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Evaluation of degradation degree of dental ceramic/polymer composites for permanent fillings

Summary — The aim of this study was to evaluate the degradation processes that take place in the dental hybrid composites intended for permanent fillings. The mixture of bis-GMA and TEGMA resins was used as the polymer matrix. Ceramic glass of various particle sizes as well as nanosilica were used as the composite fillers. The specimens were exposed to 0.1 M NaOH solution for 6, 24 or 168 h, and to water for 168 h. Degradation was evaluated by Scanning Electron Microscopy (SEM) microstructure observation and mechanical testing, such as flexural strength and microhardness. SEM investigations indicate that after the exposure to NaOH solution, the resin is partially dissolved and some filler particles have rinsed out. This deteriorates significantly the mechanical properties of ceramic/polymer composites.

Key words: dental fillings, methacrylate composites, ceramic fillers, alkaline environment, degradation, mechanical properties.

OCENA STOPNIA DEGRADACJI KOMPOZYTÓW CERAMICZNO-POLIMEROWYCH STOSOWANYCH JAKO STAŁE WYPEŁNIENIE STOMATOLOGICZNE

Streszczenie — Przedmiotem badań były kompozyty metakrylanowe na podstawie 2,2′-bis[4-(2-hydroxy-3-metakroiloksypropoksy)fenylo]propanu (bis-GMA) i dimetakrylanu glikolu trietylenowego (TEGDMA) napełnione mikronapełniaczem szklanym o różnych wymiarach cząstek (3 μm lub 5 μm — odpowiednio kompozyty K4M3 i K4M5), także z dodatkiem nanokrzemionki (kompozyt K4M5/10 nano) (tabela 2). Próbki kompozytów przetrzymywano (do 168 h) w 0,1 M roztworze NaOH oraz w wodzie; stopień degradacji oceniano na podstawie zmian wytrzymałości na zginanie (R_f) i mikrotwardości (*HV0.2*) (tabele 3 i 4, rys. 1, 2). Metodą skaningowej mikroskopii elektronowej oceniano też zmiany mikrostruktury próbek kompozytów wywołane degradacją w roztworze NaOH (rys. 3). Stwierdzono, że zmniejszenie wymiarów cząstek napełniacza polepsza odporność na degradację.

Słowa kluczowe: wypełnienia stomatologiczne, kompozyty metakrylanowe, napełniacze ceramiczne, środowisko alkaliczne, degradacja, właściwości mechaniczne.

The most popular materials currently used for dental fillings are ceramic/polymer composites which increasingly replace amalgam due to the possible toxicity of mercury and the unpleasant dark color. An important reason for a wider use of dental resins is their durability and the stability of properties in the environment of oral cavity. During the degradation processes the polymer chains are cleaved to form oligomers and finally — monomers, whose functional groups differ from those of the polymer [1]. Water can enter the polymer bulk, which may be accompanied by swelling. The intrusion of water triggers chemical polymer degradation, leading to the formation of oligomers and monomers. Progressive degradation changes the microstructure of the bulk as the results of the formation of pores, through which the degradable components are released [1]. There are some factors that influence the rate of this reaction: the type of chemical bond, pH, copolymers compositions, water uptake and hydrophilicity of the polymer matrix [2]. The organic acids produced by bacterial metabolism in the oral environment are acetic, propionic and lactic acids [3, 4]. The acetic and propionic acids show a softening effect on the polymers, whereas the lactic acid does not affect their properties [5].

Degradation of dental composites proceeds especially fast in an alkaline environment because of their reaction with the OH^- ions, and is related to the hydrolysis of the silane couplings of ceramic component and the dissolution of the filler [6]. This process is very slow in water, artificial saliva [7, 8] and at low pH environment [9]. An increase in pH accelerates the reaction [10]. The exposure to NaOH solution was considered to be an appropriate method to quickly estimate the durability of the composites *in vitro*.

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Hosoda et al. [11, 12] report that, in alkaline environments, the surface of the methacrylate resins, being polymer matrix of the composites, undergoes structural changes. They immersed the composites in 0.1 N NaOH solution at 60 °C for one week and examined them by scanning electron microscopy. It was found that the alkaline environment and the alkaline earth elements, such as Ba, present in the filler particles, accelerated the degradation of the composite resin, manifested in a filler dissolution and resin exfoliation and destruction.

The subjects of our investigations, presented here, were methacrylic composites filled with glass microfillers. These materials were exposed to water and to a 0.1 M NaOH solution in order to compare the durability of their mechanical properties in various environments. The principal goal was to determine the influence of microfiller particle size and the addition of 10 vol. %, of nanosilica on stability of flexural strength and microhardness. The changes of microstructure were also evaluated.

EXPERIMENTAL

Materials

The materials studied in the present work were the composites based on the bis-GMA (bisphenol A-glycidyl) resin reinforced with a ceramic glass microfiller or nanofiller + 10 vol. % of nanosilica. The composites were developed at Warsaw University of Technology. The chemical composition of the microfiller (of melting point 1470 °C, elaborated and made by Glass and Ceramic Institute in Warsaw) is given in Table 1. The microfiller has a symbol K-4M and was prepared in two forms which differ in grain size distribution. The average particle size amounted to either ~ 3 μm or 5 μm (K4M3 and K4M5, respectively). The filler was silanized (temp. 60 °C) using γ-metacryloyloxypropyltrimethoxysilane in order to obtain the better bonding with the polymer matrix. Nanosilica was a commercial material (R-709) made by Degussa company, with average particle size equal to 40 nm. Table 2 shows the compositions of this way fabricated ceramic/polymer composites. The composition of polymer matrix, which part was 40 wt. %, is given below:

— Bis-GMA (bisphenol-A-glycidyl) — 58.81;

— TEGDMA (triethylene glycol dimethacrylate) — 40.49;

— Photoinitiator (camphorquinone) — 0.16;

— Activator 2-(diethyloamino)ethyl methacrylate — 0.49;

— Inhibitor (butylated hydroxytoluene, BHT) — 0.05.

After manual homogenization the composites were cured by exposing them to UV-rays. Main parameters of curing lamp "Demetron LC" (KerrHave) were: output wavelength range — 400—515 nm and output light intensity — 600—950 mW/cm^2, room temperature, mean time 140 s.

Table 1. Chemical composition of the filler

Glass symbol	Kind of oxide and its weight percentage						
	SiO_2	P_2O_5	Al_2O_3	BaO	SrO	Na_2O	F
K-4M	22.11	5.22	18.76	25.39	17.17	2.28	9.07

Table 2. Kinds of ceramic/polymer composites (polymer matrix — see text)

Microfiller kind and content, vol. %	Average size of microfiller particles, μm	Designation of a composite
K4M, 60	3.203	K4M3
K4M, 60	5.113	K4M5
K4M, 50 + nanosilica, 10	5.113	K4M5/10 nano

Methods of testing

The specimens of dimensions 25×2×2 mm were exposed to distilled water for 168 h and to 0.1 M NaOH for 6, 24 or 168 h at the room temperature. Before exposure they were ground with abrasive paper from 80 to 2000 and polished with Al_2O_3 suspension. After each exposure the microstructure of the materials was examined by SEM (Hitachi 3500 N). The degradation processes can be assessed by the measurements of mechanical properties [13]. The flexural strength (R_f) and microhardness *HV0.2* were measured to characterize the mechanical properties. To determine the flexural strength, three — point bend tests were performed using a testing machine MTS Q — test on three samples per "state". The microhardness was measured by a Zwick hardness tester.

RESULTS AND DISCUSSION

The mechanical properties of the composite samples with various filler particle sizes before exposure are shown in Table 3. The composites containing the filler of larger particles show much better mechanical properties. This may indicate that bonding between the filler particles and polymer matrix is "weak point" of investigated materials.

Table 3. Mechanical properties of various kinds of the composites in the initial state

	K4M3	K4M5	K4M5/10 nano
Flexural strength, MPa	40	97	92
HV0.2	49	60	60

The results obtained for the composite K4M5/10 nano show that the mechanical properties can also be improved by adding a certain amount of nanosilica. It should also be noted that two of the investigated materials (K4M5, K4M5/10 nano) fulfilled the requirement of the ISO 4049 standard in terms of flexural strength (≥80 MPa).

The mechanical properties of composite materials depend, in particular, on the filler content. An increase in its volume fraction results in the improvement in mechanical properties. However, above certain level of the filler content the material becomes incoherent. In our previous studies, an optimum volume fraction of the filler was estimated at 60 % [14]. So just such its content we used in this work.

Our current study concerns the influence of the particle size on the mechanical properties of the composites before and after their exposure to an aggressive environment.

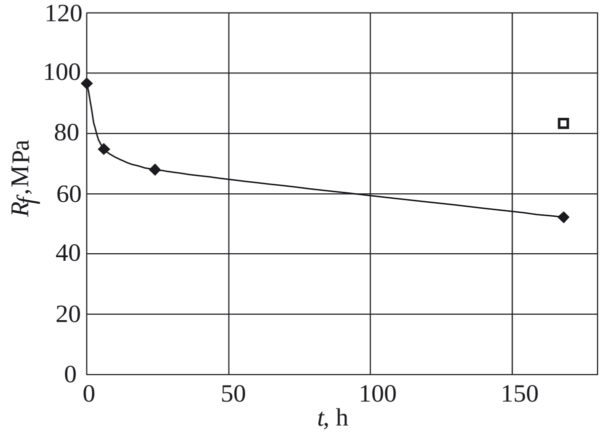

Fig. 1. Influence of the exposure time (t) in 0.1 M NaOH (♦) and in water (□) on the flexural strength (R_f) of the composite K4M5

The influence of the exposure time on the mechanical properties of the composite material in 0.1 M NaOH and water is illustrated in Fig. 1. So, the flexural strength decreases with the exposure time increase. This indicates that during the exposure either to water or NaOH solution, the material undergoes the degradation, which is much faster in NaOH solution. This may be due to the reaction of a filler with the OH^- ions, which leads to the dissolution of the filler or may be related to the hydrolysis of the silane couplings.

Fig. 2 shows how the particle size affects the degradation processes. The diagrams evidently confirm that the mechanical properties of the composites are significantly worsened after an exposure to both environments. The properties' drop is more significant in NaOH solution.

In order to evaluate the degradation processes, the relative decrease in mechanical parameters was calculated from the following equation:

$$d = (\nu_0 - \nu_f) \cdot 100/\nu_0\ [\%] \tag{1}$$

where: *d — decrease in parameters*, ν_0 *— initial value*, ν_f *— value after 168 h in 0.1 M NaOH* (H_2O).

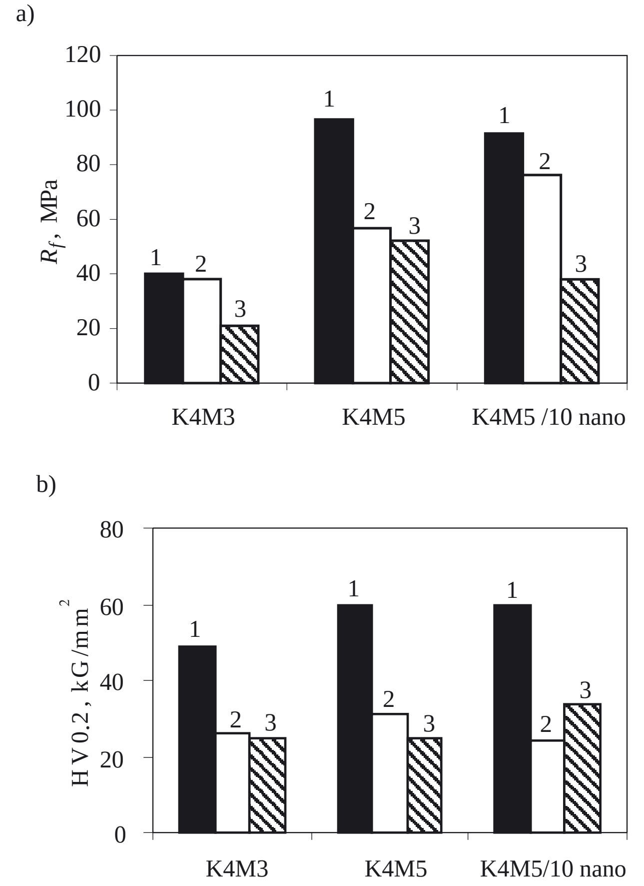

Fig. 2. Effect of filler particle size on mechanical properties of the composites after the 168 h exposure in distilled water (2) and in 0.1 M NaOH (3) compared with the initial state (1); a) flexural strength (R_f), b) microhardness (HV0.2)

The results of this analysis are shown in Table 4. From these data one can conclude that the degradation processes (decrease in the mechanical parameters) are less advanced in the composite with smaller filler particles.

There is no correlation between presence of the nanosilica and decrease of the mechanical parameters.

Table 4. Average decrease in the mechanical properties after exposure to 0.1 M NaOH and to water

	NaOH		H_2O	
	decrease R_f, %	decrease *HV0.2*, %	decrease R_f, %	decrease *HV0.2*, %
K4M3	48	49	5	47
K4M5	46	59	41	48
K4M5/10 nano	59	44	17	59

To find the reasons of observed changes in mechanical properties of the composites, caused by degradation, SEM microstructure observations were performed. The microstructure of selected composites after various times of exposure to the NaOH solution are shown in Fig. 3. The NaOH solution causes the dissolution of the

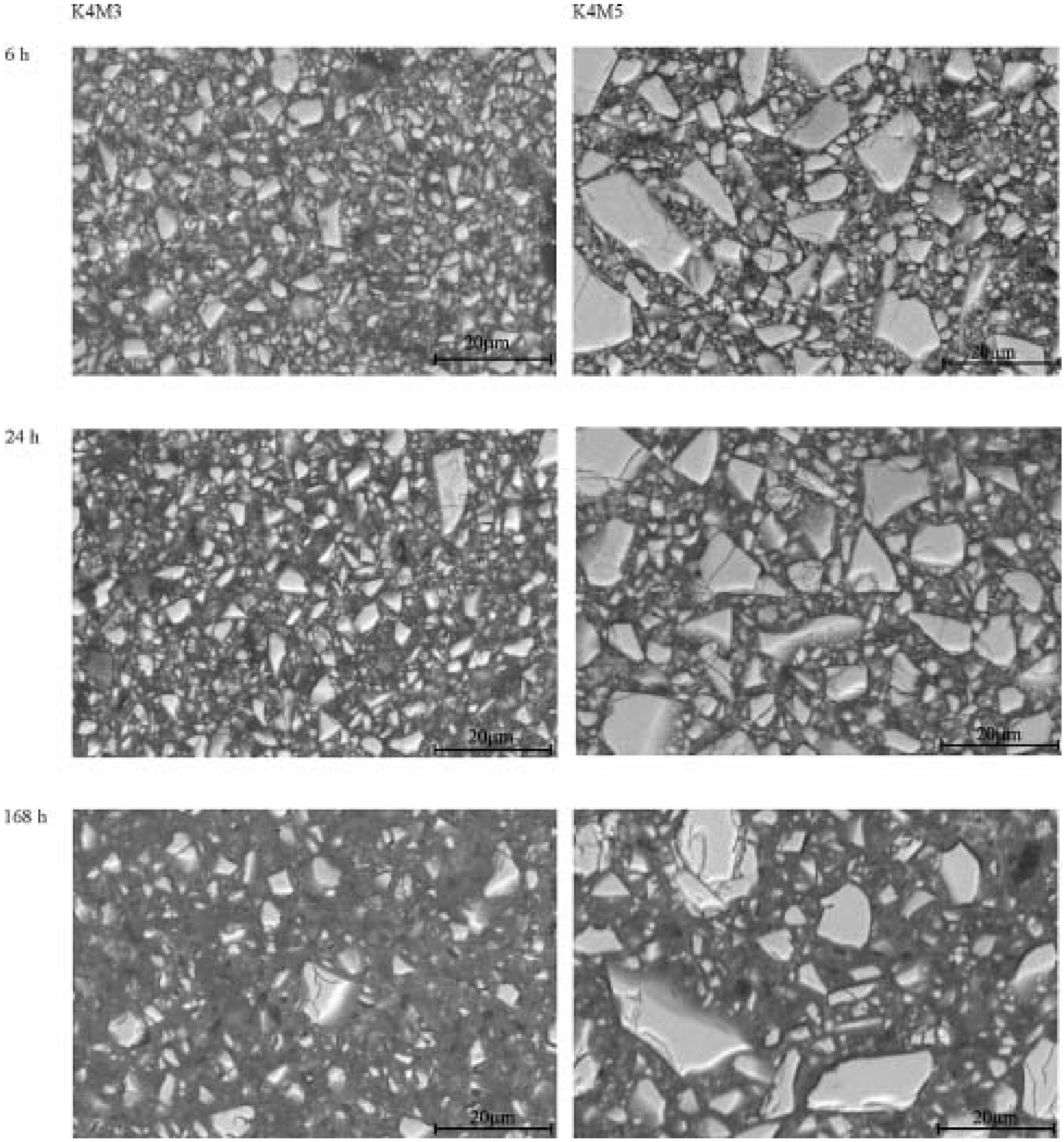

Fig. 3. Microstructure of the composites K4M3 and K4M5 after the 6, 24 or 168 h exposure to 0.1 M NaOH solution

resin and as a result ceramic particles protrude from the resin surface (for 6 h and more for 24 h). After exposure time 168 h the reduction of the volume fraction of ceramic filler was observed. It seems that the resin dissolves and some filler particles fall out. This may be a reason of the decrease in mechanical properties. The microstucture changes do not indicate unequivocally, that a decrease in mechanical parameters is more significant for composite with microfiller with the mean particle size of 5 μm. Moreover, the exposure to NaOH solution resulted in numerous cracks in the filler particles being formed. This may also cause a more significant decrease in mechanical properties of the ceramic/polymer composites, due to the fact that a material can become incoherent.

CONCLUSIONS

The conclusions drawn from the present study are:

— The mechanical properties of ceramic/polymer composites are strongly affected by the exposure either to water or 0.1 M NaOH solution. The microhardness as well as the flexural strength are substantially reduced by both of these media. Adverse effect of NaOH solution is significantly greater.

— The degradation is more significant in composites with larger microfiller particles. SEM investigations indicate that after the exposure to NaOH solution the resin is partially dissolved and some filler particles fall out. This leads to a significant deterioration of the mechanical properties of ceramic/polymer composites intended for dental application.

— It should be noted that the study was performed in an extreme (strongly alkaline) conditions. However, such conditions may give information useful for estimating the "time in-service" for these materials. Further investigations in acidic environment are planned.

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