



Improving mechanical properties of flowable dental composite resin by adding silica nanoparticles

Poboljšanje mehaničkih svojstava tečnog kompozita dodavanjem nanočestica silicijum-dioksida

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Abstract

Background/Aim. The main drawback of flowable dental composite resin is low strength compared to conventional composite resin, due to a low amount of filler, necessary for achieving low viscosity and ease of handling. The aim of this study was to improve mechanical properties of flowable dental composite resin by adding small amount of nanoparticles, which would not compromise handling properties. **Methods.** A commercially available flowable dental composite resin material was mixed with 7 nm aftertreated hydrophobic fumed silica and cured by an UV lamp. Four sets of samples were made: control sample (unmodified), the sample containing 0.05%, 0.2% and 1% nanosilica. Flexural modulus, flexural strength and microhardness were tested. One-way ANOVA followed by Tukey's test with the significance value of $p < 0.05$ was performed to statistically analyze the obtained results. Furthermore, differential scanning calorimetry (DSC) and SEM analysis were performed. To assess handling properties, slumping resistance was determined. **Results.** It was found that 0.05% is the most effective nanosilica content. All the tested mechanical properties were improved by a significant margin. On the other hand, when 0.2% and 1% nanosilica content was tested, different results were obtained, some of the mechanical properties even dropped, while some were insignificantly improved. The difference between slumping resistance of unmodified and modified samples was found to be statistically insignificant. **Conclusions.** Low nanosilica addition proved more effective in improving mechanical properties compared to higher additions. Furthermore, handling properties are unaffected by nanosilica addition.

Key words:

composite resins; surface properties; material testing; nanoparticles; silicon dioxide.

Apstrakt

Uvod/Cilj. Osnovni nedostatak tečnih kompozitnih materijala u odnosu na konvencionalne kompozitne materijale su lošija mehanička svojstva. Ovo je posledica manje količine neorganskog punioca u materijalu u odnosu na standardne kompozitne smole kako bi se dobio materijal manje viskoznosti. Cilj ovog rada bio je poboljšanje mehaničkih svojstava tečnog kompozita dodavanjem male količine nanočestica, čime se ne utiče na način upotrebe ovih materijala. **Metode.** Komercijalni tečni kompozitni materijal umešan je sa modifikovanom hidrofobnom nanosilikom veličine čestica 7 nm, i polimerizovan LED svetlosnim izvorom. Napravljene su četiri grupe uzoraka: kontrolna grupa (nemodifikovana), grupa sa dodatkom 0,05%, 0,2% i 1% nanosilike. Ispitivan je modul elastičnosti, savojna čvrstoća i mikrotvrdoća, dok su rezultati statistički obrađeni jednostrukom analizom ANOVA i Tukey-ovim testom sa faktorom značajnosti $p < 0,05$. Takođe, izvršene su i diferencijalnoskenirajuća kalorimetrija (DSC) i SEM analize. Za određivanje mogućnosti rukovanja, iskorišćena je metoda otpornosti na sleganje. **Rezultati.** Ispitivanja su pokazala da najmanja koncentracija nanosilike od 0,05% značajno povećava sva mehanička svojstva. S druge strane, dodatak od 0,2% i 1% daje različite rezultate, gde mehanička svojstva čak opadaju ili se povećavaju, ali ne u značajnoj meri. Otpornost na sleganje kod nemodifikovanih i modifikovanih uzoraka nije bila statistički značajna. **Zaključak.** Nizak sadržaj nanosilike pokazao se kao efikasniji u poboljšanju mehaničkih svojstava u poređenju sa višim sadržajima nanosilike. Način upotrebe uzoraka kod kojih su dodate nanočestice nije bio promenjen u odnosu na uzorke nemodifikovanog tečnog kompozita.

Ključne reči:

smole, kompozitne; površina, svojstva; materijali, testiranje; koloidi; silicijum dioksid.

Introduction

The first generation of flowable dental resin composites was introduced in the middle of 1990s¹. They were developed in response to requests for easy handling properties². The low viscosity of the flowable composite simplifies their clinical placement and increases the range of applications in clinical practice^{3,4}. Flowable composites were created by reducing the filler content by 20–25%¹ to reduce the viscosity of the mixture. As a result, these materials are less rigid and have a modulus of elasticity 20–30% lower than conventional hybrid composites^{5,6}, but higher volumetric shrinkage and polymerization shrinkage stress⁶. Flowable composites have been proposed as liners⁷, fissure sealants and restorative materials for small cavities⁸. Their usage is indicated in non stress bearing areas, because of their low mechanical properties. It was shown that the mechanical properties of flowable composites, such as diametral tensile strength, compressive strength, and fracture toughness, are generally about 60–90% of those of conventional composites^{1,9}. Furthermore, flow composite wear resistance is lower compared to conventional composites and especially highly filled composites¹⁰.

As flowable composites exhibit a relatively low viscosity, one notable way of improving their mechanical properties is adding nanoparticles. Conventional composite mechanical properties, radiopacity and optical properties have been improved by addition of inorganic nano particles. The most common particles are titanium dioxide^{11–13} and silica¹⁴, which were added to the composite resin. However, this research may be one of the first studies of flow composites reinforced with nanoparticles.

In this work, an attempt was made to increase flexural strength, flexural modulus of elasticity and hardness of a typical commercially available flowable dental composite resin, by adding silica nanoparticles, without an adverse effect on handling properties. This paper is the result of continuing collaboration program among Faculty of Medicine, Faculty of Technology and Faculty of Technical Sciences of the University of Novi Sad, Serbia.

Methods

In this paper, commercially available Ivoclar Vivadent Te-Econom Flow[®] composite resin material was used as a basis. This material is based on dimethacrylate paste (Bis-GMA, Triethylene glycoldimethacrylate, Urethane dimethacrylate), with inorganic fillers. In addition to this, initiators, stabilizers and pigments were present, with an overall content of 1% wt¹⁵. Te-Econom flow was mixed with Evonik AEROSIL[®] R812 fumed silica aftertreated with hexamethyldisiloxane (HMDS), having hydrophobic properties and particle size of 7 nm¹⁶. Mixing was done by using a Proxxon FBS12 100 W 3000–15000 min⁻¹ precision drill/grinder, with a Dentsply lentulo spiral-paste carrier #4 attached. The lentulo spiral was immersed in composite resin material – nanosilica mixture, poured into a 2 ml predarkened syringe tube, as shown in Figure 1. After one hour mixing, the drill/grinder with lentulo attached was extracted, syringe plunger was inserted into the sy-

ringe tube and the mixture was injected into elastomer molds, made from Bego WiroSil[®]. Curing was done by exposure to LED curing unit (Bluephase C8, 8-mm tip, Ivoclar Vivadent AG). All photopolymerizing steps were performed with a light guide held perpendicularly and within 2 mm of the material surface. The high power curing mode (HIP) was employed throughout the study, while the light output from the curing unit was verified by a built-in radiometer. The intensity of curing light was 1,000 mW/cm² and the length of exposure was 20 s (disc samples) and 20 + 20 s (square samples). After curing, 1500 grit SiC paper was used to get the desired shape and dimensions of samples. Dimensions were verified by a Hyundai micrometer, accurate to 0.01 mm.

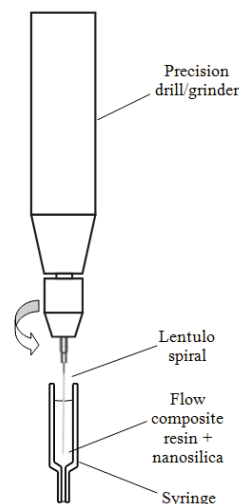


Fig. 1 – Mixing method, by using a precision drill/grinder, lentulo spiral and syringe tube.

Control samples without nanosilica addition were compared to three sets of samples with nanosilica in various concentrations. Three sets of nanocomposite resin material samples were made: with 0.05%, 0.2% and 1% nanosilica. Flexural modulus of elasticity and flexural strength were determined by using a Toyoseiki AT-L-118B tensile testing machine, with a crosshead speed of 50 mm/min. The 3-point bending method was used with the distance between the supports of 20 mm. Specimens dimensions were 2 × 2 × 22 mm. Flexural modulus of elasticity was calculated in accordance to the following equation:

$$E = \frac{Fl^4}{4dbh^3}$$

where l is the distance between the supports [mm], d is the displacement [mm] for a given load F in [N], b is specimen width [mm] and h is specimen height [mm].

Flexural strength was calculated by using the following equation:

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

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].

Microhardness was determined by using a Huyin HVS-1000 Vickers microhardness tester, by applying 100 g load and 15 s dwell time. Microhardness was measured on 6 mm diameter samples with a height of 2 mm. The common Vickers microhardness and microhardness equation was used:

$$HV = \frac{1.8544 F}{d^2}$$

where F is applied load [daN] and d is indentation diagonal [mm].

To determine handling properties of unmodified and modified materials, slumping resistance was used. It was determined by using the methodology shown in the work by Lee et al.¹⁷. Namely, an equal amount of flow composite placed into a syringe was extruded onto a slide glass. The resulting bubble was left to slump for 10 s and after that was light – cured. Afterwards, it was measured by a micrometer accurate to 0.01 mm in two aspects, its height and diameter. Height to diameter ratios indicate the slumping resistance: if this ratio is high, slumping resistance is lower and vice versa. These measurements were repeated 10 times for each sample at room temperature.

Mechanical properties and slumping resistance of various samples were statistically analyzed using the ANOVA one-way analysis of variance, followed by Tukey's test with the significance value of $p < 0.05$ ($\alpha = 0.05$).

To determine thermal properties of obtained materials, differential scanning calorimetry (DSC) analysis was performed. A TA Instruments Q20 DSC device was used, in the temperature range from 40 to 250° C.

Fracture surfaces were examined by JEOL JSM-6460LV scanning electron microscope (SEM), operating at

25 kV. The specimens were previously coated with gold, using the Balltec SCD-005 device. Per one sample from each flexural strength group was observed. For the purpose of testing, the sample with mechanical properties closest to the average was chosen.

Results

The flexural modulus of elasticity, flexural strength and Vickers microhardness results of the control samples (without nanosilica) and samples with different silica content, as well as the results of one-way ANOVA statistical analysis are shown in Tables 1–3, respectively. The statistical analysis results are represented by the p -parameter. If $p < 0.05$, the difference between the unmodified and nanosilica modified sample is significant.

The flexural modulus of elasticity of nanosilica modified samples was higher than that of the unmodified (control) sample for all the tested samples with various nanosilica content (0.05%, 0.2%, 1%) (Table 1). However, only the samples containing 0.05% and 0.2% nanosilica exhibited statistically significant difference in relation to the unmodified sample. The highest flexural modulus of elasticity was found on the smallest nanosilica content, with a decreasing trend towards higher concentrations. It can be noted that by adding nanosilica, the standard deviation increases, which was the reason why the sample containing the highest concentration of nanosilica (1%) exhibited statistically insignificant rise in flexural modulus of elasticity.

Table 2 shows the results of flexural strength of unmodified and modified samples. It can be seen, that the flexural strength of samples containing 0.05 and 1% was higher than that of the control samples. However, the flexural

Table 1
Flexural modulus of elasticity of the control sample and nanosilica modified samples, with p -values included (derived from ANOVA)

Nanosilica content (%)	Flexural modulus of elasticity E [GPa]		p
	mean	standard deviation	
0 (control sample)	3.01	0.18	–
0.05	3.81	0.25	0.00461*
0.2	3.54	0.23	0.00572*
1	3.43	0.24	0.05838

*Values of $p < 0.05$ indicate that the difference between the control sample and nanosilica modified sample is significant with the probability of 95%.

Table 2
Flexural strength of the control sample and nanosilica modified samples, with p -values included (derived from ANOVA)

Nanosilica content (%)	Flexural strength σ_{SM} [MPa]		p
	mean	standard deviation	
0 (control sample)	99.48	1.82	–
0.05	103.92	1.75	0.01902*
0.2	94.20	2.45	0.02509*
1	101.58	5.00	0.47356

*Values of $p < 0.05$ indicate that the difference between the control sample and nanosilica modified sample is significant with the probability of 95%.

Table 3
Microhardness HV0.1 of the control sample and nanosilica modified samples, with p -values included (derived from ANOVA)

Nanosilica content (%)	Microhardness HV0.1		p
	mean	standard deviation	
0 (control sample)	26.67	0.85	–
0.05	31.40	1.14	0.00024*
0.2	29.80	2.21	0.07095
1	25.40	1.44	0.10959

*Values of $p < 0.05$ indicate that the difference between the control sample and nanosilica modified sample is significant with the probability of 95%.

strength of the sample with 0.2% nanosilica was lower than that of the unmodified sample. It must be noted that, similarly to the previous results, standard deviations of modified samples were higher than that of unmodified, except from the sample containing 0.05% nanosilica. This particular sample was the only one tested with flexural strength statistically significantly higher than the control sample. On the other hand, sample with 0.2% nanosilica, although its p -factor was lower than 0.05, its flexural strength was not significantly higher compared to the unmodified sample.

The microhardness (HV0.1) results are shown in Table 3. The highest microhardness was measured on sample containing 0.05% nanosilica. Microhardness drops as the nanosilica content rised. Furthermore, the microhardness of a sample containing 1% nanosilica was lower than the control sample. Statistically, only the sample with 0.05% nanosilica had a significantly higher microhardness compared to the control sample. Standard deviations of all the modified samples were higher than that of the unmodified samples.

A lateral view of cured flowable composite without and with nanosilica is shown in Figure 2. It can be seen that the shape of the bubbles obtained with various nanosilica concentrations is the same. Slumping resistance represented by bubble height to diameter ratios is shown in Table 4. Al-

though there was a moderate rise in the bubble aspect ratio, the difference between the control sample (non-modified) and nanosilica added samples (0.05 and 0.2%) was not statistically different, as indicated by the factor p .

DSC curves of dimethacrylate paste and nanosilica composites showed that a silica content in the examined range, did not have an influence on the glass transition temperature (T_g), (Figure 3), where T_g for all samples was between 95.22 and 95.88°C. Glass transition temperature

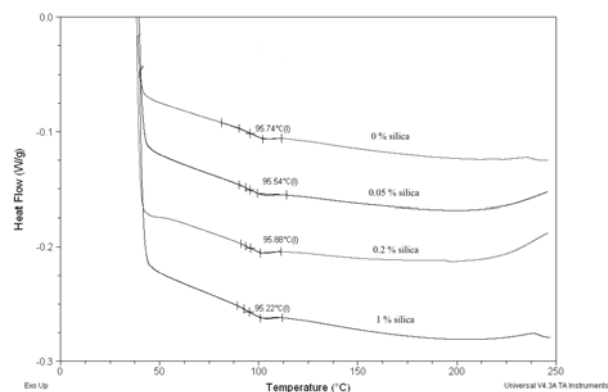


Fig. 3 – Differential scanning of calorimetry (DSC) thermograms of Te-Econom Flow®/silica nanocomposites.



Fig. 2 – A lateral view of cured flowable nonmodified and modified samples after 10 s slumping at room temperature.

Table 4
Aspect ratios of unmodified and modified samples, with p -values included (derived by ANOVA)

Nanosilica content (%)	Aspect ratio		p
	mean	standard deviation	
0 (control sample)	0.541	0.035911	–
0.05	0.543	0.038449	0.941059*
0.2	0.553	0.038536	0.501769*
1	0.580	0.041927	0.051052*

*Values of $p > 0.05$ indicate that the difference between the control sample and nanosilica modified sample is not significant with the probability of 95%.

variations are usually correlated to the polymer immobility in interfacial layer¹⁸. Thus, this indicates that the interfacial layer is relatively thin, meaning that a small amount of polymer is immobilised, having a low influence on Tg.

SEM micrograph showing clustered silica nanoparticles before mixing is shown in Figure 4. Fracture surface micrographs obtained by scanning electron microscopy (SEM) are shown in Figure 5. Figure 5 reveals a similar fracture mode for all the samples, unmodified and modified. A brittle type of fracture was noticed, with clearly visible inorganic filler particles. However, the secondary electron (SE) and especially the backscattering (BS) mode of operation at higher magnifications showed the existence of chemically different particles in comparison to the material matrix (Figure 6). These particles had the size of approximately 100 × 50 nm, which was considerably larger than the average of 7 nm of the Evonik AEROSIL® R812 fumed silica aftertreated with

HMDS. Therefore, the detected particles may closely correspond to inorganic particles, fractured in the process of material testing.

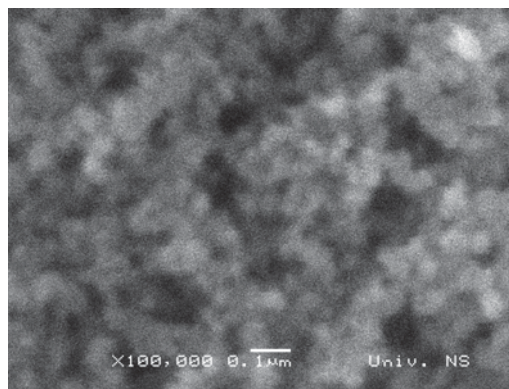


Fig. 4 – Clustered silica nanoparticles before mixing.

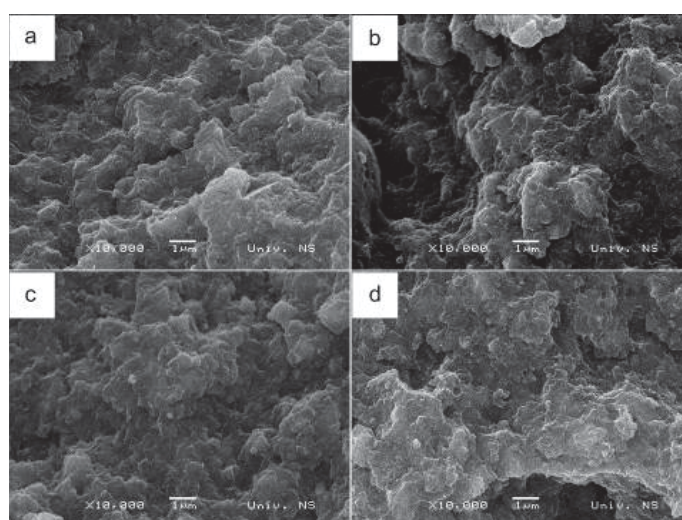


Fig. 5 – Fracture surfaces showing similar morphology:
a) unmodified; b) modified with 0.05%; c) with 0.2%; d) with 1% nanosilica.

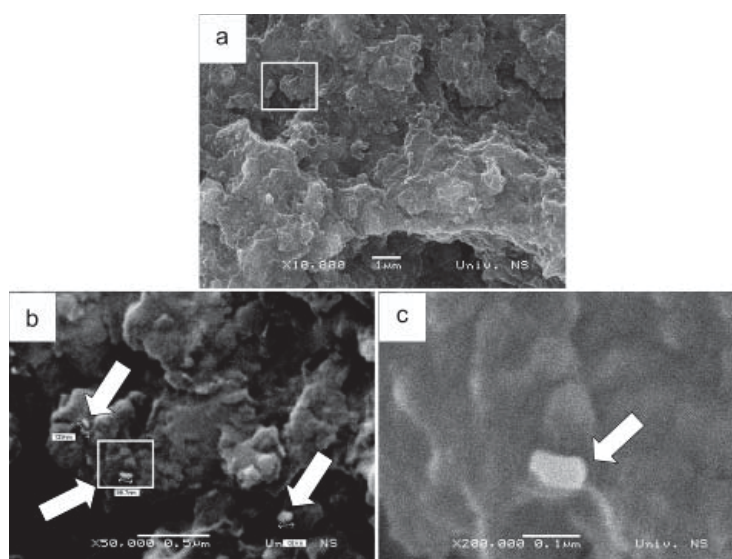


Fig. 6 – A sample modified with 1% nanosilica, showing inorganic filler particles:
a) Fig. 5d fracture surface – detail square is magnified in b); b) Arrows show inorganic particles in BS mode – detail square is magnified in c); c) An inorganic particle, magnified.

Discussion

The presented results of mechanical properties undoubtedly indicate that nanosilica content is not proportional to the benefits of such modification. Namely, even when relatively low nanosilica concentrations are considered, high and medium nanosilica content (1 and 0.2%) do not offer the highest rise in mechanical properties. Furthermore, samples containing 0.2% and 1% nanosilica have even lower flexural strength and microhardness than the unmodified sample, respectively (Tables 2 and 3). However, flexural modulus of elasticity of all the modified samples is higher in comparison to the unmodified sample. This proves that the most pronounced benefit of adding nanoparticles is the rise in flexural modulus of elasticity. This result has been noticed by other authors as well¹⁹⁻²¹. On the other hand, although average values of flexural modulus of elasticity are higher compared to the unmodified, control sample, the difference is not significant for all the samples. Although 1% nanosilica added composite resin offers 14% higher flexural modulus of elasticity, the difference is not significant, due to the fact that the standard deviation is higher for the modified in comparison to unmodified samples.

Overall, the optimal nanosilica content is the lowest, 0.05%. Such concentration offers significantly higher flexural modulus of elasticity, flexural strength and microhardness in all the tests performed in this study. This result is in accordance with some of the latest published results, where higher nanoparticle concentrations might lead to an uncontrollable and stochastic forming of agglomerates¹². By agglomerating, a large number of nanosilica particles become joined together, leading to nonhomogenous strengthening due to a nonuniform distribution of nanoparticles²². An indirect confirmation of the agglomerate occurrence in higher nanosilica concentrations comes from DCS thermograms.

Namely, DSC thermograms show marginally small variations in T_g, which means that the overall interfacial layer volume of all the modified samples is the same, regardless the nanosilica content. Uniform distribution of nanoparticles of the same size would result in a significant difference in T_g, in favor of the higher nanosilica content, however, this does not occur. The main reason might be agglomeration in the samples containing higher amount of nanosilica. Nevertheless, this theory deserves further attention of researchers, especially by testing low nanoparticle addition in other polymer and composite materials.

All the benefits reflected by mechanical properties were not gained at the cost of handling properties. This was shown by the slumping resistance results, which show statistically insignificant differences between the results obtained by using unmodified and nanosilica modified samples.

Conclusion

According to the presented results obtained by testing the Te-Econom Flow material it could be concluded that low nanosilica addition is more effective in rising mechanical properties of modified composite resin samples, compared to higher nanosilica additions. Also, flexural modulus of elasticity, flexural strength and microhardness may be improved at lower cost than if a higher nanosilica addition is considered. More effective reinforcement of the basic material with lower amount of nanosilica may be the result of agglomeration, which affect more the samples containing a higher amount of nanosilica. Low nanosilica addition of up to 1% does not result in a statistically significant change in slumping resistance, indicating unchanged handling properties. Other basic material and nanoparticle type require careful optimization in term of nanoparticle concentration to achieve optimal mechanical properties.

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