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KOMPOZYTY
COMPOSITES

Krzysztof Pałka[1]*, Jarosław Bieniaś[2], Agata Niewczas[3], Małgorzata Muzyka[4]

[1, 2, 4] Lublin University of Technology, Department of Materials Engineering, 36 Nadbystrzycka St., 20-618 Lublin, Poland
[3] Medical University of Lublin, Department of Conservative Dentistry, 7 Karmelicka St., 20-081 Lublin, Poland
** Corresponding author. E-mail: k.palka@pollub.pl*

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MICROHARDNESS OF RESTORATIVE COMPOSITES AFTER EXPOSURE IN PHYSIOLOGICAL SOLUTION

Restorative materials used in dentistry are required to have long-term durability in the oral cavity. In some cases the interaction of these materials with oral fluids may involve dissolution or degradation of surface layers. Such a fluid absorption may affect the mechanical properties of the materials and inflict damaging dimensional changes. This study was conducted to compare the effect of 4-week storage period in physiological solution on the surface microhardness measured in Vickers units, between materials with micro- and nano-fillers. Vickers microhardness was assessed in two nano-filler materials: Filtek Supreme and Grandio and two of micro filler materials: Filtek Silorane and Gradia stored in physiological solution at 37°C for 4 weeks. Measurements were taken at 1st, 14th and 28th day. The statistical evaluation was done by one-way analysis of variance. Materials with nanofiller showed a higher microhardness at the beginning of the study as compared with the materials with microfillers. The microhardness of Filtek Supreme significantly diminished in the final stage of the study, whereas that of Grandio showed decreasing tendency but without significant difference. Similar changes were observed for Gradia, however, they exhibit a much lower microhardness throughout the study period. Filtek Silorane based on the new silorane resin manifested different changes of microhardness as compared with other materials tested. Microhardness of Filtek Silorane increased to 65.6 HV0,02 at 14 days of storage, then slightly decreased to 61.56 HV0.02 at the end of the test period. The results suggest that the amount of filler did not appear to improve the surface microhardness of materials. Restorative materials based on Bis-GMA matrix showed influence of storage time in physiological solution on microhardness value. Results obtained for Filtek Silorane showed the lack of microhardness reduction caused by stability of silorane resin matrix in water environment.

Keywords: **restorative composite materials, micro and nano fillers, Vickers microhardness, storage**

MIKROTWARDOŚĆ KOMPOZYTÓW STOMATOLOGICZNYCH PO EKSPOZYCJI W SOLI FIZJOLOGICZNEJ

Wymagania stawiane kompozytom stomatologicznym dotyczą dużej trwałości w warunkach panujących w jamie ustnej. W niektórych przypadkach interakcje ze środowiskiem jamy ustnej mogą wywołać degradację powierzchni kompozytowych materiałów wypełnień. Celem niniejszej pracy było określenie wpływu 4-tygodniowej ekspozycji w roztworze fizjologicznym na mikrotwardość materiałów kompozytowych. Do badań wytypowano materiały z mikrowypełniaczem - Filtek Silorane i Gradia oraz z nanowypełniaczem - Filtek Supreme i Grandio. Pomiary mikrotwardości wykonano metodą Vickersa przy obciążeniu 0,1962 N w 24 godz. po utwardzeniu oraz po 14 i 28 dniach ekspozycji w soli fizjologicznej w temperaturze 37°C. Wyniki oceniano statystycznie z zastosowaniem jednoelementowej analizy wariancji przy *p* < 0,05. Kompozyty z nanowypełniaczem wykazywały wyższą początkową twardość niż materiały z wypełniaczem mikro. Dla kompozytu Filtek Supreme obserwowano statystycznie istotne obniżenie twardości po 14 i 28 dniach w stosunku do mierzonej po utwardzaniu. Kompozyt Grando wykazuje również tendencję obniżania mikrotwardości, również istotną statystycznie po 14 i 28 dniach w stosunku do wartości początkowej. Materiały z mikrowypełniaczem wykazują niższą twardość oraz mniejsze zmiany mikrotwardości, jednakże odchylenia te nie są statystycznie istotne. Mikrotwardość kompozytu Filtek Silorane zwiększyła się do 65,6 HV0,02 po 14 dniach ekspozycji, a następnie nieznacznie obniżyła do 61,56 HV0,02 w ostatnim dniu testu. Uzyskane wyniki wskazują na brak jednoznacznej zależności wpływu ilości wypełniacza na mikrotwardość kompozytów stomatologicznych. Kompozyty na bazie żywicy Bis-GMA wykazują istotne zmiany mikrotwardości po ekspozycji w soli fizjologicznej. Wyniki uzyskane dla kompozytu Filtek Silorane wskazują na brak zmian w mikrotwardości, wynikający ze stabilności żywicy siloranowej w roztworach wodnych.

Słowa kluczowe: **kompozyty stomatologiczne, mikro- i nanowypełniacze, mikrotwardość Vickersa, przechowywanie**

INTRODUCTION

Restorative filling materials used in dentistry are required to have long-term durability in the oral cavity. This is a complex environment where the material is in constant contact with saliva, a fluid that contains a variety of inorganic and organic species, accompanied by the bacterial flora complex. In some cases the interaction of these materials with oral fluids may involve dissolution or degradation of surface layers while in others, the interaction may involve leaching out of unbound or loosely bound components or an uptake of fluids into the structure of the material. Such a fluid absorption may affect the mechanical properties of the materials and cause damaging dimensional changes [1-8].

The effect of fluid absorption depends on numerous factors including not only the rate and amount of fluid (water) absorbed, but also the mechanism of absorption itself. Any absorption causing a dimensional change, has potentially important clinical consequences and can be harmful for the material. Water sorption may cause some undesirable effects such as softening of the resin matrix, resin degradation, reduction of stain-resistance and a leakage of filler elements, by degradation of the silane present in the interface between matrix and particles [5]. The main noticeable effect of fluid absorption is the decrease in microhardness. The softening effect occurs in such ”natural” fluids like water [6-9], ethanol [1, 5] and in organic acids and food simulating solutions [4]. Another problem deals with softening effect in bleaching and fluoride agents or various finishing procedures.

The ability of restorative dental materials to withstand the functional force and exposure to various substances in the mouth is an important requirement for their clinical performance for a considerable period of time. In this study the microhardness of four commercial dental composites containing micro- and nanoparticles was investigated. The main objective was to identify the effect of storage in physiological solution on properties of dental composites. Samples were tested without any treatment (control) to compare with samples stored in physiological solution.

MATERIALS AND METHODS

Four kinds of commercial composites were investigated in this study. Table 1 shows the trade names of these materials, sizes and amount of reinforcing fillers and manufacturers. All materials used had shade A3. For microhardness measurement, a form from PMMA plate was made with thickness of 1 mm. In the plate there were five holes drilled with an internal diameter of 6 mm. Each mold was placed on a strip (universal strips of acetate foil) that was placed on a microscopic glass slide. An amount of resin-composite sufficient to slightly overfill the mold was extruded from the tube. The material was then packed in a place using a nitride plated resin-composite instrument. Another strip was placed on the top of the mold and further covered with a second glass slide and pressed to extrude the excess material and to obtain a uniformly smooth specimen surface. Each specimen was light cured continuously for 40 seconds from the top of the specimen using Astralis7 (Halogen curing light, Ivoclar-Vivadent) with a light intensity about 750 mW/cm^2.

The distance between the head of light pipe and the samples was steady and amounted to ~0,5 mm. After hardening within 40 s time, the specimens were situated in the incubator (37°) for 24 hours. Next they underwent the microhardness tests. Vicker’s method with the use of Hanneman hardness tester (Zeiss) was used. Loading values equaled 0.1962 N. There were 10 microhardness measurements taken for each specimen. After the test, specimens were immersed in 20 ml of the physiological solution (pH = 7) contained within a dark bottle that was put in incubator (37°C). Next microhardness tests were performed after 14 and 28 days. Each specimen was then blotted dry using a filter paper then subjected to microhardness. The results were statistically analyzed with the use of Statistica 8 (StatSoft Inc.). For all statistical tests performed a result was considered statistically significant at the value of $p < 0.05$.

TABLE 1. **Material data**
TABELA 1. **Dane materiałów użytych w badaniach**

Material	Manufacturer	Type	Filler content wt. %	Particle size
Filtek Supreme	3M ESPE	nano	59.5	nanoclusters: 0.6÷1,4 μm; 5÷20 nm
Grandio	Voco GmbH	nanohybrid	87	20÷50 nm
Filtek Silorane	3M ESPE	microhybrid	76	0.1÷1 μm
Gradia	GC	micro	73	average 0.85 μm

RESULTS AND DISCUSSION

Mean values of measurements including standard deviations are presented in Figures 1-4. Significant differences are presented for the types of selected materials.

Microhardness of Filtek Supreme and Grandio obtained after curing are significantly different from those obtained in the second and third stage of the study. In cases of nanocomposites, Filtek Silorane and Gradia there were no significant differences observed in the results of microhardness.

Microfilled composites, Filtek Supreme and Grandio were significantly harder at the beginning of tests as compared with other materials tested. Furthermore, both materials were softened during storage time, Grandio diminished its microhardness in a linear manner while Filtek Supreme in an exponential one, with asymptotic value of about 65 HV0.02. There was also a large drop of microhardness observed for Filtek Supreme on the 14th day of storage (Figs. 1 and 2).

There was a significant difference observed between microhardness in the first and last stage of tests in both cases of tested materials. In nanomaterials Grandio and Filtek Supreme, the particles type (spherical, microhybrid or nanoclustered, respectively) could apparently lead to increased creep during curing, allowing tension releases. Grandio contains a smaller amount of resin than Filtek Supreme (according to manufacturer's information) and the degradation of resin caused by the physiological solution is considerably lower [5]. Therefore, micro-hardness diminished from 109.38 and 120.40 HV0.02 respectively to mean value of 80.98 and 65.94 HV0.02. Nano-particles have quite a large surface in comparison to their volume and therewith higher surface energies. In order to fill the gaps between the spherical particles, the sphere sizes must be varied. In Grandio composite spherical nano-particles (silicium dioxide, 20÷50 nm) and glass ceramic particles of fine-tuned size were used, which classifies Grandio as a nanohybrid composite.

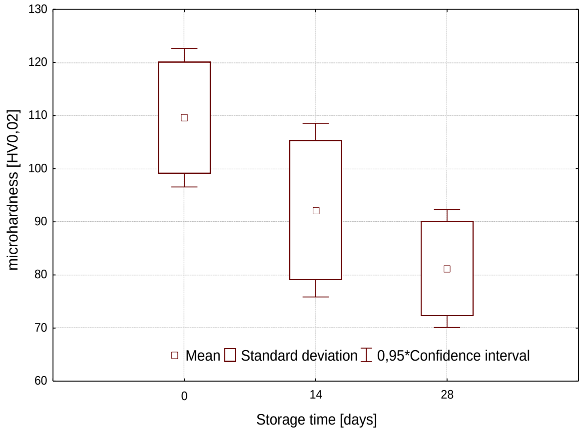

Fig. 1. Microhardness of Grandio in function of storage time

Rys. 1. Mikrotwardość materiału Grandio w zależności od czasu ekspozycji

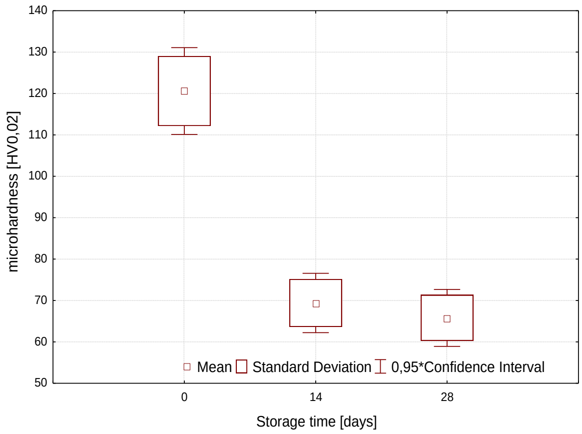

Fig. 2. Microhardness of Filtek Supreme in function of storage time

Rys. 2. Mikrotwardość materiału Filtek Supreme w zależności od czasu ekspozycji

The average microhardness of the Filtek Silorane composite slightly increased in the first stage of test. In the third stage, reduction of microhardness was observed, however, microhardness of the last step was higher than the one in the first stage. In fact, there was no significant difference observed between microhardness in every stage of test (Fig. 3). Water sorption for Filtek Silorane restorative is very low [9] due to the hydrophobicity of the silorane matrix, which results in a very low tendency for hydrolytic degradation of composite resin. The filler content in Silorane is similar to Gradia, but the second one showed considerably lower microhardness.

Microhardness of Gradia composite had the lowest value of all materials tested. 24 hours after curing the microhardness had value of 34.54 HV0.02, two-weeks time of storage in physiological solution decreased it to 29.46 HV0.02 and then another two weeks of immerse slightly increase the microhardness to 30.12 HV0.02. In fact, there was also no significant difference observed between microhardness in every stage of test (Fig. 4).

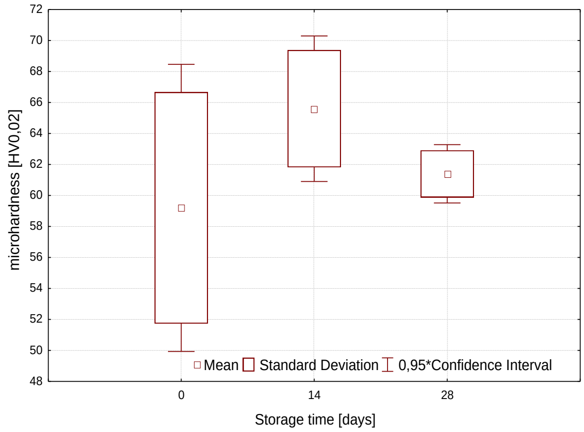

Fig. 3. Microhardness of Filtek Silorane in function of storage time

Rys. 3. Mikrotwardość materiału Filtek Silorane w zależności od czasu ekspozycji

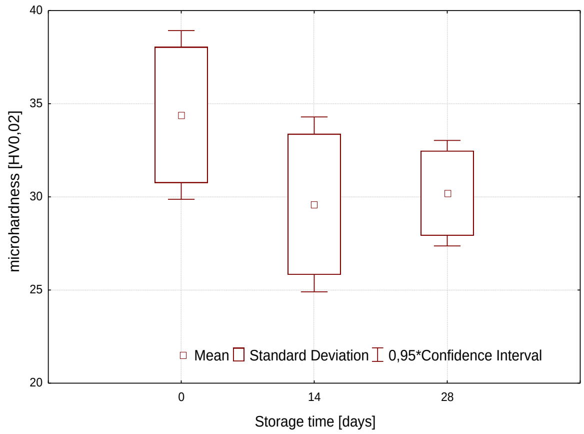

Fig. 4. Microhardness of Gradia in function of storage time

Rys. 4. Mikrotwardość materiału Gradia w zależności od czasu ekspozycji

The Gradia composite material is composed of 73% wt. of filler (silica with average particle size of 0.85 μm and prepolymerized filler) in methacrylate monomers matrix. Filtek Silorane consists of 76% wt. fine quartz particles and radiopaque yttrium fluoride. Silica appears to be a worse filler than fine quartz, particularly in association with relatively larger prepolymerized filler. Penetration of intender may cause cracking of prepolymerized filler particles resulting in the reduction of microhardness. From the filler side, Filtek Silorane restorative is to be classified as a microhybrid composite. The quartz surface is modified with a silane layer which was specifically matched to the silorane technology, in order to provide the proper interface of the filler to the resin [9].

CONCLUSIONS

Restorative materials based on Bis-GMA matrix showed the strict relation of storage time in physiological solution with microhardness value. The results obtained for Filtek Silorane exclusively revealed the lack of microhardness reduction caused by stability of silorane resin matrix in water environment. The type of filling material and size also exerted influence on microhardness, this produced the conclusion that hybrid materials were generally more stable (Grandio and Filtek Silorane).

Acknowledgments

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