



# Effect of silica filler on properties of PMMA resin

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## ABSTRACT

**Purpose:** Of this paper was to investigate the effect of silica nanofiller addition to PMMA-based denture material. The null hypothesis was that no difference exists between the mean flexural strength, hardness, sorption among materials without and with different content of silica filler.

**Design/methodology/approach:** The nanosilica was introduced into “powder” component of commercially available PMMA resin for dentistry in concentrations 2, 5 and 10%. The SEM observations were made to confirm dispersion quality. To confirm presence of silica filler the X-ray microanalysis have been made. The influence of nanosilica addition on flexural strength, flexural modulus, hardness and sorption were investigated. Samples were stored at distilled water and ethanol solution. Statistical analysis were prepared with the one-way or the two-way analysis of variance ANOVA ( $\alpha=0.05$ ), and Newman-Keuls significant difference post hoc test was used to determine the differences between mean values ( $\alpha=0.05$ ).

**Findings:** The result show that all investigated properties were changed after silica filler addition. Initially flexural strength decreased, but after accelerated again in ethanol incised. Flexural modulus and hardness increased. Sorption was decreased in both aging liquids.

**Research limitations/implications:** Limitations resulting from the specificity of the conditions of laboratory tests and aging conditions so it does not allow to fully translate obtained results to expected results of clinical trials.

**Practical implications:** The PMMA drawback is still insufficient mechanical properties, so it can be easily damaged during an accidents or when a patients applies high mastication force to the denture which show areas for further mechanical properties improvement. One of the ways of improving the mechanical properties of PMMA based materials may be nanoparticle addition, including commonly used nanosilica fillers.

**Originality/value:** Influence of destructive plasticizing solutions on chosen properties of materials with different concentrations of silica fillers have been investigated.

**Keywords:** PMMA; Denture; Silica filler; Aging; Flexural strength; Hardness; Sorption

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## PROPERTIES

## 1. Introduction

The importance of poly(methyl-methacrylate) (PMMA) resins in dentistry is absolutely evident. The PMMA based materials are still the leading material for dentures today. The injection-molded thermoplastic materials, such as acetal or polyamide, constitute only a partial alternative [1] and show lower modulus of elasticity than the PMMA materials [2]. Despite that acetal or polyamide allows to improve esthetics of the denture [3], due to lower modulus of elasticity than in the case of wires clasp, the dentures made of those polymers present lower retentive force [4]. Additionally injection-molded denture base materials show the tendency to color deterioration [5] and higher *Candida* spp. biofilm formation than PMMA materials [6], though they have lower sorption and solubility [7] and are residual monomer [8]. The advantages of PMMA based materials also include esthetic properties like color true to life and transparency, good adaptation to teeth, ease of operation during dentures manufacturing processes and possibility of repair [9]. However PMMA drawback is still insufficient mechanical properties, so it can be easily damaged during an accident or when a patient applies high mastication force to the denture which shows areas for further mechanical properties improvement [10-12]. One of the ways of improving the mechanical properties of PMMA based materials may be nanoparticle addition, including commonly used nanosilica fillers. Nanosilica fillers have been successfully used with many polymeric and dental composite materials, and experimental studies have shown favorable effects on mechanical properties [13-17]. Nevertheless, nanoparticle loading also may have consequences in decreased mechanical properties [18,19].

In this research study, the effect of silica nanofiller addition to PMMA-based denture material was investigated. The approach used was aimed at determining general properties by testing flexural strength, hardness and sorption. Flexural strength and flexural modulus are one of the most important mechanical properties of acrylic resins. International standard for dentistry base polymers [20] for heat cured denture base resins established that minimal limit of flexural strength shall not be less than 65 MPa and flexural modulus at least 2 GPa. Hardness is not standardized by ISO standard for denture base materials but has been found to be sensitive to the residual monomer content in the polymerized materials and it can be used as an indirect method of evaluating polymerization depth of resin-based composite materials [22,23].

Sorption and solubility can cause dimensional instability which can cause internal stresses that may

result in crack formation [24,25]. Liquids like water also interact with the polymer chains and generate some effects like reversible loosening or plasticization of the structure, solvation or reversible rupture of weak interchain bonds, and irreversible disruption of the polymer matrix [26]. Studies on the water sorption of denture resin have shown that sorbed water can be one of the causes of the decrease of mechanical properties [25,27]. It should be also noted that leaching out of traces of unreacted monomer and water-soluble additives into the oral environment can also produce a soft tissue reaction [9]. Consequently, the sorption and solubility are the serious problems that affect durability, and for those materials should be as low as possible. According to this ISO standard [20] water sorption for heat-cured denture base materials should not exceed  $32 \mu\text{g}/\text{mm}^3$ . In this work all investigations were made for samples stored in distilled water and ethyl alcohol solution to determine destructive effect of plasticizing solutions on modified materials.

The null hypothesis was that no difference exists between the mean flexural strength, hardness, sorption among materials without and with different content of silica filler.

## 2. Materials and methods

As a matrix material commercially available heat cured denture base resin Vertex Rapid Simplified (Vertex-Dental B.V., The Netherlands) was used. The nanosilica filler after treated with a methacrylsilane AEROSIL R711 (EVONIK Industries, Germany) was added to "powder" component in concentrations by weight 2, 5 and 10% and mixed with planetary ball mill Pulverisette 5 (Fritsch, Germany) at 400 rpm for 10 minutes.

The polymerized material samples  $40 \times 40 \times 1,5$  mm for SEM examinations were prepared with standard flasking procedures with dental stone and before investigations were immersed in liquid nitrogen, broken and silver sputtered. The observations were made on obtained fractures with Zeiss SUPRA 35 scanning electron microscope at the accelerating voltage of 5 and 8 kV.

The X-ray microanalysis has been made on the Zeiss SUPRA 35 scanning electron microscope using the secondary electrons detection. To confirm presence of silica filler (qualitative microanalysis) the X-ray microanalysis has been made with the EDAX Trident XM4 dispersive radiation spectrometer at the accelerating voltage of 15 kV.

The samples for flexural strength were made with two stages technique, as described in [20]. First, the wax plates  $65 \times 40 \times 5$  mm were prepared and flasking were made using standard procedures with dental stone. Acrylic plates (investigate materials and control group) was polymerized in the usual way according with manufacturer instructions. For each experimental combination (material-aging conditions) two plates were prepared and next 5 samples from it were cut. The samples were preliminarily wet-ground to align it on abrasive papers (Struers A/S: Copenhagen, Denmark) in the grit size sequence 120, 220 and 320 to eliminate any possible unevenness and to standardize the dimensions. Following this grinding process, the dimensions controlled with caliper were  $64 \times 10$  mm  $\times$  3.3 mm. The obtained PMMA samples were thoroughly rinsed, and their surfaces were wet-ground by 500-grit abrasive paper to remove the scratches made by the previous grinding procedure and finally their surfaces were polished with 6  $\mu$ m diamond paste (Struers A/S: Copenhagen, Denmark). The samples were aged at  $37 \pm 1^\circ\text{C}$  in distilled water for  $50 \pm 1$  h and 14 days  $\pm$  2 h and in ethyl alcohol solution for 14 days  $\pm$  2 h.

After aging the specimens were inserted in universal testing machine (ZWICK Z250, Zwick GmbH & Com: Ulm, Germany) with no delay (Fig. 1) and flexural testing was performed at a cross-head speed of 5 mm/min. The flexural strengths ( $\sigma$ ) in MPa were calculated according to the formula below:

$$\sigma = \frac{3F_{\max} * l}{2bh^2} \quad (1)$$

where  $F_{\max}$  is the maximum force (N);  $l$  is the distance between the supporter arms of the machine in mm (50 mm);  $b$  is the width of the specimens in mm;  $h$  is the height of the specimens in mm ( $b$  and  $h$  were measured immediately prior to water storage).

Flexural modulus ( $E$ ) in GPa was calculated from the following equation:

$$E = \frac{F_1 l^3}{4bh^3 d} \quad (2)$$

where  $d$  is the deflection in mm corresponding to load  $F_1$  at a point in the straight-line portion of the load-deflection curve.

The samples for hardness test were made similar like for flexural strength test, but from each material five plates (dimensions  $50 \times 50 \times 5$  mm) were prepared. The plates were preliminarily wet-ground to align it on abrasive papers (Struers A/S: Copenhagen, Denmark) in the grit size

as described above to get final thickness of 4 mm, finally their surfaces were wet-ground by 500-grit abrasive paper and polished with 6  $\mu$ m diamond paste (Struers A/S: Copenhagen, Denmark). The samples were aged at  $37 \pm 1^\circ\text{C}$  in distilled water for  $50 \pm 1$  h and 14 days  $\pm$  2 h and in ethyl alcohol solution for 14 days  $\pm$  2 h. For hardness measurements ball indentation hardness test were used [21]. A 5 mm diameter steel ball was intended into a specimen with an initial load of 9.8 N and is increased to a 358 N or 132 N load for samples stored in distilled water or ethanol solution respectively for 30 seconds. The depth of the resulting deformation was measured and the surface area of the impression was calculated, and the hardness ( $H$ ) was expressed in  $\text{N}/\text{mm}^2$  (MPa). Measurements were made 10 times at randomly chosen locations on 5 specimens for each condition, the mean value was recorded, and the hardness values was then calculated.

The sorption of the obtained composites was determined using a method based on the ISO standard. Test samples measuring 50 mm in diameter and 0.5 mm in thickness were cured in stainless steel molds. Cross-linked samples were removed from the mold with tweezers, and their quality was examined to determine whether it contained any bubbles or the surfaces were flat. Fifteen samples of each material were created, five for each material-aging conditions combination. The samples were weighed on an AS 110/C/2 analytic scale (Radwag: Radom, Poland) with a measurement accuracy of 0.1 mg and were placed inside desiccators containing freshly dried silica gel. Next the desiccators were placed in a dryer at  $37 \pm 1^\circ\text{C}$ . The samples drayed and were weighed every 24 h, until the daily changes in mass were no higher than 0.2 mg. Stable values were registered as conditioned mass ( $m_1$ ). After drying, the diameter and thickness of the samples were measured. Next the samples were placed in a chamber and aged at  $37 \pm 1^\circ\text{C}$  in distilled water for 7 and 14 days  $\pm$  2 h and in ethyl alcohol solution for 14 days  $\pm$  2 h. After aging, the samples were successively removed from liquids, visible moisture was removed using filter paper and the samples were additionally air-dried for approximately 15 s and next mass  $m_2$  was registered. The samples were again dried as described previously until they reached a stable mass, denoted as  $m_3$ . The sorption was calculated using the following equations:

$$W_{sp} = \frac{m_2 - m_3}{V} \quad (3)$$

where  $W_{sp}$  is sorption in  $\mu\text{g}/\text{mm}^3$ ,  $m_2$  is the mass after aging in  $\mu\text{g}$ , and  $m_3$  is the mass after the second drying step,  $V$  is the sample volume in  $\text{mm}^3$ .

The results were subjected to statistical analysis with a Statistica 10 software. The distributions of the residuals were tested with Shapiro-Wilk test and the equality of variances were tested with Bartlett test. When the distributions of the residuals were normal and the variances were equal the one-way or the two-way analysis of variance ANOVA ( $\alpha = 0.05$ ), and Newman-Keuls significant difference *post hoc* test was used to determine the differences between mean values ( $\alpha = 0.05$ ).

### 3. Results

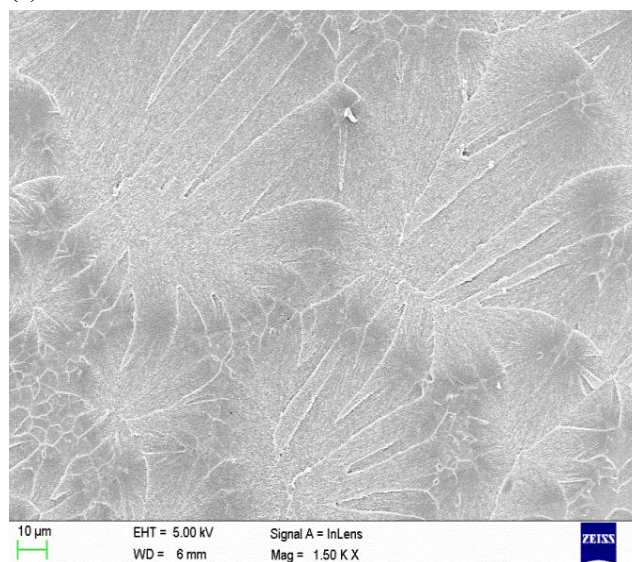
For commercially available resin typical structure showing presence of peerless from “powder” component of “powder-liquid” system have been noted (Fig. 1). The presence of nanosilica in materials has been confirmed with X-ray microanalysis (Figs 2b, 2c). The SEM investigation show that dispersion of silica fillers in prepared materials was not homogenous (Fig. 2). Numerous small aggregations measuring from few dozen nanometres to few hundred have been observed (Fig. 2a). Also large aggregations measuring more than 1  $\mu\text{m}$  have been detected (Fig. 2c) and the number of those aggregations increased with the increasing of the filler content. Especially in material with 10% of filler content extra-large aggregations measured even over 10  $\mu\text{m}$  have been observed (Fig. 2d). Some areas measuring 10-20  $\mu\text{m}$  were free from silica filler, which was related with primary morphology of the “powder” component.

The flexural strength results were presented in Fig. 3. The statistically significant influence of filler concentration and aging liquid on the flexural strength were noted (Table 1 and Table 2). After two-days in distilled water for filled materials flexural strength decreased with increasing the filler content. After two weeks in distilled water the flexural strength values for materials with additive were still lower than for resin without filler, but for composite with 10% of filler it increased significantly. Aging in ethanol solution decreased strongly flexural strength of all materials, but for composite materials higher values were noted than for unmodified resin. The best results were noted for material with 2% of filler.

The flexural modulus results were presented in Fig. 4. The statistically significant influence of filler concentration and aging conditions on the flexural modulus were noted (Table 3 and Table 4). Increasing filler content caused increasing of flexural modulus values (Fig. 4), but only

after two weeks in distilled water statistically significant differences were noted (Table 4). Aging in ethanol solution reduced by half flexural modulus values. The most softening effect of the aging was the most visible for unmodified resin, and the lowest for material with the 10% of silica filler.

(a)



(b)

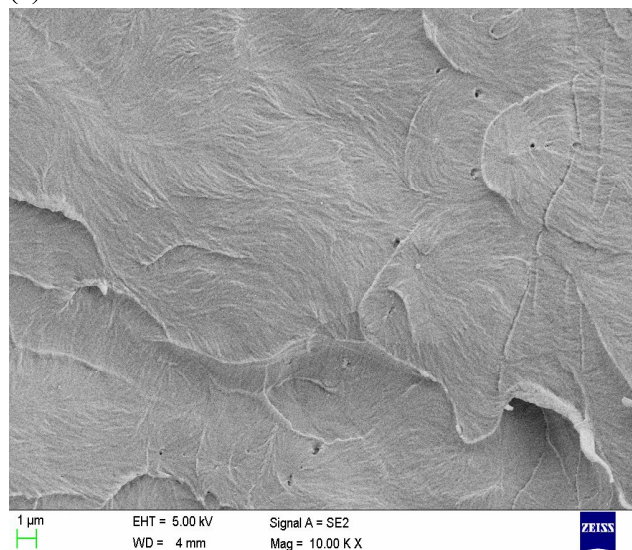


Fig. 1. Exemplary micrographs showing fracture of the resin without silica filler; typical structure after using “powder-liquid” system clear visible with peerless from “powder component (a) and enlargement showing fillers-free material (b)

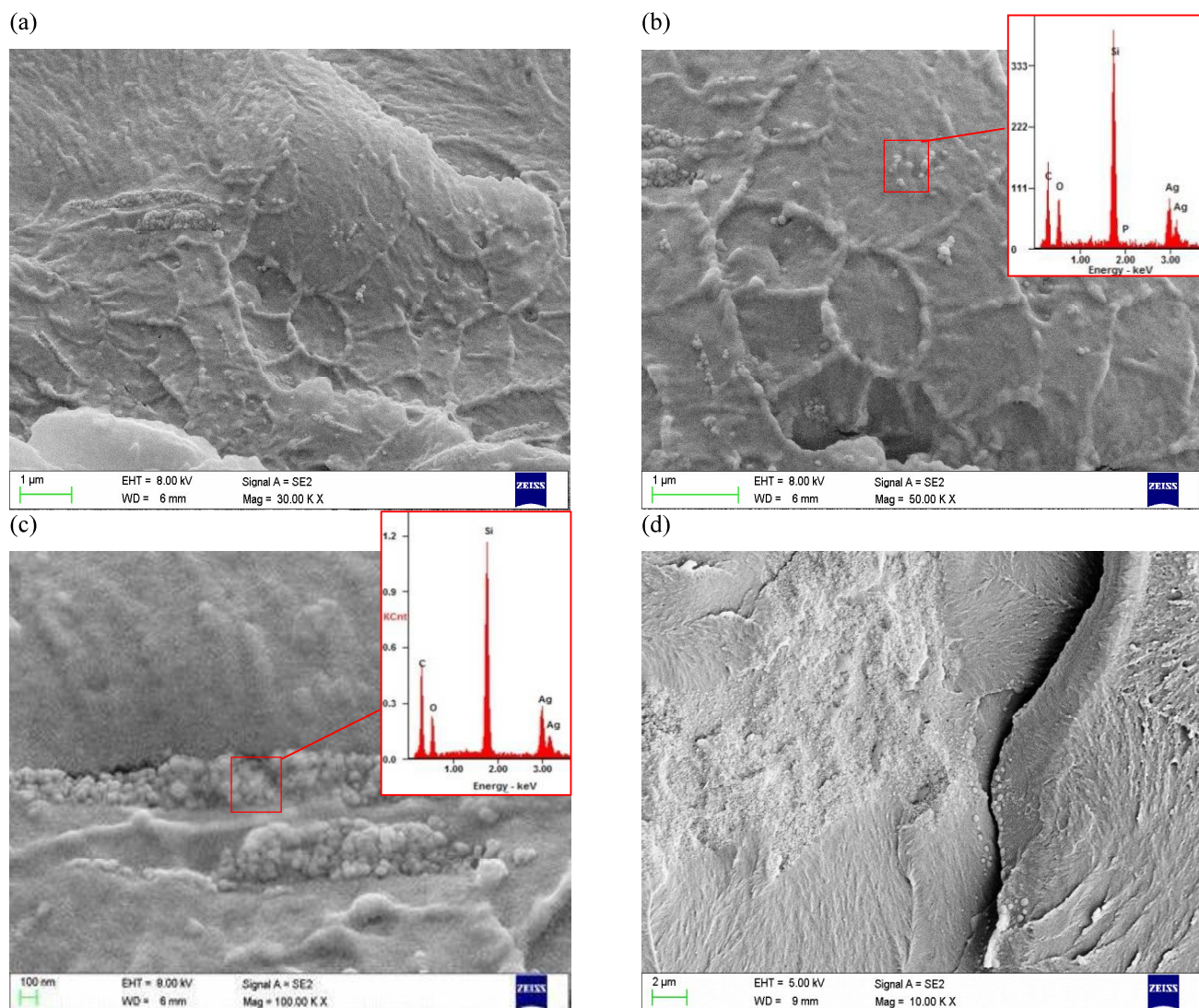


Fig. 2. Micrographs showing fracture of the composite with 2% of silica filler (a) and two exemplary enlargements with the results or microanalysis (b) and (c), extra-large aggregation from material with 10% of silica filler (d)

Table 1. The two-way analysis of variance results for flexural strength (statistically significant when  $P < 0.05$ )

	Sum of squares	Degrees of freedom	Mean square	F-test statistic value	P
Aging conditions	14796.4	2	7398.2	212.5	<0.0001
Filler content	1156.5	3	385.5	11.1	<0.0001
Aging conditions × Filler content	2029.6	6	338.3	9.7	<0.0001

Table 2. The results of multiple comparisons with Newman-Keuls *post hoc* test for flexural strength,  $P < 0.05$  indicated significant difference\*

Aging solution, aging time	Filler content, %			
	0	2	5	10
DW, 48 hours	A; z	A,B; z	B; z	C; z
DW, 14 days	A; z	B; z	B; z	B; y
ETH, 14 days	A; y	B; y	B; z	A,B; x

\*Groups with the same uppercase letters; (A-C) for each row and lowercase letters; (x-z) for each column are not significantly different at the  $P < 0.05$  level

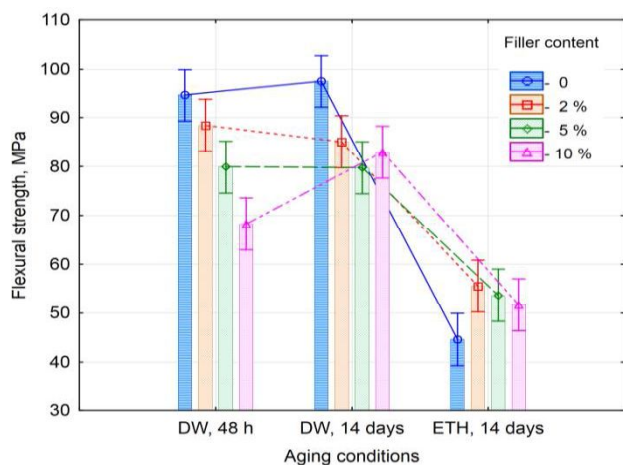


Fig. 3. Flexural strength of investigated materials with different nanosilica content under different aging conditions

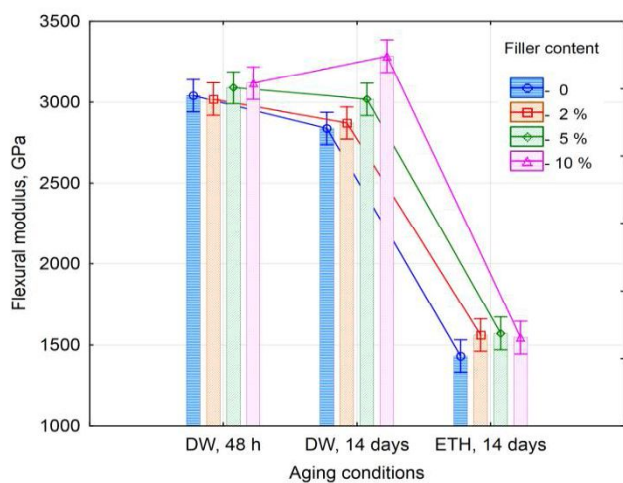


Fig. 4. Flexural modulus of investigated materials with different nanosilica content under different aging conditions

The hardness results were presented in Fig. 5. The statistically significant influence of filler concentration and aging conditions on the hardness were noted (Table 5 and Table 6). Increasing filler content caused increasing of hardness values (Fig. 5), but in distilled water only for the highest filler content it was statistically significant (Table 6). However in ethanol solution increasing of filler content limited more strongly plasticizing effect of ethanol. Aging in ethanol solution reduced by more than three times the hardness values. The largest hardness reduction after aging was observed for unmodified resin, and the lowest for material with the 10% of silica filler. Prolonged aging

in distilled water (from 2 to 14 days) for all materials reduced hardness.

Table 3.

The two-way analysis of variance results for flexural modulus (statistically significant when  $P < 0.05$ )

	Sum of squares	Degrees of freedom	Mean square	F-test statistic value	P
Aging conditions	30421724	2	15210862	1232,8	<0.0001
Filler content	391006	3	130335	10,6	<0.0001
Aging conditions × Filler content	325811	6	54302	4,4	0.0013

Table 4.

The results of multiple comparisons with Newman-Keuls test for flexural modulus,  $P < 0.05$  indicated significant difference\*

Aging liquid, aging time	Filler content, %			
	0	2	5	10
DW, 48 hours	A; z	A; z	A; z	A; z
DW, 14 days	A; y	A; z	B; z	C; y
ETH, 14 days	A; x	A; y	A; y	A; x

\*Groups with the same uppercase letters; (A-C) for each row and lowercase letters; (x-z) for each column are not significantly different at the  $P < 0.05$  level

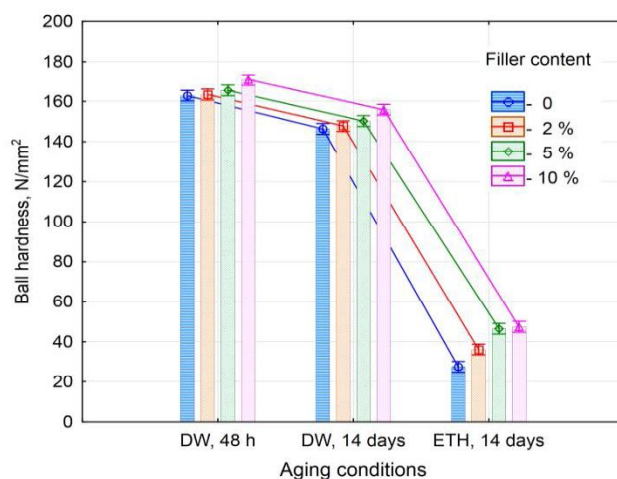


Fig. 5. Ball hardness of investigated materials with different nanosilica content under different aging conditions

Table 5. The two-way analysis of variance results for ball hardness (statistically significant when  $P < 0.05$ )

	Sum of squares	Degrees of freedom	Mean square	F-test statistic value	P
Aging conditions	189439.7	2	94719.9	10655.7	<0.0001
Filler content	1338.2	3	446.1	50.2	<0.0001
Aging conditions × Filler content	443.8	6	74.0	8.32	<0.0001

Table 6. The results of multiple comparisons with Newman-Keuls *post hoc* test for ball hardness,  $P < 0.05$  indicated significant difference\*

Aging liquid, aging time	Filler content, %			
	0	2	5	10
DW, 48 hours	A; z	A; z	A; z	B; z
DW, 14 days	A; y	A; y	A; y	B; y
ETH, 14 days	A; x	B; x	C; x	C; x

\*Groups with the same uppercase letters; (A-C) for each row and lowercase letters; (x-z) for each column are not significantly different at the  $P < 0.05$  level

Table 7. The results of one-way analysis of variance for sorption after 14 days aging in ethanol solution and distilled water (statistically significant when  $P < 0.05$ )

Aging liquid	Sum of squares	Degrees of freedom	Mean square	F-test statistic value	P
Ethanol solution	28179.3	3	9393.1	300.3	<0.0001
Distilled water	111.2	3	37.1	22.4	<0.0001

Table 8. The results of multiple comparisons with Newman-Keuls *post hoc* test for sorption after 14 days aging in ethanol solution and distilled water

Aging liquid	Filler content, %			
	0	2	5	10
Ethanol solution	A	B	C	D
Distilled water	A	A	B	C

\*Groups with the same uppercase letters; (A-D) for each row are not significantly different at the  $P < 0.05$  level

The sorption values after 14 days aging in distilled water for all materials were approximately from seven to ten times smallest like after aging in ethanol (Figs 6, 7). The statistically significant influence of filler concentration on sorption were noted, and F-test statistic values indicated that this influence was much stronger when samples were stored in ethanol solution (Table 7). Increasing filler content resulted in significant decreasing of the sorption values (Table 8). In distilled water for materials with 10% of filler sorption compared to the starting material decreased by 19%, but in ethanol solution it decreased by 37%.

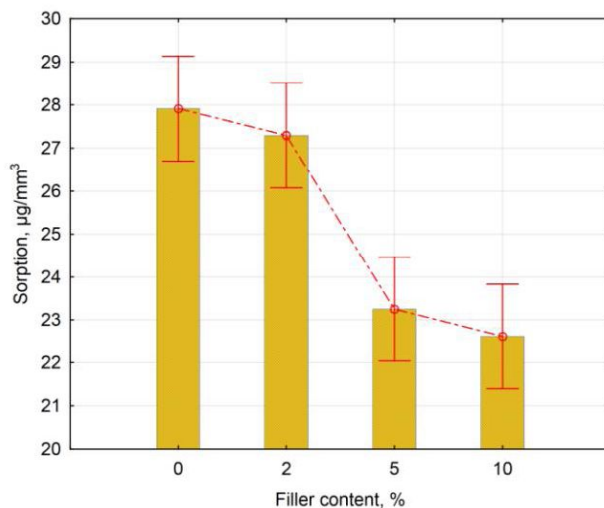


Fig. 6. Sorption after 14 days aging in distilled water

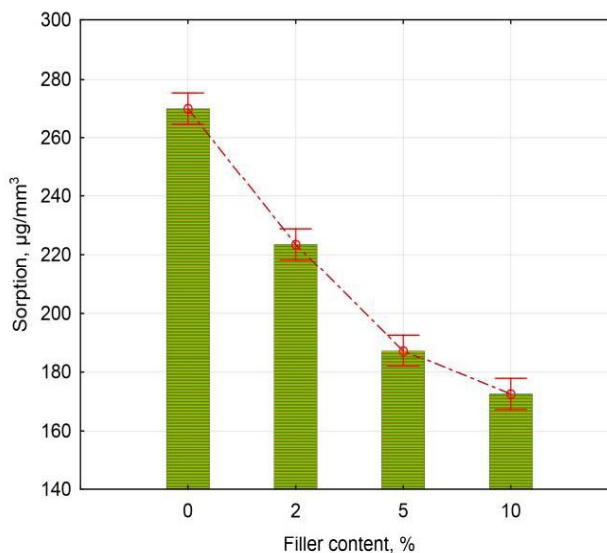


Fig. 7. Sorption after 14 days aging in ethanol solution

## 4. Discussion

One of the ways of improving changing the properties of PMMA denture base materials can be nanoparticle addition, including nanosilica fillers. Nanofillers, including silica fillers, has been successfully used with many dental composite materials, but experimental studies have shown some favorable [13-17] and unfavorable effects of their use [18,19]. The effect of addition silica nanofillers on the chosen mechanical properties of commercially available denture base materials were investigated previously in some studies, but usually low fillers concentrations (up to 1%) were used [17,19,28]. In this study we used average filler concentrations from 2% up to 10%. The results obtained in this investigations allow the rejection of the null hypothesis. As the nanoparticle content was increased, the flexural strength, flexural modulus, hardness and sorption were changed and this changes were materials and aging condition dependent.

Raszewski et al. [28] reported that the low addition of different silica fillers may decrease or increase flexural strength, but noted effects were different after 1 and 7 day of storage in distilled water. Mc Nally et al. [29] show that mechanical properties of PMMA resin with low silica fillers addition were similar or worse like for control group. Sodagar et al. [19] investigated effect of different nanoparticles added to the monomer component (including SiO<sub>2</sub>) on flexural strength of PMMA denture base resin and reported that SiO<sub>2</sub> nanoparticles caused significant reduction of the flexural strength of composites, and this effect was directly correlated with the content of nanoparticles. Their investigations were made for samples stored in distilled water and stay in accordance with our results in the same the same aging conditions for highest filler content. However in our study also longer aging time in distilled water were used, which allowed to reduce unfavourable changes. For material with 10% of silica filler the increase of flexural strength was noted, which may be related with the continues of crosslinking during aging at 37°C in water. Additionally after aging in strongly destructive medium (ethanol solution) for filled materials much higher flexural strength values were noted, with show protective role of filler. The initial unfavourable changes in flexural strength noted with the increasing filler content were probably related with the increasing of number and size of filler agglomerations confirmed during SEM investigations. The creation of agglomerates may cause a theoretical decrease in the number of "particles", which can lead to the formation of gaps between the reinforced areas [17], so during flexural testing the crack from the gaps may

propagate and can lower the flexural strength. It should be also remembered the mixing filler into component commercially available denture base materials like "powder" or "liquid" have always limited effectiveness, because PMMA pearls from "powder" component after polymerization procedure stay in only slightly changed form, as can be seen on Fig. 1. Polymerized "pearls" (powder) are produced to reduce polymerisation shrinkage and it is important to retain it. So it should be noted that effective way for fillers addition should be realized during pearls production with suspension polymerization and additionally during "liquid" component production.

Investigation show also increase flexural modulus with increasing fillers content probably as a result of reaction of methyl group from methacrylsilane treated silica filler with MMA from the resin components. Raszewski et al. [28] also noted increasing of flexural modulus after addition of three surface treated silica fillers.

The hardness values increased in our study after filler additions and increasing filler content reduced plasticizing effect of aging solutions. Balos et al. [17] obtained also hardness increase for low silica additions.

Raszewski et al. [28] reported that the sorption values after addition of 0,5% different silica nanofillers were in overall similar like for unmodified material, but for resin with Aerosil R812 it decreased, which is in accordance with our results.

Registered sorption reduction with increasing nanofiller content corresponds well with hardens measurements results, because decreed mass of absorbed plasticizing solution caused smallest hardness reduction. It should be noted, that this effect was stronger for longer aging time and more destructive aging media, so it can be more visible for long-term conditions, but this speculation need further investigations.

## 5. Conclusions

Within the limits of this study, the following conclusions were formulated:

- The silica filler addition caused reduction of flexural strength after storage in distilled water, with was probably related with increasing number and size of filler agglomerations.
- After aging in ethanol solution the materials with nanofiller addition show higher flexural strength in comparison to resin without filler.
- The flexural modulus and hardness increased when higher nanofiller content was used, and this effect was



more visible when more destructive aging conditions were applied.

- Introducing silica nanofillers into the PMMA denture base resin reduced sorption of the plasticizing liquids during aging.
- The reduced sorption noted for materials with nanofillers can be a major cause of their more favorable properties after two week in ethanol solution and distilled water in comparison to the results after 48 h in distilled water.
- The method of nanofillers incorporation with mixing to the commercially available PMMA denture base resin components shows the limitations resulting from its original morphology.

### Additional information

Selected issues related to this paper are planned to be presented at the 22<sup>nd</sup> Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10<sup>th</sup> anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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