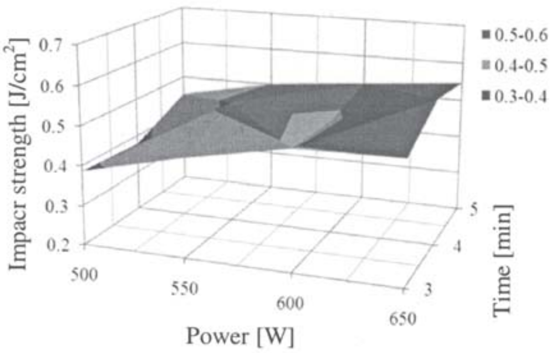

Fig. 3. Flexural strength in relation to power and time

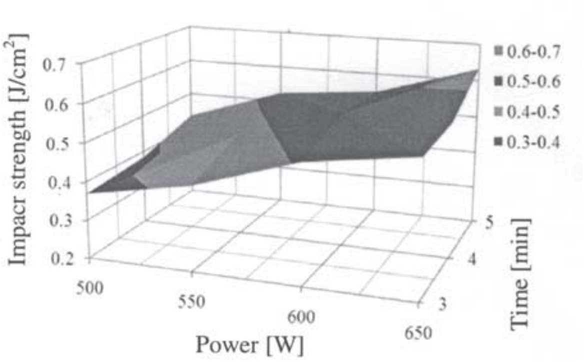

Fig. 4. Flexural strength in relation to power and time

Table 2
IMPACT STRENGTH AND P-VALUES

Material	Sample	Impact strength KO $[J/cm^2]$	P
Simgal-R	0	0,341	
	500/3	0,386	0.35192*
	500/4	0,378	0.46915*
	500/5	0,450	0.10698*
	550/3	0,447	0.07540*
	550/4	0,515	0.03291
	550/5	0,501	0.02220
	600/3	0,497	0.09080*
	600/4	0,491	0.10085*
	600/5	0,524	0.00873
	650/3	0,502	0.02490
	650/4	0,570	0.01596
	650/5	0,547	0.06870*
Akrilat-R	0	0.367	
	500/3	0.369	0.93083*
	500/4	0.384	0.61825*
	500/5	0.434	0.11463*
	550/3	0.419	0.15450*
	550/4	0.475	0.02687
	550/5	0.524	0.00855
	600/3	0.507	0.00091
	600/4	0.556	0.00036
	600/5	0.549	0.00071
	650/3	0.546	0.00139
	650/4	0.556	0.00032
	650/5	0.633	0.00152
Ufi-Gel Hard C	0	0.267	

**Values P>0.05 indicate that, the difference between untrated and treated samples is not significant (probability of 95 %).*

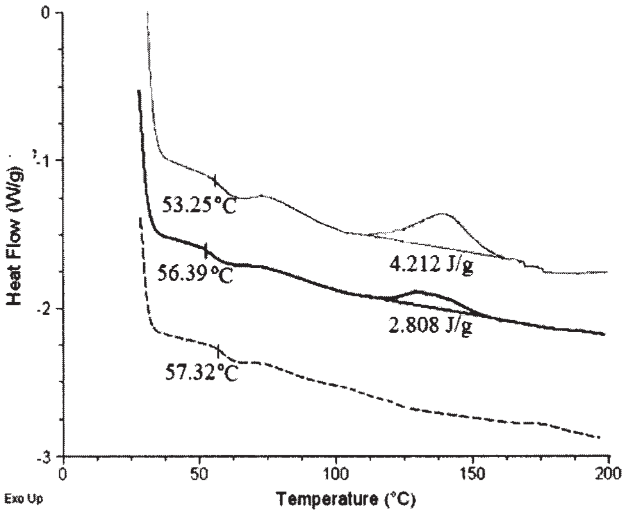

Fig. 5. Representative Simgal-R DSC curves: thin line – untreated, thick line – 500/4, dashed line – 650/3

Table 3
GLASS TRANSITION TEMPERATURE AND ENTHAPLY OF POLYMERIZATION

Material	Sample	Glass transition temperature [°C]	Enthalpy of polymer-ization [J/g]
Simgal-R	0	53.25	4.212
	500/3	56.32	3.417
	500/4	56.39	2.808
	500/5	52.91	1.593
	550/3	56.21	2.612
	550/4	56.31	0.888
	550/5	57.11	0.850
	600/3	56.33	1.125
	600/4	53.22	1.384
	600/5	53.67	0.844
	650/3	57.32	0
	650/4	55.69	0
	650/5	52.78	0
Akrilat-R	0	53.18	4.242
	500/3	53.25	3.661
	500/4	54.10	2.921
	500/5	56.41	2.203
	550/3	58.05	2.331
	550/4	56.23	1.691
	550/5	54.67	1.032
	600/3	52.02	1.055
	600/4	56.95	1.243
	600/5	51.98	0.787
	650/3	58.18	0
	650/4	62.75	0
	650/5	54.96	0

In untreated condition, flexural and impact strength are higher for Akrilat-R. The same trend is noticed for maximum values in treated condition. Compared to Ufi-Gel Hard C, Simgal-R and Akrilat-R have higher mechanical properties, especially flexural strength. The main reason is that Ufi-Gel Hard C is basically a PEMA.

A typical DSC curve is shown in figure 5. Glass transition temperatures and enthaplies of transition are shown in table 3.

From table 3, it can be seen that glass transition temperatures are all in the region from 51.98 and 62.75°C.

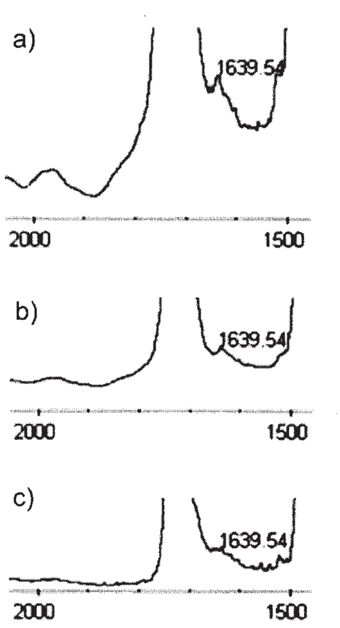

Fig. 6. Representative Akrilat-R FTIR curves: a) untreated sample, b) 500/4, c) 650/4 (Wavenumbers 1639.54 cm^{-1}, C=C group).

Table 4
METHYL-METHACRYLATE MONOMER CONTENT

Sample	Material	
	Simgal-R	Akrilat-R
0	6,5	7,4
500/3	5,2	4,7
500/4	5,1	4,0
500/5	5,2	4,2
550/3	4,9	4,2
550/4	4,8	3,0
550/5	4,2	2,9
600/3	4,3	3,1
600/4	3,4	2,7
600/5	3,0	2,7
650/3	3,1	2,6
650/4	3,7	<2,0
650/5	3,1	<2,0

However, enthalpies of polymerization values are smaller as the irradiation power and time increase. Furthermore, at 650 W and 3, 4 and 5 min, polymerization does not occur, indicating that the tested material does not contain monomer (table 3, fig. 5).

FTIR results are shown in table 4, while representative FTIR curves are shown on figure 6. The results of FTIR analysis shown that methyl-methacrylat monomer content decreases, as the power and time microwave irradiation settings increase. This is in good agreement with the results of enthalpy of polymerization obtained by DSC analysis.

Visual examination of samples from both materials revealed that at irradiation power of 650 W and 5 min time, the surface of the samples becomes rough and irregualar, figure 7. Furthermore, the sample becomes bent and the color is changed, making this power/time setting unacceptable from the aestetics and patient mouth fitting points of view. This is the result of excessive heating from the turntable, which limits the available irradiation parameters to 650 W and 4 min.

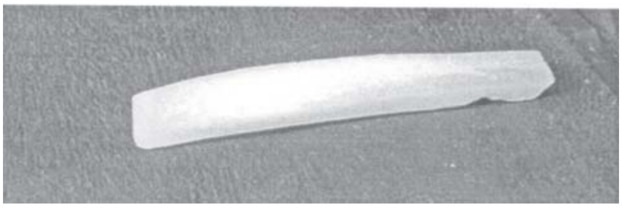

Fig. 7. Akrilat-R sample treated at 650 W and 5 min. It can be seen that the surface texture is coarser and the sample is bent

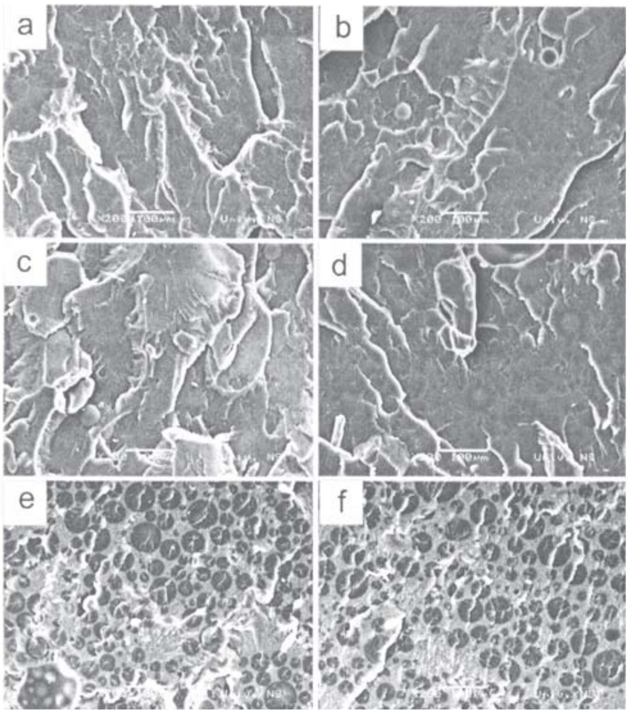

Fig. 8. Fracture mode: a) untreated Simgal-R, b) treated Simgal-R, c) treated Akrilat-R, d) untreated Akrilat-R, e) untreated Ufi-Gel Hard C, f) treated Ufi-Gel Hard C

The fracture mode obtained by SEM observation shows a typical brittle rupture by "quasi-cleavage" mechanism, figure 8. The observation indicated that fracture mode is not gradiually influenced by microwave irradiation. However, fracture mode of Simgal-R and Akrilat-R is similar, and different from Ufi-Gel Hard C, which is expected, since they belong to a different type of polymer materials.

Conclusions

According to obtained results, some conlusions can be drawn.

Microwave post-polimerization treatment increases both flexural and impact strengths of both tested PMMA reline resins.

The rise in tested mechanical properties is the result of decreasing methyl-methacrylate monomer content, by the additional heat generated through microwave irradiation. Residual monomer acts as empty space, or a microvoid, which, under load may propagate and cause fracture.

The highest irradiation parameters, power of 650 W and 5 min time induce an excessive heat, that may cause unwanted changes in sample surface texture and bending. This is unacceptable from the point of view of aestetics and patient's mouth fitting.

Optimal microwave parameters, for achieving the highest flexural strength are: 650/3 for Simgal-R and 650/4 for Akrilat-R. For impact strength, the optimal parameters are: 650/4 for both Simgal-R and Akrilat-R.

Lower methyl-methacrylate content for microwave treated samples makes them more biocompatible, by reducing the risk of irritation and alergic reaction. The achieved monomer content makes them suitable for all but the most sensitive patients, offering considerably higher flexural and impact strength at lower cost than the most modern materials, such as Ufi-Gel Hard C.

By applying microwave post polymerization treatment, the resulting product may become more durable and user – friendly, while still having a lower cost.

References

1.JEROLIMOV, V.: Osnove stomatoloskih materijala, Sveuciliste u Zagrebu, Zagreb, 2005.

2.TALLGREN, A., J. Prosthet. Dent. **89**, nr. 5, 2003, p.427

3.FUJII, K., Dent. Mater. J. **8**, nr. 2, 1989, p.243

4.LEE, S.Y., LAI, Y.L., HSU, T.S., Eur. J. Oral. Sci. **110**, nr. 2, 2003, p.179

5.FLETCHER, A.M., PURNAVEJA, S., AMIN, W.M., RITCHIE, G.M., Moradians, S, Dodd, A.W., J. Dent. Res. **62**, nr. 2, 1983, p.118

6.LAMB D.J., ELLIS, B., PRIESTLEY D., 1983. J. Dent. **11**, nr. 1, 1983, p.80

7.BLAGOJEVIC V, MURPHY V.M., 1999. J Oral. Rehabil. **26**, nr. 10, 1999, p.804

8.VERGANI, C.E., SEIKO, S.R., PAVARINA, A.C., dos Santos Nunes Reis J.M., J. Prosthet. Dent. **93**, nr. 6, 2005, p.577

9.BALOS, T., BALOS, S., MARKOVIC, D., Mogucnosti poboljsanja mehanickih osobina autopolimerizujuceg akrilata Simgal-R, 1. Kongres stomatologa Vojvodine, Novi Sad, Srbija, p.61

10. BALOS, S., SIĐANIN, L., GERIC, K., Uticaj mikrotalasnog zracenja na savojnu cvrstocu autopolimerizujuceg PMMA biopolimera, XXXII Savetovanje proizvodnog masinstva sa medunarodnim ucescem, Novi Sad, Srbija, p.487

11. BALOS, S. MSc Thesis, Uticaj mikrotalasnog zracenja na mehanicke karakteristike PMMA biopolimera, University of Novi Sad, Novi Sad, Serbia

12. GEURTSEN, W. Medizinische Hochschule Hannover, 09.1998

13. VODA, M., BORDEASU, I., MESMACQUE, G., CHITAC, V., TABARA, I. Mat. Plast., **44**, nr. 3, 2007, p. 254

14. MAICAN, E, BAYER, M., TABARA A. I., BALASOIU, V., Mat. Plast., **45**, nr. 2, 2008, p. 184

15. ANTON, L. E., BORDEASU, I., TABARA, I., Mat. Plast., **45**, nr. 2, 2008, p. 190

16. TODIC, V., LUKIC, D., STEVIC, M., MILOSEVIC, M., Mat.Plast.**45**, nr.4, 2008, p.381

Manuscript received: 28.04.2009