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Effect of particle size and particle surface pretreatment of fillers on selected properties of model ceramic-polymer composites used as dental fillings

Summary: The properties of polymer matrix composites used as dental fillings are strongly affected by the presence and surface treatment of ceramic glass fillers. The proper selection of the size of filler particles, which determine mechanical properties, is a crucial problem in design of ceramic-polymer composites for dental fillings. The goal of the work was to determine the influence of average filler particle size and the effect of surface treatment on selected mechanical properties of composites based on mixture of acrylic resins: 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA).

Key words: ceramic-polymer composites, dental materials, ceramic fillers, particle size, silanation, mechanical properties.

WPŁYW WYMIARÓW CZĄSTEK ORAZ OBRÓBKI POWIERZCHNIOWEJ NAPEŁNIACZY NA WYBRANE WŁAŚCIWOŚCI MODELOWYCH KOMPOZYTÓW CERAMICZNO-POLIMEROWYCH STOSOWANYCH NA WYPEŁNIENIA STOMATOLOGICZNE

Streszczenie — Materiałami badanymi w pracy były kompozyty oparte na mieszaninie dwóch żywic metakrylanowych, zawierające 40—60 % obj. napełniaczy ceramicznych (głównie krzemionkowych) o różnym średnim wymiarze cząstek. Określono wpływ tych wymiarów (w przedziale 13 nm—3 μm) czterech typów napełniaczy na maksymalny ich udział w kompozycji (MVFF) a także na wytrzymałość na zginanie (R_f) (rys. 2) i mikrotwardość *HV 0,2* (rys. 3). Zbadano również zależność wartości *MVFF*, R_f i *HV 0,2* od ilości 3-(metakryloiloksy) propylotrimetoksysilanu (MPTMS) — środka zastosowanego do powierzchniowej obróbki (silanizacji) proszkowych napełniaczy kompozytów zawierających mikronapełniacz "K3M" (rys. 4, 6, 7) lub mikrokrzemionkę (rys. 8, 9). Stwierdzono, że średni wymiar cząstek napełniacza wywiera istotny wpływ na oceniane właściwości materiałów: kompozyty z mikronapełniaczem (wymiar 500 nm) charakteryzują się zdecydowanie większą wartością R_f i mikrotwardością niż kompozyty wzmacniane mikrokrzemionką (wymiar 3 μm). Wykazano też, że kompozyty zawierające silanizowany napełniacz ceramiczny wykazują lepsze właściwości mechaniczne niż kompozyty z niesilanizowanym proszkiem.

Słowa kluczowe: kompozyty ceramiczno-polimerowe, materiały dentystyczne, wypełniacze ceramiczne, wymiary cząstek, silanizacja, właściwości mechaniczne.

The most popular materials currently used for stomatology inlays are ceramic-polymer composites which increasingly substitute amalgams showing unpleasant dark color and being possibly toxic due to the presence of mercury [1]. The ceramic-polymer composites mainly contain acrylic resins and glass ceramic fillers.

The properties of dental composites depend on the filler type, volume fraction of a filler incorporated to the resin, and the size of the filler particles. Mechanical properties of the composites improve with an increase in filler volume fraction [2]. However, the flexural strength reaches the highest value for a certain volume fraction of a filler and above this point starts to decrease. As a result optimum performance cannot be achieved simply by maximizing the volume fraction of a filler. However, additional optimization of the properties can be achieved by an appropriate selection of the distribution of filler particle sizes [3, 4]. It should be noted that commercially available materials differ in particular in volume fraction of ceramic phase and their particle sizes [2].

One of the important factors influencing mechanical properties of composites is the bonding between particles and the polymeric matrix. The recent developments of ceramic filler preparation technology and chemical coupling of the particles have led to a significant improvement in the clinical performance of dental composites, which were introduced in 1960s. The general procedure includes a pretreatment of inorganic particles with coupling agents, which improve particle wetting and chemical bonding of the filler particles to the organic matrix [5, 6].

Inorganic fillers in dental composites are typically silanized to improve their bonding to organic matrix and increase the "service life" of dental materials [7, 8].

Composites with silanized fillers exhibit superior mechanical parameters, wear resistance and higher resistance to water sorption compared to composites containing non-silanized fillers [9]. In addition, silanes improve dispersion of the fillers in a matrix [10].

The aim of the present work was to determine the influence of the average filler particle size and surface treatment on mechanical properties of composites based on a mixture of two selected acrylic resins (see [11]).

As this study is mostly related to technological aspects of dental composites, its purpose was to determine the influence of: (1) average particle size on maximum proper volume fraction of a filler in the composite, and (2) amount of 3-(methacryloyloxy)propyltrimethoxysilane used as silanizing agent on this volume fraction of fillers and on mechanical properties of the composites. Three kinds of fillers, differing especially in average particle, were used: nanosilica (13 or 40 nm), microsilica (500 nm) and microfiller (3 μm).

EXPERIMENTAL

Materials

The materials studied were composites based on the mixture of two acrylic resins: 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane bis-GMA and triethylene glycol dimethacrylate (TEGDMA), reinforced with silica glass fillers. The composition of the polymer matrix was as follows (in wt. %): bis-GMA — 58.81, TEGDMA — 40.49 (both resins from Aldrich), camphorquinone (photoinitiator) — 0.16, (diethylamine)ethyl methacrylate (activator) — 0.49, butylated hydroxytoluene (BHT, inhibitor) — 0.05.

Density of this the polymeric base amounts 1.33 g/cm^3.

Several kinds of silica glass fillers was used, namely:

— Commercial nanosilica fillers (made by Degussa company: "Aerosil DT4", "VP DT5", "Aerosil R709"). These fillers were supplied after surface silanization. The average particle size ranged from 13 nm (for "Aerosil DT4") to 40 nm (for "VP DT5" and "Aerosil R709"). The particles were of spherical shape. However, silicas "VP DT5" and "Aerosil R709" differed in bulk density (400 g/l and 150 g/l, respectively). Densities of all these nanosilicas were equal 2.2 g/cm^3.

— Spherical microsilica particles with an average particle size of 500 nm and a very narrow particle size distribution. Density of microsilica was 2.4 g/cm^3. This filler was silanized by us using 3-(methacryloyloxy)propyltrimethoxysilane (MPTMS, "DYNSYLAN MEMO" manufactured by Degussa). Three concentrations of MPTMS were used: 0.15, 1.5 or 3 wt. % per powder mass of microsilica. MPTMS was dissolved in toluene (used in the amount dependent on silane amount introduced) by mixing for 10 minutes in an evaporator a temperature of 80 °C. Then the powder was added, mixture was mixed at 80 °C for 30 minutes and the toluene was evaporated.

Table 1. Chemical composition of microfiller "K3M"

Type of oxide	SiO_2	B_2O_3	Al_2O_3	BaO
Weight %	50	9	8	33

— Microfiller "K3M"with an average particle size of 3 μm and density 3.0335 g/cm^3 elaborated and produced by the Glass and Ceramic Institute in Warsaw. The chemical composition of "K3M" is given in Table 1. This ceramic glass microfiller was also silanized using MPTMS and the same procedure as for microsilica.

Curing

After manual homogenization, the compositions (polymeric base + filler) were cured at room temperature, for a mean time 170 s by exposing to UV-rays. Main parameters of "Demetron LC" curing lamp (KerrHave) were: output wavelength in the range 400—515 nm and output light intensity 600—950 mW/cm^2.

Methods of testing

For testing the mechanical properties of the composites the flexural strength (R_f) and microhardness (*HV0.2*) were measured. To determine R_f value three-point bend tests were performed using a "MTS Q-test" testing machine. The specimens of dimensions 25×2×2 mm were subjected to bend tests under a strain rate 0.75 mm/min according to ISO — 4049. The microhardness was measured using a Zwick hardness tester equipped with a square based pyramidal Vickers' diamond indenter at a load of 200 G for 15 s.

The microstructures of some of the composites were examined using a "Hitachi S-3500" scanning electron microscope (SEM).

Before the microhardness measurements and SEM examinations the specimens were polished with 500 grit sandpaper and then with diamond paste.

RESULT AND DISCUSSION

Figure 1 shows the influence of type of silica on the maximum volume fraction of a filler (*MVFF*) which can be introduced into a composite by manual mixing. The highest *MVFF* value (74 %) was obtained for microsilica.

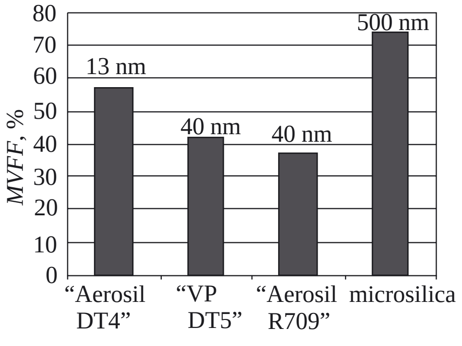

Fig. 1. Influence of type of silica maximum volume fraction of a filler (MVFF) (numbers over the columns show the average particle size)

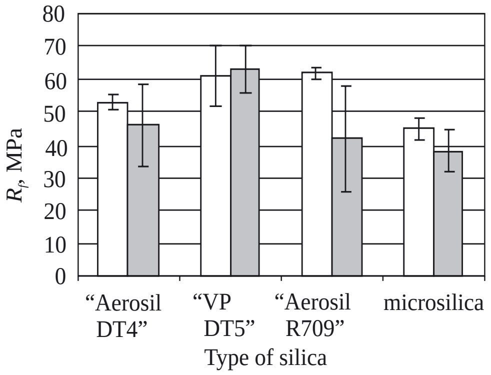

Fig. 2. Influence of silica type on flexural strength (R_f) of composites; □ — maximal volume fraction of silica, ■ — 40 vol. % of silica

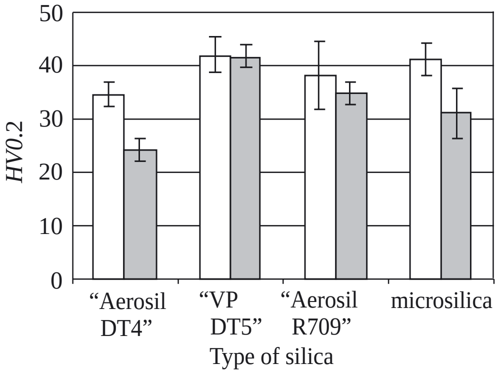

Fig. 3. Influence of silica type on microhardness (HV0.2) of composites; columns denotations as. Fig. 2

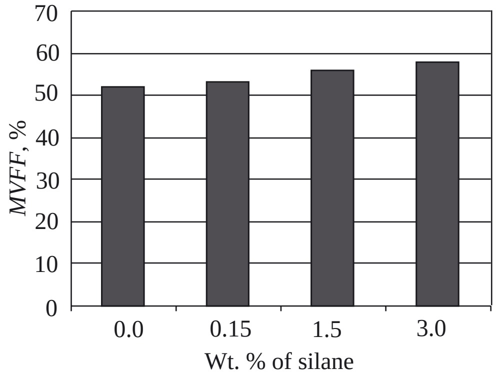

Fig. 4. The influence of silane amount on MVFF value of microfiller "K3M" in a composite

However, this amount of silica does not correspond to the best mechanical properties. In fact, the composite containing microsilica shows the lowest flexural strength (Fig. 2). The lowest *MVFF* — 37 % — was obtained in the case of "Aerosil R709". "VP DT5" nanosilica which has the same average particle size but higher bulk density let achieve a slightly higher *MVFF* value (Fig. 1). The amount of filler used in determination of flexural strength (40 %, Fig. 2) exceeded that *MVFF* value and the composites obtained were brittle.

The best mechanical properties were obtained for composites containing "VP DT5" nanosilica. They show the highest values of flexural strength and microhardness (Fig. 3). The worst flexural strength was found for the composite containing microsilica: both the materials with maximum volume fraction of a filler and that with 40 vol. % of filler exhibited the lowest R_f values.

From the results obtained one can conclude that there is no direct correlation between the volume fraction of nanosilica and the mechanical properties of composites. Usually the higher volume fraction of a filler have a beneficial effect on the properties. However, this is not true for nanofiller as in this case the mechanical properties are governed mainly by the interface bonding. The composites containing nanosilica of average particle size eqal 40 nm exhibited higher values of both flexural strength and microhardness than the composite with nanosilica of particle size 13 nm — the latter of very small particles may form clusters which were not homogenized during mixing.

As the interface can strongly influence the mechanical properties of composites, the investigation aimed at determining the influence of amount of 3-(methacryloyloxy)propyltrimethoxysilane on the maximum volume fraction of fillers and on these mechanical properties. The quantity of silane having a beneficial effect on *MVFF* of microfiller "K3M" in a composite was established. By using a greater amount of silane, it was possible to obtain composites having a higher *MVFF* value (Fig. 4).

Figure 5 shows the microstructures of composites reinforced with "K3M" microfiller which was pre-treated with various amounts of silane. In all cases, uniform distribution of a filler can be observed. However, the composites showed different mechanical properties.

The optimum amounts of silane for microsilica and microfiller "K3M" were determined by consideration of the mechanical properties. The best properties were found for the composite containing microfiller "K3M" silanized with 1.5 wt. % of MPTMS. The flexural strength of this composite — 86 MPa — was almost twice higher than of composite with unsilanized microfiller (47 MPa) (Fig. 6).

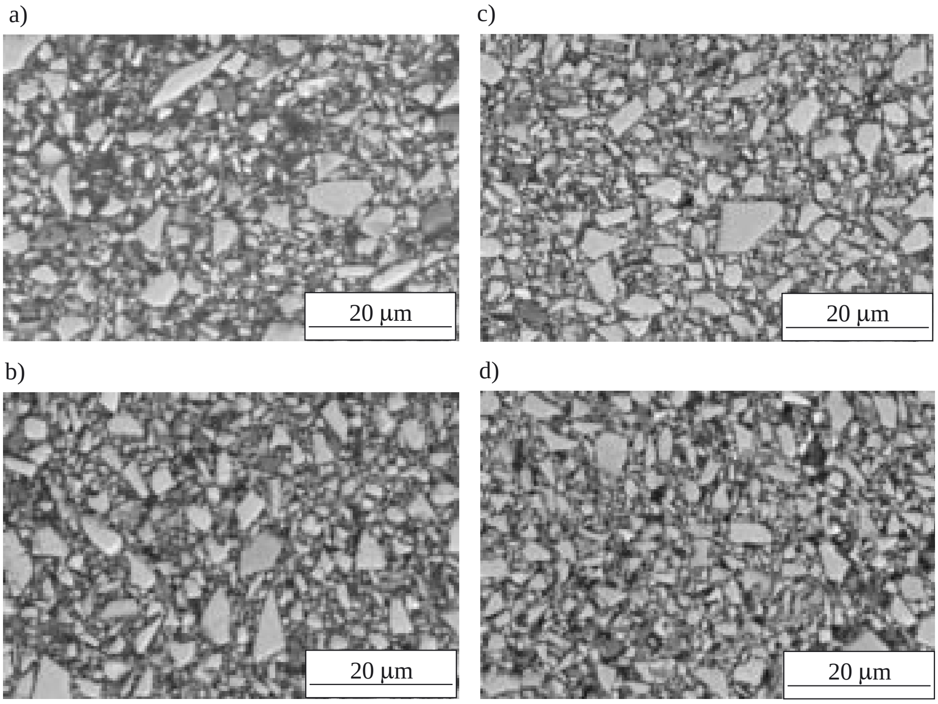

Fig. 5. Microstructure of composite containing microfiller "K3M": a) without silanation, b) after silanation with 0.15 wt. % of silane, c) after silanation with 1.5 wt. % of silane, d) after silanation with 3 wt. % of silane

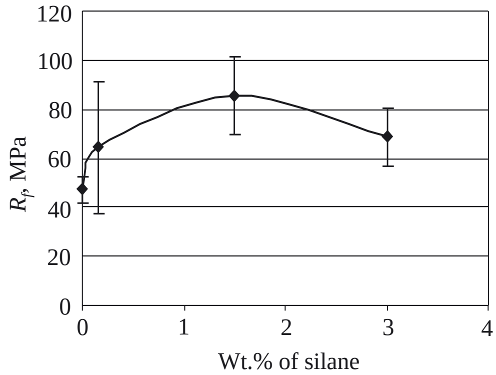

Fig. 6. Influence of silane content on flexural strength (R_f) of composites reinforced with microfiller "K3M" (maximal volume fraction)

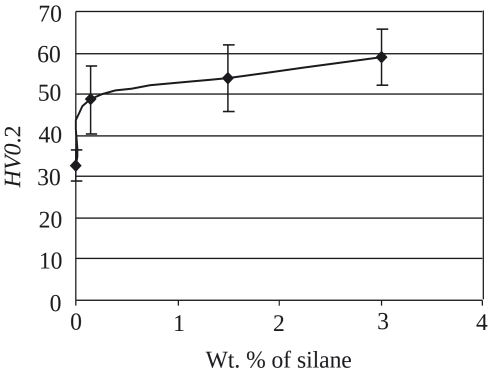

Fig. 7. Influence of silane content on microhardness (HV0.2) of composites reinforced with microfiller "K3M" (maximal volume fraction)

The flexural strength values of composites containing microfiller "K3M" silanized with 0.15 or 3 wt. % of silane were comparable and amounted to 64 MPa and 69 MPa, respectively. This means that 0.15 wt. % of MPTMS is not sufficient to cover the surface of the powder. In the case of the highest amount of silane (3 wt. %) the highest volume fraction of microfiller can be introduced into a composite. However, the mechanical properties of such composites are lower than for a composite containing microfiller "K3M" pretreated with 1.5 wt. % of silane.

The microhardness of composites with microfiller "K3M" depends also on the relative concentration of silane (Fig. 7), namely as the concentration of silaning compound increases, so does the microhardness. Without silane the *HV0.2* value was 33, whereas for 3 % of silane this increased to 59.

On the basis of the above-mentioned results of mechanical properties investigations, the optimum silane concentration for "K3M" microfiller pretreatment is 1.5 wt. %.

Similar experiments were carried out for microsilica. In that case, one volume fraction of a filler (50 vol. %) and three amounts of silane (the same as previously) were used.

The flexural strength values of composites containing microsilica without silanation are substantially lower that in the case of composites containing the "K3M" microfiller (Fig. 8).

The amount of silane used during silanation influences the R_f value of the composites with microsilica, namely the flexural strength rises as the concentration of silane increases. The best mechanical properties were

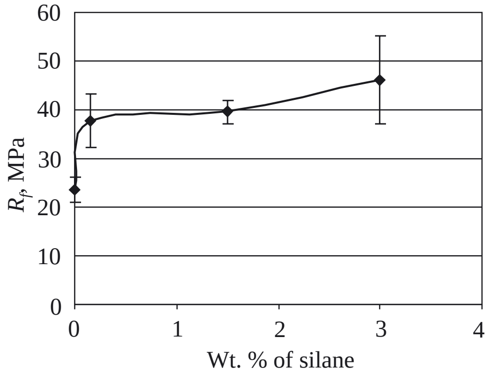

Fig. 8. Influence of silane concentration on flexural strength (R_f) of composites reinforced with microsilica (50 vol. %)

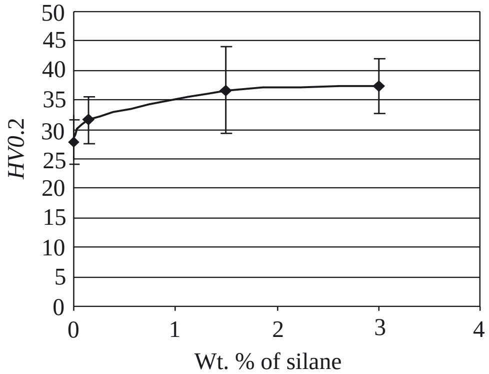

Fig. 9. Influence of silane concentration on microhardness (HV0.2) of composites reinforced with microsilica (50 vol. %)

found for a material with microsilica silanized with 3 wt. % of 3-(methacryloyloxy)propyltrimethoxysilane — the highest content of silane. For this composite, the flexural strength is twice better than that of the composite containing microsilica without silane coupling.

The effect of MPTMS concentration on microhardness of the composites is less significant but general dependence is maintained though scatter of results is much wider (Fig. 9).

The higher amount of silane necessary here to obtain the optimum properties of microsilica containing composites is due to the larger interfacial surface area than in the case of microfiller "K3M".

CONCLUSIONS

From the results the following conclusions can be drawn:

— The type of the filler has an influence on the mechanical properties of the investigated materials.

— Composites with the microfiller show flexural strength and microhardness substantially superior to those of composites reinforced with microsilica.

— Surface treatment (silanation) of ceramic glass filler strongly improves composites' properties.

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REFERENCES

1. Hol P. J., Vamnes J. S., Gjerdet N. R., Eide R., Isren R.: *Environment. Res. Sect. A* 2001, **87,** 141.
2. Ikejima I., Nomoto R., McCabe J. F.: *Dent. Mat.* 2003, **19**, 206.
3. Tanimoto Y., Kitagawa T., Aida M., Nishiyama N.: *Acta Biomat.* 2006, **2**, 633.
4. Venhoven B. A. M., De Gee A. J., Werner A., Davidson C. L.: *Biomaterials* 1996, **17**, 735.
5. Kaas R. L., Kardos J. L.: *Polym. Eng. Sci.* 1971, **11**, 11.
6. Słomkowski S.: *Polimery* 2006, **51**, 87.
7. Luo J., Seghi R., Lannutti J.: *Mat. Sci. Eng. C* 1997, **5**, 15.
8. Debnath S., Wunder S. L., McCool J. I., Baran G. R.: *Dent. Mat.* 2003, **19**, 441.
9. Luo J., Lannutti J. J., Seghi R. R.: *Dent. Mat.* 1998, **14**, 29.
10. Wang J. W., Ploehn H.: *J. Appl. Polym. Sci.* 1996, **59**, 345.
11. Siejka-Kulczyk J., Lewandowska M., Kurzydłowski K. J.: *Polimery* 2006, **51**, 742.