



Flexural strength and modulus of autopolymerized poly(methyl methacrylate) with nanosilica

Savojna čvrstoća i modul elastičnosti autopolimerizovanog polimetilmetakrilata sa nanočesticama silicijum-dioksida

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Abstract

Background/Aim. Autopolymerized, or cold polymerized poly(methyl methacrylate) class of materials have a lower mechanical properties compared to hot polymerized poly(methyl methacrylate), due to a limited time of mixing before the polymerization process begins. The aim of this study was to test the effect of different relatively low nanosilica contents, in improving mechanical properties of the cold polymerized poly(methyl methacrylate). **Methods.** A commercially available autopolymerized poly(methyl methacrylate) denture reline resin methyl methacrylate liquid component was mixed with 7 nm after treated hydrophobic fumed silica and subsequently mixed with poly(methyl methacrylate) powder. Three nanosilica loadings were used: 0.05%, 0.2% and 1.5%. Flexural modulus and strength were tested, with one way ANOVA followed by Tukey's test. Furthermore, zeta potential, differential scanning calorimetry, scanning electron microscopy and energy dispersive X-ray analyses were performed. **Results.** Flexural modulus and strength of poly(methyl methacrylate) based nanocomposites were statistically significantly increased by the addition of 0.05% nano-SiO₂. The increase in nanosilica content up to 1.5% does not contribute to mechanical properties tested, but quite contrary. The main reason was agglomeration, that occurred before mixing of the liquid and powder component and was proved by zeta potential measurement, and after mixing, proved by scanning electron microscopy and energy dispersive x-ray analyses. **Conclusions.** Addition of 7 nm 0.05% SiO₂ is the most effective in increasing flexural modulus and strength of autopolymerized poly(methyl methacrylate).

Key words: methylmethacrylate; acrylates; denture rebasing; materials testing; stress, mechanical; nanoparticles; silicon dioxide; elasticity; calorimetry, differential scanning.

Apstrakt

Uvod/Cilj. Autopolimerizujući ili hladno polimerizujući polimetilmetakrilatni materijali imaju niže mehaničke osobine u odnosu na toplo polimerizujuće polimetilmetakrilate, zbog ograničenog trajanja mešanja pre početka procesa polimerizacije. Cilj ovog rada bio je da se ispita efekat relativno niskih sadržaja nanosilike u cilju povećanja mehaničkih osobina hladno polimerizujućeg polimetilmetakrilata. **Metode.** U tečnu metilmetakrilat komponentu komercijalnog autopolimerizujućeg polimetilmetakrilatnog materijala za podlaganje zubnih proteza umešane su nanočestice veličine 7 nm, a potom je modifikovana tečnost pomešana sa prahom polimetilmetakrilata. Ispitana su tri sadržaja nanosilike: 0,05%, 0,2% i 1,5%. Izvršena su ispitivanja modula elastičnosti i čvrstoće. Rezultati su statistički analizirani uz primenu jed-nostruke statističke analize ANOVA i Tukey-testom. Takođe, izvršeno je merenje zeta potencijala tečne komponente, diferencijalna skenirajuća kalorimetrija, skenirajuća elektronska mikroskopija i energetska disperzivna rentdenska analiza. **Rezultati.** Modul elastičnosti i čvrstoća bili su statistički značajno povećani dodatkom 0,05% nano-SiO₂. Povećanje sadržaja nanosilike na 1,5% nije doprinelo povećanju ispitivanih mehaničkih osobina, naprotiv. Osnovni razlog bio je pojava aglomeracije, pre mešanja praha i tečne komponente, dokazana merenjem zeta-potencijala, kao i nakon mešanja, a dokazana je skenirajućom elektronskom mikroskopijom i energetskom disperzivnom rendgenskom analizom. **Zaključak.** Najefikasniji sadržaj nanosilike za povećanje modula elastičnosti i čvrstoće autopolimerizovanog polimetilmetakrilata je 0,05%.

Ključne reči: metilmetakrilati; akrilati; zubna proteza, podlaganje; materijali, testiranje; stres, mehanički; koloidi; silicijum dioksid; elastičnost; kalorimetrija.

Introduction

Poly(methyl-methacrylate) (PMMA) is one of the most widely used polymer materials due to the convenient combination of properties such as transparency, aesthetics, and biocompatibility. Such properties enabled it to be used for denture bases, of which, the vast majority are made of PMMA¹. A special type of PMMA is autopolymerized, that is, it is synthesized by the successive addition of free radical building blocks. Free radicals can be formed via separate initiator molecules formed by the reaction between the materials powder and liquid components^{1, 2}. The autopolymerized PMMA has been widely used to provide better retention of removable prostheses in cases of alveolar resorption, as well as for denture repair in case of crack or fracture³. However, their mechanical properties are lower if compared with the heat-polymerized PMMA used for denture bases⁴. The main reason is a higher amount of unconverted monomer which acts as a microvoid. This causes stress concentration which can initiate internal or external cracks making the material less resistant^{5, 6}. There are various methods of improving the mechanical properties of autopolymerized MMA such as: heat post-treatment, which can be achieved by hot water treatment⁷ and by microwave post-irradiation⁸⁻¹¹. These methods can be used only when the autopolymerized PMMA material is already applied to the denture, so the heat input may cause the denture to deform, that is, change its shape and therefore become unsuited to the geometrical configuration of the patients mouth¹². An alternative approach is the introduction of rods or particles in the material, to obtain a composite material that would exhibit an increase in mechanical properties compared to the autopolymerized PMMA.

In the work by Carlos and Harrison¹³ ultra high molecular weight polyethylene (UHMWPE) was added to the PMMA to reinforce added to acrylic resin denture base material. However, the results showed that impact strength and hardness were reduced. The studies by Chow et al.^{14, 15} showed that the addition of hydroxyapatite at maximum content of 5% can increase fracture toughness. At the same time, flexural strength decreased, most probably due to agglomeration of the particles.

The addition of up to 15% of ZrO₂ can significantly increase the impact strength of the PMMA¹⁶. A study by El-lakwa et al.¹⁷ showed that Al₂O₃ addition can significantly increase flexural strength of PMMA. These studies led to the tests done by Alhabet et al.¹⁸, where various Al₂O₃/ZrO₂ particle ratios in the PMMA matrix showed a positive effect in increasing flexural strength and modulus as well as fracture toughness, however, tensile strength and modulus were reduced. Obviously, the particle type, size, content, surface properties and distribution all influence the composite mechanical properties. An approach used in works by Balos et al.^{19, 20} comprised of the addition of relatively low (under 2%) of hydrophobic SiO₂ particles to improve the mechanical properties (microhardness, flexural strength, flexural modulus and fracture toughness) of flow dental composites, as well as PMMA denture bases. Low SiO₂ particle addition

of 0.05% proved to be beneficial for all tested mechanical properties. The main reason was a lower agglomeration and more convenient distribution on reinforcing particles.

The aim of this study was to test the effect of different contents of relatively low nanoparticle content, added to the autopolymerized PMMA material, and to determine mechanical properties of nanocomposite, in terms of modulus and flexural strength.

Methods

The material used in this study was a commercial PMMA denture reline resin Simgal (Galenika, Zemun, Serbia), supplied separately in powder and liquid. The powder consisted of the PMMA, benzoyl peroxide and inorganic pigments, while the liquid being the MMA monomer and the tertiary amine. Benzoyl peroxide and tertiary amine initiate the radical polymerization process. Samples were prepared in accordance with manufacturers instruction, with powder to liquid ratio of 2 : 1 in weight. PMMA was modified with hydrophobic properties: AEROSIL R812 (Evonik, Essen, Germany) 7 nm SiO₂ with hydrophobic properties and specific surface area of between 195 and 245 m²/g. Nanoparticles were weighed on analytical balance (Adventurer Pro Ohaus, Parsippany, NJ) with an accuracy of 0.0001 g and subsequently mixed with the liquid component by using a magnetic stirrer MM-530 (Tehnica, Zelezniki, Slovenia) for 10 min. Afterwards, the ultrasonic bath PS-20A (Challenger, Selangor, Malaysia) was used for 10 min, to prevent agglomeration, while the final mixing was done in magnetic stirrer again for 2 min, to obtain stabilized solution of nanoparticles in the liquid component. To determine the size of the particles in the liquid component, Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) analyzer was applied. The liquid component was then mixed with powder component and the obtained mix was poured into square Al-alloy molds. Then, after polymerization, 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 micrometer, accurate to 0.01 mm at 3 locations. Five specimens were used for each testing, for each of the following sample groups: control group (unmodified), the group with 0.05, 0.2 and 1.5 (wt.)% nanoparticles in relation to the overall weight of the liquid and powder component.

The flexural modulus and flexural strength were determined by using an AT-L-118B (Toyoseiki, Tokyo, Japan) tensile testing machine, with a crosshead speed of 50 mm/min. 3 point bending test was used, with the distance between the supports of 40 mm. Specimens dimensions were 6 x 2.5 x 45 mm.

The flexural modulus was calculated by using the following equation:

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

where l is the distance between the supports [mm], Δd is the displacement range [mm] for a given testing load range ΔF

[N], b is specimen width [mm] and h is specimen height [mm].

The flexural strength was calculated by using the following equation:

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

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].

To evaluate the significance between the results of mechanical properties of different sample groups, 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 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. The glass transition temperatures were determined on the basis of the second heating.

The fracture surfaces were examined by JSM-6460LV (JEOL, Tokyo, Japan) scanning electron microscope (SEM), operating at 25 kV, both in secondary electron and back-scattering electron mode. The specimens were previously coated with gold, using the SCD-005 (Bal-tec/Leica, Wetzlar, Germany) device. Furthermore, to examine particles found on fracture surfaces, energy-dispersive X-ray spectroscopy (EDX) was used.

Results

The size distribution of particles in the liquid component of the PMMA material used in this study is shown in Figure 1. General trends are similar to single peak shaped distribution in liquid components used for obtaining specimens with 0.05% and 0.2% nanosilica. In the liquid specimen used for obtaining the specimen with 1.5% nanosilica, 2 peaks can be seen, with a secondary peak set at 52 nm particle size. Also, the only existing (0.05% and 0.2% SiO₂) and primary peak (1.5% SiO₂) was found at slightly elevated particle size as the content of particles increases.

The flexural modulus and strength, standard deviations and the results of statistical analysis of control and modified specimens are shown in Figures 2 and 3. It can be seen that the mechanical properties vary in accordance to the nanoparticle type added. SiO₂ 7 nm particles offered a significantly increased flexural modulus at 0.05% and strength at 0.05% and 0.2% contents. The highest flexural modulus and strength were obtained with the lowest, 0.05% nanoparticle loading. At 1.5% loading, mechanical properties were lower compared to control specimen group. The statistical difference between the modified specimen (1.5% SiO₂) in terms of flexural modulus was significant compared to the control specimen, without nanoparticles added. However, in terms of flexural strength this difference was not significant.

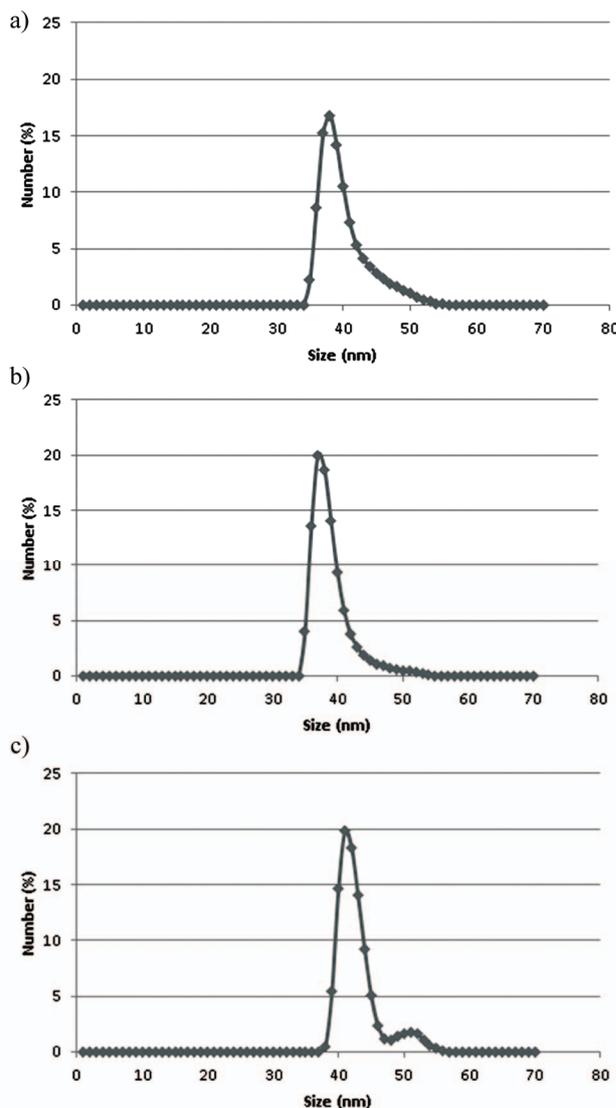


Fig. 1 – Particle size in liquid component with different contents of nanosilica: a) 0.05%; b) 0.2%; c) 1.5%.

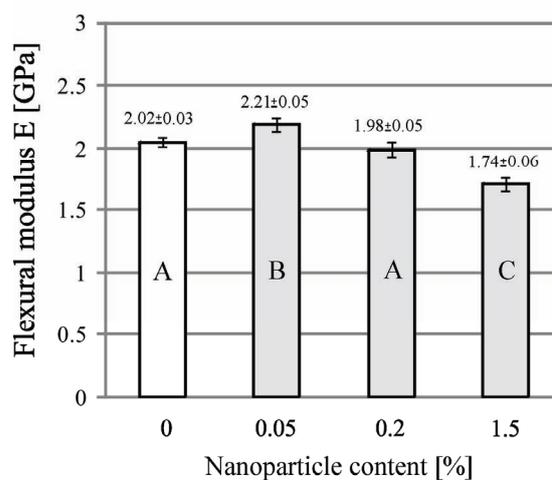


Fig. 2 – Flexural modulus and standard deviations of tested materials. Different letters indicate statistically significant differences at a level of 95%.

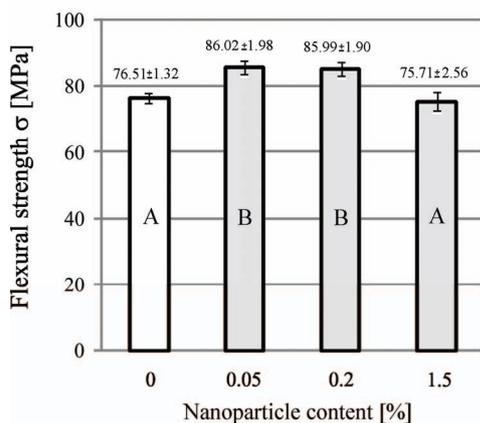


Fig. 3 – Flexural strength and standard deviations of tested materials. Different letters indicate statistically significant differences at a level of 95%.

Differential scanning calorimetry (DSC) curves shown in Figure 4 reveal that the addition of nanoparticles increase glass transition temperatures (T_g) at all contents. The increase in the T_g was moderate and ranges up to 5°C. The highest increase is in specimen groups modified with 0.05% and 0.2% SiO_2 .

The representative fracture surfaces are shown in Figure 5. It can be seen that a brittle fracture mode was present in all specimens, with a characteristic river pattern. Furthermore, the fracture surface showed that the crack propagated between basic material powder particles (Figure 5a, d) and partially through them (Figure 5b, c).

Another feature of the fracture surfaces was the presence of agglomerates, (Figure 6). In Figure 6, SiO_2 agglomerate was shown in secondary electron SEM mode, as degradation of the polymer matrix underneath the agglomerate during the energy dispersive X-ray (EDX) testing process.

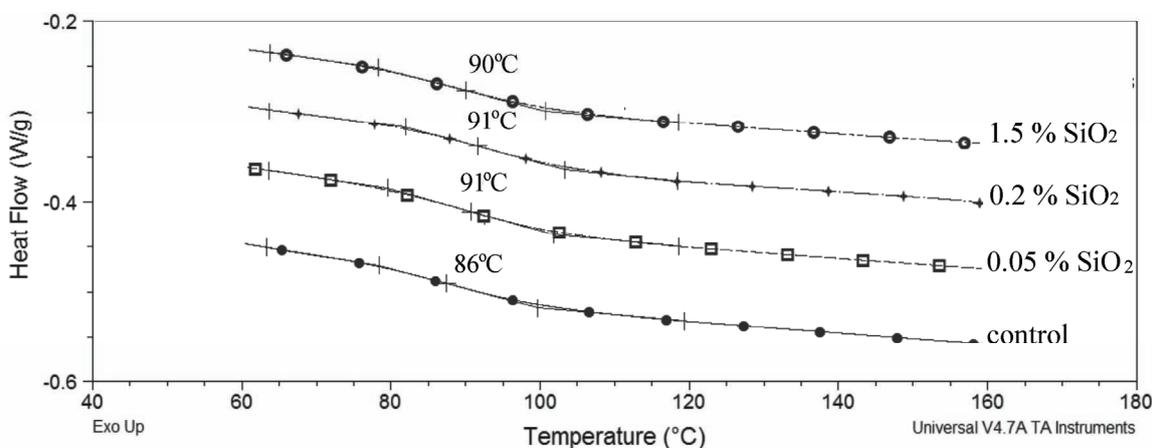


Fig. 4 – Differential scanning calorimetry (DSC) curves of prepared samples with different type and content of nanoparticles.

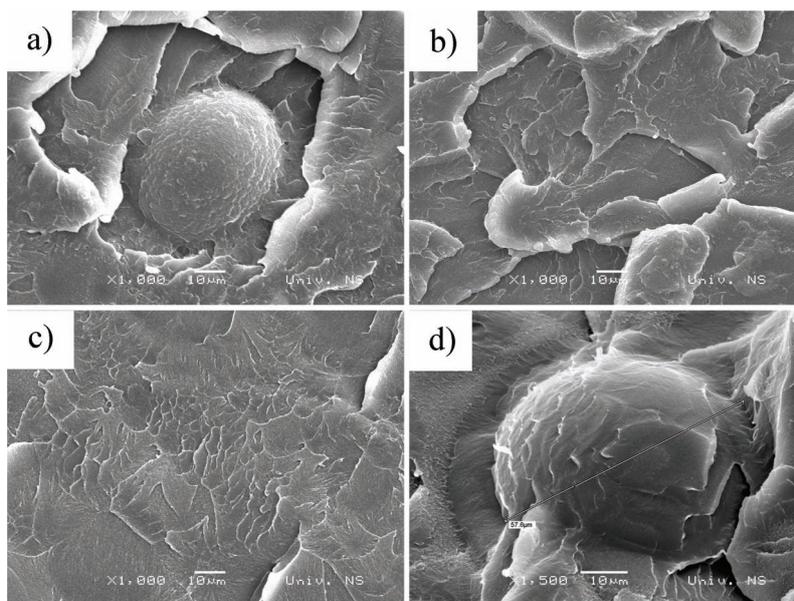


Fig. 5 – Fracture surfaces scanning electron microscope (SEM): a) control specimen; b) 0.05% SiO_2 ; c) 0.2% SiO_2 ; d) 1.5% SiO_2 .

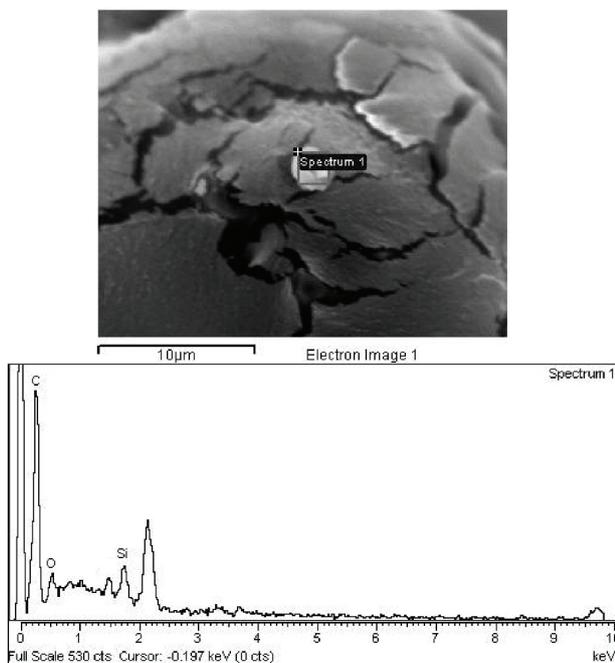


Fig. 6 – Energy dispersive X-ray (EDX) analysis of 1.5 % SiO₂ added to a poly (methyl-methacrylate) specimen.

Discussion

The results presented in this paper show a strong correlation between flexural modulus, flexural strength, glass transition temperatures (T_g), fracture surfaces and EDX analysis. Various investigations suggest that T_g of nanocomposites vary depending on different factors, such as the type of polymer matrix, type and size of nanoparticles and method of preparation^{21–23}. The change in the T_g value of the composite is mainly associated with the immobility of the polymer macromolecules in the interfacial layer within few nanometers of the nanoparticle surface. If the interfacial layer is thin and a small amount of polymer is immobilized, the change in the T_g value is not expected^{24, 25}. The ideal polymer nanocomposite material has a well dispersed nanoparticles with sufficiently small distances between them, so interfacial layers contact each other forming a homogenous reinforced field²³. Interfacial layer thickness can be calculated using the following equation (3)²⁴:

$$D = \frac{d_p}{2} \left[a \sqrt{\left(a_d \frac{1 - y_p}{y_p} \right)} - 1 \right] \quad (3)$$

where: d is the interfacial layer thickness, d_p is the nanoparticle diameter, a_d is the fraction of monomer (polymer) that forms the interfacial layer and y_p is the nanoparticle content in the nanocomposite²⁴. Equation 3 shows that the interfacial layer thickness is directly proportional to the nanoparticle diameter. The results shown in this paper suggest that mechanical properties (flexural modulus and strength) are pro-

portional to T_g . However, in specimens containing 1.5(wt.%) of SiO₂ nanoparticles, T_g is lower compared to other nanoparticle contents. This result suggests that agglomeration occurs. Namely, as agglomerates are considerably larger than nanoparticles (shown in Figure 5), their larger size can cause the increased thickness of interfacial layer. However, as the overall number of agglomerates is considerably lower than the overall number of nanoparticles, the impact of a larger number of interfacial layers may have beneficial effect on increasing the T_g . This finding is supported by the detection of relatively large agglomerates compared to initial particle size in the higher nanoparticle content (1.5%). Also, the deterioration in mechanical properties was generally obtained with the highest nanoparticle content of 1.5%, which can indicate that agglomerates affect the mechanical properties. These results are supported by previous investigations^{19, 20}. Agglomerates influence the drop in mechanical properties in several ways. The most obvious is the decrease in the effective number of reinforcing particles, causing gaps between the interfacial layers (reinforced fields)^{19, 20, 25}. This is confirmed with the results of fracture surface examination. In specimens containing 1.5% SiO₂ fracture surfaces, as well as, in control specimens, the crack propagates between powder particles, while in other specimen groups, the crack propagates through the powder particles. This indicates that the inter powder particle polymer material, polymerized during material synthesis in the control and 1.5% SiO₂ specimen groups is significantly less resistant compared to powder material, so the crack propagates through it, rather than through powder particles. This correlates well to flexural modulus and strength obtained with the control and 1.5% SiO₂ content specimen groups. Another negative effect of higher nanoparticle contents is that large agglomerates can fracture under load, while their fragment or fragments can remain firmly bonded to the PMMA matrix, that is, to the interfacial layer. It must be noted that agglomerates fracture at lower local stresses than nano or micro particles of the same size. The main reason for such behavior is their relatively low cohesive strength, due to the presence of relatively weak secondary bonds (Van der Waals forces, hydrogen, capillary, or by adsorption of foreign substances) between individual nanoparticles^{26, 27}, compared to the ionic or covalent bonds within ceramic fillers. After agglomerate fracture, the stress is suddenly transmitted to the matrix, causing matrix overload and premature failure^{20, 28}.

Conclusion

The incorporation of 7 nm SiO₂ nanoparticles into autopolymerized poly(methyl methacrylate) is beneficial for improving flexural modulus and strength. The most effective content is 0.05% SiO₂. The highest applied concentrations of 1.5% are proved to be ineffective to the level that flexural modulus and strength are lower than that of the unmodified specimen. Agglomeration plays an important role in reducing mechanical properties compared to the control unmodified specimens.

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