SHORT COMMUNICATION

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Autopolymerized poly(methyl methacrylate) reinforced with aluminum trioxide nanoparticles

Autopolimerizovani poli(metilmetakrilat) ojačan nanočesticama aluminijum trioksida

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Abstract

Background/Aim. Mechanical properties, most significantly flexural strength of cold polymerized acrylic dental materials, used for denture reparation are lower compared to the equivalent hot polymerized materials. This paradox can be rectified by the application of alumina nanoparticles, which was the aim of this work. **Methods.** The liquid component of the commercial autopolymerized denture reline resin was modified with 0.05%, 0.2% and 1.5% (wt) 13 nm hydrophobic Al_2O_3. These mixtures, along with the unmodified liquid, were mixed with the powder component to form test specimens. Flexural modulus and strength were tested, while the results were statistically evaluated by the one-way ANOVA analysis followed by Tukey's test. Differential scanning calorimetry, scanning electron microscopy and energy dispersive X-ray analysis were performed to assess the heat and fracture surface features. **Results.** A statistically significant increase in flexural modulus was obtained only for 0.2% nanoparticle content, while flexural strength was significantly increased for specimens modified with 0.05% and 0.2% nanoparticles. Moreover, the rise of nanoparticle content to 1.5% contributed the formation of agglomerates, giving unsatisfactory mechanical properties. Also, the rise in glass transition temperature was noted for the most effective 0.05 and 0.2% Al_2O_3 contents. **Conclusion.** The 0.2% 13 nm Al_2O_3 loading is the most effective in improving the tested mechanical properties of cold polimerized poly(methyl methacrylate) reline resin.

Key words:
acrylates; calorimetry, differential scanning; denture rebasing; elasticity; materal testing; nanoparticles; polymethyl methacrylate; stress, mechanical.

Apstrakt

Uvod/Cilj. Mehaničke osobine, u najvećoj meri savojna čvrstoća, hladno polimerizovanih akrilata za reparaturu proteza, manja je u odnosu na toplo polimerizovane akrilate. Taj paradoks može biti rešen upotrebom nano čestica, što je bio cilj ovog rada. **Metode.** Tečna komponenta komercijalnog autopolimerizujućeg polimetilmetakrilata za podlaganje proteza modifikovana je sa 0,05%, 0,2% i 1,5% (wt) hidrofobnim Al_2O_3 nanočesticama promera 13 nm, testiranih merenjem zeta potencijala. Te mešavine, zajedno sa nemodifikovanom tečnom komponentom, pomešane su sa prahom kako bi se dobili uzorci za ispitivanje. Izvršeno je ispitivanje savojnog modula elastičnosti i čvrstoće, uz primenu jednostruke analize varijanse (ANOVA) sa *Tukey* testom. Toplotne karakteristike su ispitane diferencijalnom skenirajućom kalorimetrijom, dok su površinska svojstva prelomljenih površina ispitana skenirajućim elektronskim mikroskopom i energetskom disperzionom analizom. **Rezultati.** Statistički značajno povećanje savojne čvrstoće dobijeno je samo kod uzoraka sa 0,2% nanočestica, dok je to u slučaju savojnog modula elastičnosti nađeno kod uzoraka sa 0,05% i 0,2% nanočestica. Povećanje sadržaja nanočestica na 1,5% doprinosilo je pojavi aglomerata, što je negativno uticalo na mehaničke osobine. Povećanje temperature ostakljivanja postignuto je kod najefikasnijih koncentracija nano Al_2O_3 od 0,05% i 0,2%. **Zaključak.** Za najveći stepen povećanja mehaničkih osobina hladno-polimerizujućeg polimetilmetakrilata potreban je sadržaj od 0,2% nanočestica Al_2O_3 promera 13 nm.

Ključne reči:
akrilati; kalorimetrija, diferencijalno skenirajuća; zubna proteza, podlaganje; elastičnost; materijali, testiranje; koloidi; polimetilmetakrilat; stres, mehanički.

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Introduction

Poly(methyl methacrylate) (PMMA) has been used traditionally as a shatterproof replacement for glass due to its convenient properties, such as transparency, which results in a broad array of applications, including aircraft canopies, protective goggles, automobile running lights, as well as construction panels and dentures [1]. Today, around 90% of all dentures are made from PMMA [2, 3]. However, PMMA also has disadvantages, the most notable being insufficient ductility and strength, which leaves room for further improvement [4]. Mechanical properties of denture base can be increased in a number of ways. The addition of metal wire and unidirectional glass fibers can significantly increase the strength of dentures [5]. Moreover, ultra-high-molecular-weight polyethylone (UHMWPE) was used to reinforce the denture [6]. An increased flexural modulus and reduced flexural strength were obtained by adding rigid rod polymer fillers [7]. ZrO_2 and Al_2O_3 particulate fillers [8, 9], as well as the combination of these two filler types [10–12] were used, with a profound increase in strength and toughness.

PMMA is used for denture reline resins as well, but they are cold, rather than hot polymerized. This material is used for providing better retention of removable prostheses in cases of alveolar resorption and denture reparation in case of crack or fracture [13]. The mechanical properties of cold polymerized denture reline resin is lower as a result of a limited time for mixing the liquid and powder component, after which the radical polymerization commences. This results in an increased unconverted monomer content [14, 15]. The unconverted monomer acts as a microvoid, which weakens the material. There are several methods to decrease the monomer content, i.e., to increase the mechanical properties of denture reline resins. Post heat treatment in hot water was suggested by Lamb et al. [16] or by microwave treatment [17, 18]. A different approach is to add a certain amount of nanoparticles, aimed at reducing the mobility of polymer chains in the vicinity of the nanoparticle. An array of well-distributed nanoparticles throughout the material causes the formation of a reinforcing field increasing the materials mechanical properties [19].

The aim of this study was to test the effect of hydrophobic alumina (Al_2O_3) nanoparticles on mechanical properties (flexural modulus and flexural strength) of autopolymerized PMMA denture reline resin.

Methods

The basic material used was a PMMA denture reline resin designated as Simgal® (Galenika, Zemun, Serbia). This material consists of powder and liquid, while the mixing ratio was kept at 2:1 in weight, respectively. The liquid component was modified with AEROXIDE Alu C 13 nm Al_2O_3 (Evonik, Essen, Germany), having a specific surface area of 85–115 m^2/g. The following contents in the liquid phase were used: 0.05%, 0.2% and 1.5% (wt). The control specimen was left untreated. To obtain the correct amount of nanoparticles for mixing, the analytical balance with an accuracy of 0.0001 g was used (Adventurer Pro Ohaus, Parsippany, NJ). The mixing was done in a magnetic stirrer MM-530 (Tehtnica, Zelezniki, Slovenia) for 10 min. Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) analyzer was used to determine the size of the particles in the liquid component (Figure 1). The unmodified and modified liquid components were then mixed with the powder component and the obtained mixture was poured into square Al-alloy molds. The specimens were obtained by mechanical cutting with cooling and the abrasive papers were used to get the final specimen shape and size (prismatic, 6 × 2.5 × 45 mm). To determine the flexural modulus of elasticity and flexural strength, Toyoseiki AT-L-118B (Toyoseiki, Tokyo, Japan) universal tensile testing machine was used. Three point bend test was used, with crosshead speed of 50 mm/min. The distance between the supports was 40 mm. The flexural modulus of elasticity was calculated by using the following equation (1):

$$E = \frac{\Delta F l^4}{4 \Delta d b h^3} \quad (1)$$

where l is the distance between the supports [mm], Δd is the displacement range [mm] for a testing load range ΔF [N], b is specimen width [mm] and h is specimen height [mm].

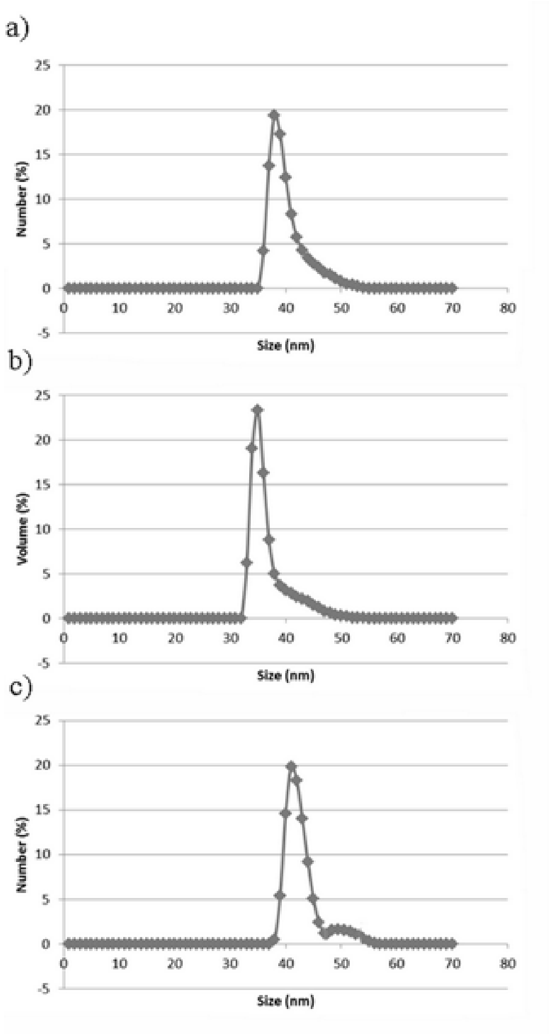

Fig. 1 – Particle distribution after mixing with liquid phase.

The flexural strength was calculated by using the equation (2):

$$\sigma = \frac{3Fl}{2bh^2} \quad (2)$$

where F is maximum force [N], l is the distance between the supports [mm], b is specimen width [mm] and h is specimen height [mm]. Five specimens were used for each of the following sample groups: the control group (unmodified), the group with 0.05%, 0.2% and 1.5% (wt) nanoparticles. One-way analysis of variance (ANOVA) followed by Tukey's test with the significance value of $p < 0.05$ was used. The tests were performed by using Minitab 16 software.

To determine the thermal properties of obtained materials, differential scanning calorimetry (DSC) analysis was performed. Q20 (TA Instruments, New Castle, DE) DSC device was applied, in the temperature range from 60 °C to 160 °C, with a scan rate of 10 °C/min. Furthermore, fracture surfaces were examined by JSM-6460LV (JEOL, Tokyo, Japan) scanning electron microscope (SEM), operating at 25 kV. The specimens were previously coated with gold, using the SCD-005 (Bal-tec/Leica, Wetzlar, Germany) device. To examine certain fracture surface features, energy-dispersive X-ray spectroscopy (EDX) was used (Oxford Instruments INCA Microanalysis system).

Results and discussion

The flexural modulus, flexural strength and standard deviations of tested materials, along with letter indicators of statistical significance between the results are given in Figures 2 and 3. It can be seen that the highest flexural modulus

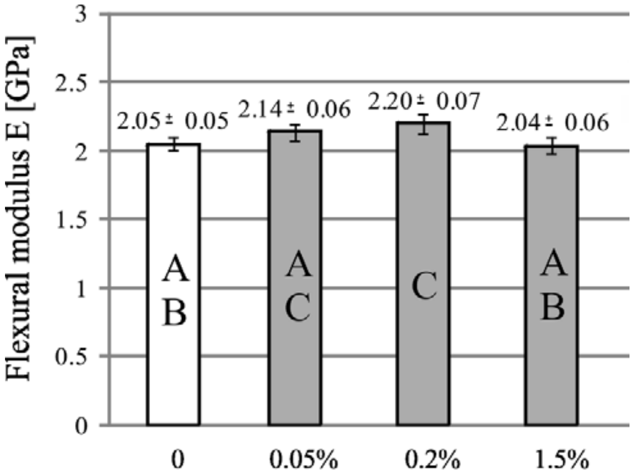

Fig. 2 –Flexural modulus and standard deviations of tested materials (different letters indicate statistically significant differences at a level of 95%).
GPa – gigapascals.

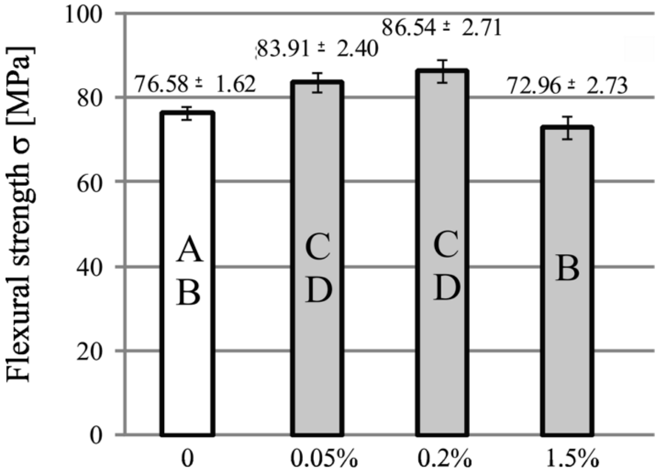

Fig. 3 –Flexural strength and standard deviations of tested materials (different letters indicate statistically significant differences at a level of 95%).
MPa – megapascals.

and strength were obtained for the specimen modified with 0.2% of Al_2O_3 nanoparticles. Both mechanical properties were significantly different from the control specimen. Specimens obtained with 0.05% nanoparticles also had a higher flexural modulus and strength; however, only in terms of strength, the difference was statistically significant. On the other hand, in specimens modified with 1.5% nanoparticles, the obtained values were lower than those of the control specimen.

The results of the DSC analysis are shown in Figure 4. The glass transition temperature (T_g) in the specimen modified with 0.05% and 0.2% nanoparticles was higher than that in the control specimen. This is the result of the layer surrounding the nanoparticles, where the mobility of the polymer chains is reduced compared to the unmodified material [19, 20]. In the specimen modified with 1.5% nanoparticles, T_g was the same as in the control specimen, probably due to a relatively thin modified layer and the limited amount of this modified material surrounding the nanofiller. This was obtained in spite of a higher addition of nanoparticles, because agglomeration occurs. This can be correlated both to the results obtained with zeta sizer, the distribution of nanoparticle size in liquid component (Figure 1) and mechanical properties shown in Figures 2 and 3. Namely, as a larger amount of polymer is immobilized, the modulus of elasticity and strength are higher, as in specimens modified with 0.05% and 0.2% of nanoparticles. This is also in accordance with a larger amount of smaller particles in the liquid component prior to mixing of the liquid and powder of the cold polymerized PMMA, as shown when Figures 1a and 1b are compared to Figure 1c. Lower mechanical properties of the specimens modified with 1.5% of Al_2O_3 are the result of larger particles (agglomerates) in the liquid phase before mixing, which, along with the results of DSC analysis indicate that the elevated agglomeration remained in the polymerized material (Figure 4).

Fracture surfaces of flexural strength testing specimens are shown in Figure 5. It can be seen that there are river marks present, typical for brittle fracture. Additionally, in Figure 5a and particularly in Figure 5c, spherical structures can be noticed. These structures are powder pre-polymerized PMMA particles that are bonded by the polymerized MMA from the liquid component of the material. The crack path passing between the PMMA powder particles indicates that there is a significant difference between the strength of the liquid-component originated matrix and powder particles. In the specimen modified with 0.2% of nanoparticles, the crack path does not avoid powder particles, indicating a smaller difference between local mechanical properties between the matrix and spherical particles. That means, the cold polymerized matrix mechanical properties in the specimen modified with 0.2% nanoparticles are higher than those in the control specimen and the specimen modified with 1.5% nano Al_2O_3.

The results of the EDX analysis for the agglomerate particle and the surrounding material are shown in Figure 6. It can be seen that the analyzed agglomerate clearly can be identified as aluminum oxide. The analyzed particle size is

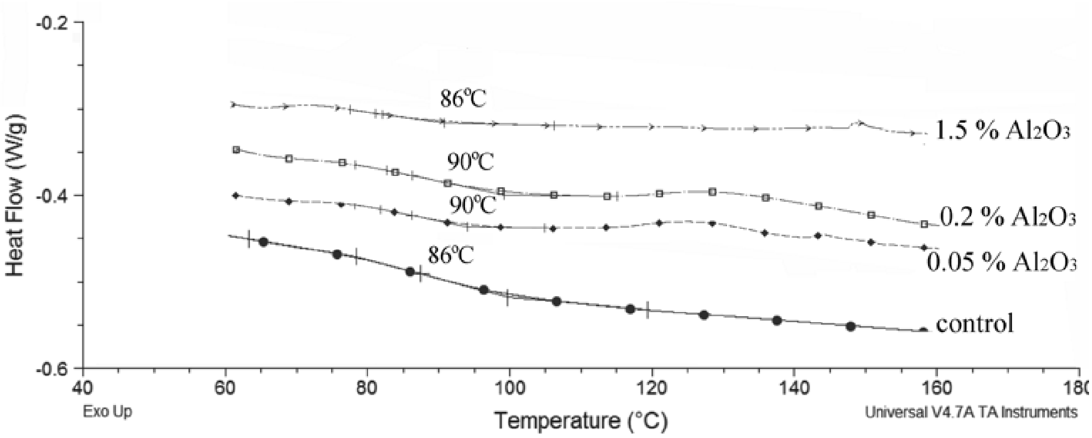

Fig. 4 – Differential scanning calorimetry (DSC) analysis results.

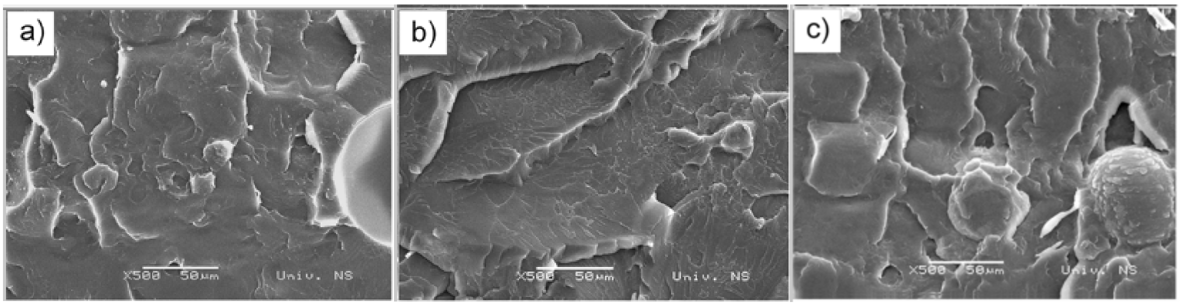

Fig. 5 – Scanning electron microscope (SEM) images of fractured surfaces: a) the control specimen; b) the specimen modified with 0.2% nanoparticles; c) the specimen modified with 1.5% nanoparticles.

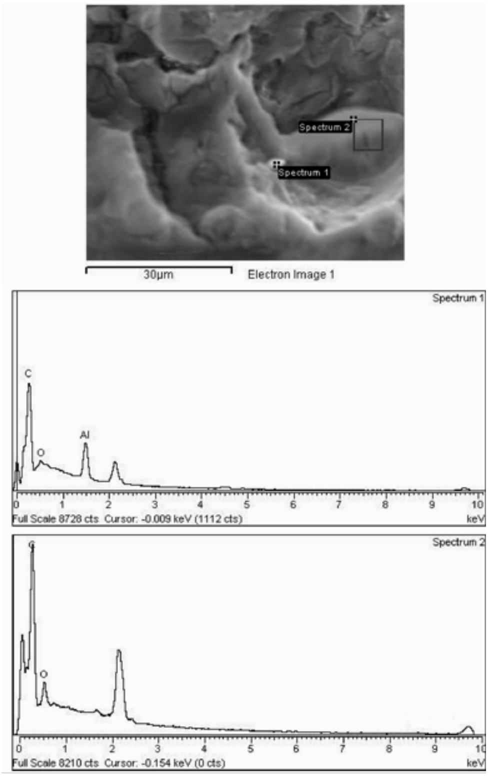

Fig. 6 – Energy-dispersive x-ray spectroscopy (EDX) analysis of agglomerate (spectrum 1) and the surrounding material (spectrum 2) of the specimen modified with 1.5% nanoparticles.

several orders of magnitude larger than nanoparticles introduced in the liquid component, as well as the measured particles in the liquid component (39–55 nm). The particle shown in Figure 6 can be classified as a relatively large agglomerate, which can explain the mechanical behavior of the material tested. As shown in Figures 2 and 3, the specimen modified with 1.5% nanoparticles has a lower flexural modulus and strength compared with the control specimen. Such results can be explained by the existence of large agglomerates that negate the effect of a relatively small volume of material surrounding the particles with reduced mobility of polymer chains. Namely, the agglomerates are collectives of nanoparticles, due to the existence of Van der Waals forces between them. As the agglomerates fracture under load, the stress is transmitted to the surrounding material, causing unstable crack propagation, weakening the material [4, 21].

Conclusion

The incorporation of 13 nm hydrophobic Al_2O_3 nanoparticles into the cold polymerized PMMA is beneficial for improving flexural modulus and flexural strength. The most effective content is 0.2% Al_2O_3, with a statistically significant rise in flexural modulus and strength compared to the control specimen. The nanoparticle loading of 1.5% proved to decrease mechanical properties compared to the control, unmodified specimens. The main reason for this behavior is the agglomeration of nanoparticles, creating particles several orders of magnitude larger, that contribute to the decrease in mechanical properties through the mechanism of fracture and unstable crack propagation.

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REFERENCES

1. *Tallgren A.* The continuing reduction of the residual alveolar ridges in complete denture wearers: A mixed-longitudinal study covering 25 years, 1972. J Prosthet Dent 2003; 89(5): 427–35.
2. *Stamenković D, Obradović-Đuričić K, Beloica D, Leković V, Ivanović V, Pavlović G,* et al. Dental materials. Belgrade: Zavod za udžbenike i nastavna sredstva; 2003. (Serbian)
3. *Jerolimov V.* The basics of dental materials. Zagreb: School of Dental Medicine University of Zagreb: 2005. (Croatian)
4. *Balos S, Pilic B, Markovic D, Pavlicevic J, Luzanin O.* Poly(methyl-methacrylate) nanocomposites with low silica addition. J Prosthet Den 2014; 111(4): 327–34.
5. *Vojdani M, Khaledi AAR.* Transverse Strength of Reinforced Denture Base Resin with Metal Wire and E-Glass Fibers. Front Dent 2006; 3(4): 159–66.
6. *Carlos NB, Harrison A.* The effect of untreated UHMWPE beads on some properties of acrylic resin denture base material. J Dent 1997; 25(1): 59–64.
7. *Vuorinen AM, Dyer SR, Lassila LV, Vallittu PK.* Effect of rigid rod polymer filler on mechanical properties of poly methyl methacrylate denture base material. Dent Mater 2008; 24(5): 708–13.
8. *Ayad NM, Badawi MF, Fatah AA.* Effect of reinforcement of high-impact acrylic resin with zirconia on some physical and mechanical properties. Arch Oral Res 2008; 4(3): 145–51.
9. *Ellakwa AE, Morsy MA, El-Sheikh AM.* Effect of aluminum oxide addition on the flexural strength and thermal diffusivity of heat-polymerized acrylic resin. J Prosthodont 2008; 17(6): 439–44.
10. *Fortulan CA, de Souza DPF.* Microstructural evolution of the Al_2O_3–ZrO_2 composite and its correlation with electrical conductivity. Mater Res 1999; 2(3): 205–10.
11. *Marti A.* Inert bioceramics (Al_2O_3, ZrO_2) for medical application. Injury Int J Care Injured 2000; 31(Suppl 4): 33–6.
12. *Santos C, Souza RC, Daguano JKMF, Elias CN, Rogero SO.* Development of Al_2O_3–ZrO_2 bioceramic composites. Salvador, Brazil: 51 Congresso Brasileiro de Ceramica; 2007, June 3–6.
13. *Balos S, Pilic B, Petrovic Dj, Petronijevic B, Sarcev I.* Flexural strength and modulus of autopolimerized poly(methyl methacrylate) with nanosilica. Vojnosanit Pregl 2018; 75(6): 564–69.
14. *Lee SY, Lai, YL, Hsu, TS.* Influence of polymerization conditions on monomer elution and microhardness of autopolymerized polymethyl methacrylate resin. Eur J Oral Sci 2002; 110(2): 179–83.
15. *Fletcher AM, Purnaveja S, Amin WM, Ritchie GM, Moradians S, Dodd AW.* The Level of Residual Monomer in Self curing denture Base Materials. J Dent Res 1983; 62(2): 118–20.

16. *Lamb DJ, Ellis B, Priestley D.* The effects of process variables on levels of residual monomer in autopolymerizing dental acrylic resin. J Dent 1983; 11(1): 80–8.
17. *Balos S, Balos T, Sidjanin L, Markovic D, Pilic B, Pavlicevic J.* Study of PMMA biopolymer properties treated with microwave energy. Mater Plast 2011; 48(2): 127–31.
18. *Balos S, Balos T, Sidjanin L, Markovic D, Pilic B, Pavlicevic J.* Flexural and impact strength of microwave treated autopolimerized Poly(Methyl-methacrylate). Mater Plast 2009; 46(3): 261-65.
19. *Fragiadakis D, Pissis P, Bokobza L.* Glass transition and molecular dynamics in poly (dimethylsiloxane)/silica nanocomposites. Polymer 2005; 46(16): 6001–8.
20. *Bera O, Pavlicevic J, Jovicic M, Stoiljkovic D, Pilic B, Radicevic R.* The Influence of nanosilica on styrene free radical polymerization kinetics. Polym Composite 2011; 33(2): 262–66.
21. *Elshereksi NW, Mohamed SH, Arifin A, Mohd Ishak ZA.* Effect of filler incorporation on the fracture toughness properties of denture base poly(methyl methacrylate). J Phys Sci 2009; 20(2): 1–12.

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