Article citation info:
PIENIAK D, NIEWCZAS A, KORDOS P. Influence of thermal fatigue and ageing on the microhardness of polymer-ceramic composites for bio-medical applications. Eksploatacja i Niezawodnosc – Maintenance and Reliability 2012; 14 (2): 181–188.

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INFLUENCE OF THERMAL FATIGUE AND AGEING ON THE MICROHARDNESS OF POLYMER-CERAMIC COMPOSITES FOR BIOMEDICAL APPLICATIONS

WPŁYW ZMĘCZENIA CIEPLNEGO ORAZ STARZENIA NA MIKROTWARDOŚĆ KOMPOZYTÓW POLIMEROWO – CERAMICZNYCH DO ZASTOSOWAŃ BIOMEDYCZNYCH*

Studies presented in this paper, concern polymer-ceramic composites applied in the conservative dentistry. The aim of the study was to evaluate a long-term impact of the humid environment and cyclic thermal loads on the microhardness of new silorane-based composites and two methacrylate-based composites. The composite samples were subjected to normal saline environment with cyclically variable temperatures (5°C and 65°C), using a special thermal shock simulator. Microhardness was measured with Vicker's method before the fatigue test and after a series of 4000 thermal cycles. It is known that microhardness of silorane-based composite in opposite to methacrylate-based composites not decrease under the influence of cyclic thermal loads. It was found slight increase of microhardness under conditions of conducted tests. The ageing studies were also conducted consisting in microhardness evaluation of the composite samples in 6 months period. During that time the samples were kept in normal saline. The studies of hardness were carried out after each month of the exposure time. No long-term impact of normal saline environment with constant temperature on the microhardness of the studied materials has been noticed.

Keywords: *thermal fatigue, ageing, microhardness, dental composite fillings.*

Badania prezentowane w niniejszej publikacji dotyczyły kompozytów polimerowo-ceramicznych stosowanych w stomatologii zachowawczej. Celem pracy była porównawcza ocena wpływu długotrwałego oddziaływania wilgotnego środowiska oraz cyklicznych obciążeń cieplnych na mikrotwardość nowego kompozytu bazującego na siloranach oraz dwóch tradycyjnych kompozytów bazujących na związkach metakrylanu. Próbki z kompozytów poddano oddziaływaniu środowiska soli fizjologicznej o cyklicznie zmiennych temperaturach (5°C i 65°C) wykorzystując specjalny symulator szoków termicznych. Wykonywano pomiary mikrotwardości metodą Vickersa przed rozpoczęciem testu zmęczenia cieplnego oraz po serii 4000 cykli termicznych. Wykazano, że w przeciwieństwie do tradycyjnych kompozytów stomatologicznych mikrotwardość kompozytu bazującego na siloranach nie zmniejsza się pod wpływem cyklicznego oddziaływania szoków termicznych odpowiadających warunkom fizjologicznym jamy ustnej. W warunkach przeprowadzonych badań stwierdzono nieznaczny wzrost tej mikrotwardości. Przeprowadzono również badania starzeniowe polegające na ocenie mikrotwardości próbek kompozytów przez okres 6 miesięcy. W tym okresie czasu próbki przechowywano w soli fizjologicznej. Pomiary mikrotwardości wykonywano po każdym miesiącu ekspozycji. Wykazano, że długotrwałe oddziaływanie środowiska soli fizjologicznej w warunkach stałej temperatury nie zmienia mikrotwardości żadnego z badanych materiałów.

Słowa kluczowe: *zmęczenie cieplne, starzenie, mikrotwardość, kompozytowe wypełnienia stomatologiczne.*

1. Introduction

Polymer-ceramic composites are commonly applied as dental fillings materials. They are used due to their aesthetic properties (wide range of colours) and good mechanical properties. Polymer composite materials based on the methacrylate compounds consist of the matrix, which is a light-cured resin (up to 40% of the structure volume) and inorganic micro- or macro-nanofillers in most cases based on the silicon compounds (above 60% of the structure volume) [2,11,17]. Additionally, composite is composed of photo-initiators and pre-adhesive agents. A short characteristic of the polymer composite compounds is given in table 1.

Recently, in dental practice more and more the new silorane-based composite are used. A silorane-based composite has been introduced with distinctive polymerization characteristic to reduced polymerization shrinkage. The silorane matrix is formed by opening-ring during polymerization process. The silorane molecule represents a hybrid built-up of siloxane and oxiran

(*) Tekst artykułu w polskiej wersji językowej dostępny w elektronicznym wydaniu kwartalnika na stronie ***www.ein.org.pl***

Table. 1. Characteristics of the selected polymer-ceramic composites applied in dentistry.

Indication	Name of the compound	Characteristics
Organic composite phase (polymer)		
Bis-GMA	Bisphenol A-Glycidyl Methacrylate	Bis-GMA monomers have a large molecular weight and they undergo free-radical polymerization creating polymer rich in cross bonds and initiators.
TEGMA	Tetraethyleneglycol Dimethacrylate	These are dissolving monomers, they make composite material less viscous, their kontent influence also the level of polymerization shrinkage.
UDMA	Urethane *Dimethacrylate*	-
PCDMA	polycarbonate *dimethacrylate*	-
Inorganic composite phase		
-	This chase consists of among the others: lithium aluminium silicates, crystalline quartz, barium-aluminium-barium-silicon glass, strontium-barium-aluminium-fluorosilicate glass, silica, silanized lime	Based on ethe smolecules size inorganic phase can be divided into macro – (1 -30 μm) of qartz, glass, ceramic or micro-fillers (0,007 do 0,04 μm) prepared of silicon dioxide or in a different way – prepolymerized as a result of technological performance (1-200 μm), agglomerated (1-25 μm) or spheroidal (20-30 μm).
Photo-initiator		
CQ	camphorquinone	Fotoinitiators are used to polymerization by the generation of free radicals (in case of light photo-polymerization with wave length of approx. 400-500 nm, blue or violet light

structural moieties [15]. The silorane-based composite opens new vistas in reduction of marginal microleakage phenomenon [5,15,19]. Based on the literature [14] it is known that silorane-based composite has very good mechanical properties: high impact resistance, flexural strength and satisfactory hardness. Whereas the stability question is unknown in conditions log-term influence humidity environment and cyclically thermal fatigue correspond to oral cavity. Therefore, authors undertake a study of comparison the influence of ageing and thermal fatigue on microhardness new silorane-based composite and properties two "traditional" methacrylate-based composites.

Microhardness is a composite property, which is correlated with resistance to wear, also in case of thermal fatigue [3]. Investigations of microhardness allow evaluating mechanical properties of the composite. As it has been demonstrated in [13] there is a strong correlation between composite microhardness and elasticity modulus values, photo-polymerization depth, and the strongest with a polymerization shrinkage degree. In the paper concerning relation between physical-mechanical properties of the polymer composites and their application [9,16] a relationship between composite microhardness and degree of its wear in in vitro simulation conditions has been shown. Additionally, a correlation with the degree of composite filler conversion has been demonstrated [6]. Microhardness studies can be also used to evaluate a local gradient of photo-polymerization, which is a specific homogeneity of composite in the area of impact of the lamp light spectrum [8,18], influence of polymerization time and the type of the lamp's light. It can be also applied as a measure of residual mechanical properties in the ageing and fatigue studies.

Undertaking in vitro thermal fatigue simulation studies of the mechanical tooth-composite filling system, the loads conditions reflecting physiological conditions in the human oral cavity should be ensured. The following parameters should be controlled: temperature of the operating liquid (artificial saliva or normal saline), retention time of the operating liquid in the container with samples, or the studied sample in the container with operating liquid, as well as number of load cycles (thermal shocks).

In the previous studies different assumptions have been made with regards to the experimental parameters. Lower operating liquid temperature applied in the experiments, was between 2 and 24ºC [7], whereas heated liquid temperature was in a range of 45ºC [4] and 60 ºC [20]. Retention time of the liquid in the container with samples was from 15 even up to 180 seconds, while number of cycles varied from 25 to 1 million thermal cycles [1,7]. Currently, most often the following experimental parameters are assumed:

- Cooled operating liquid temperature − 5 ºC,
- Heated operating liquid temperature from 55ºC to 65 ºC,
- Retention time of the operating liquid in the container with samples – 30 seconds,
- Number of thermal cycles – from a few up to a few thousands.

2. Materials and methods

In both conducted tests of thermal fatigue and ageing, the same composites applied in stomatology were considered. The commercial methacrylate-based materials, such as: Ice (SDI), Venus (Heraeus) and new silorane-based Filtek Silorane (3M ESPE) – table 2.

The examples of SEM analysis results are presented in figure 1. There are visible molecules of composite polymer phase (larger), and also molecules of inorganic filler (smaller). The latter ones are the molecules with more regular shape, often close to spherical, with a similar size of grains.

From the selected materials disk shape samples with 14 mm diameter and 1 mm thickness were made. Photo-polymerization

Table 2. List of the studied composites

Material Type	Manufacturer	Resin	Filler content (wt%)	Size of filler molecules
Ice nanohybrid	SDI	multifunctional methacrylic ester	77,5 inorganic filler	0,04 – 1,5 μm
Venus microhybrid	Heraeus-Kulzer	bisphenol-A glycidyl methacrylate (Bis-GMA) trietylen glycol dimethacrylate (TEGMA)	80 barium glass inorganic filler	0,04 -1 μm
Filtek Silorane silorane	3M ESPE	silorane	76 inorganic filler	0,04 – 1,7 μm

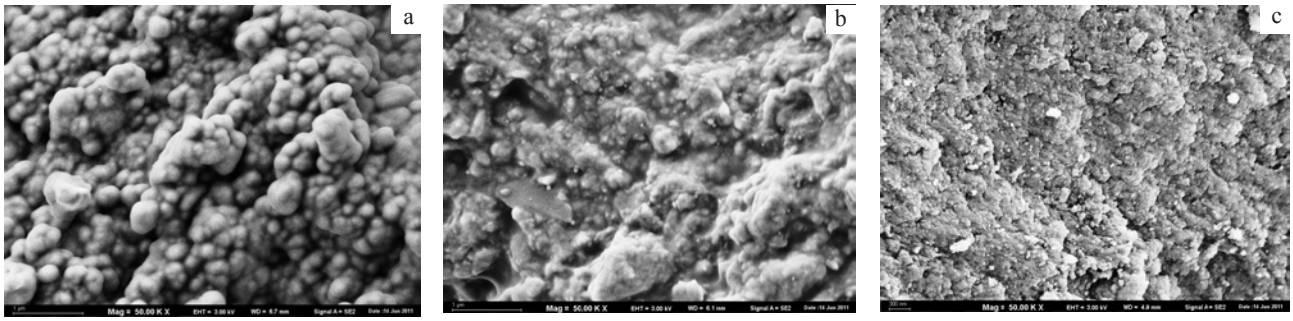

Fig. 1. SEM images of the sections of the studied materials: a) Filtek Silorane, b) Ice, c) Venus

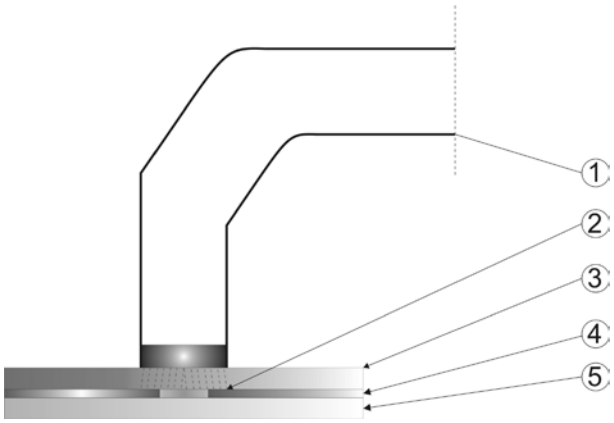

Fig. 2. Production of samples made of light-cured composites: 1 – lamp, 2 – exposed composite sample, 3 and 5 – plexiglass plates, 4 – steel form

process was conducted with the use of halogen lamp as shown in figure 2. The exposure time of the samples was 40 seconds, according to materials manufacturers' recommendations.

In these studies a thermal shocks simulator was applied, designed in order to investigate dental materials. The device was made by the staff of the Mechanical Department of Technical University in Lublin in cooperation with Medical University in Lublin.

The thermal shocks simulator (fig. 3) consists of the microprocessor control system and hydraulic system. The device enables creation of thermal shocks in the samples placed in the measuring container located in the simulator. Operation of the device consists of the cyclic pumping in and out of the operating liquid from the measuring container. The container is alternately filled with heated (65°C) or cooled operating liquid (5°C) from two independent temperature conditioning systems [11].

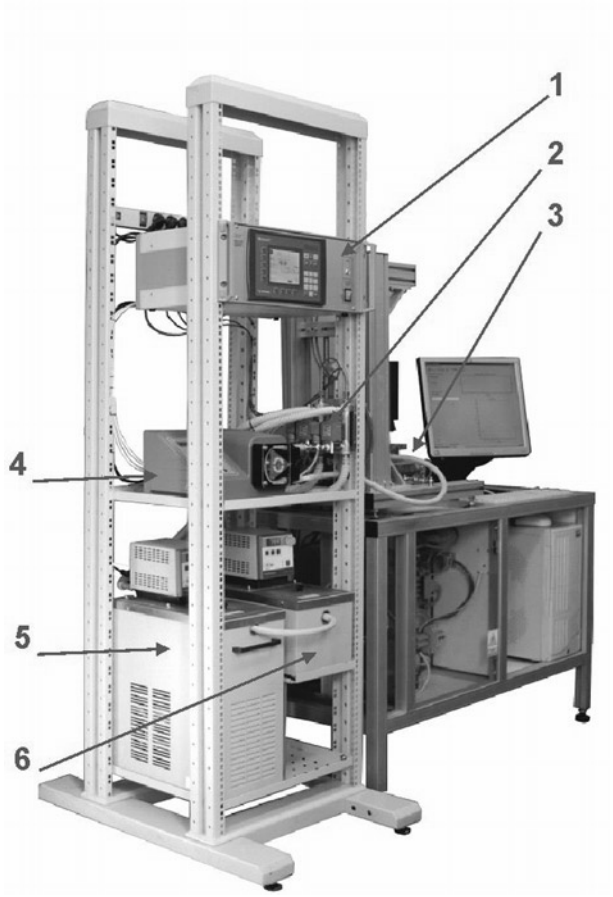

Fig. 3. Experimental stand for durability studies with specific thermal shocks module components: 1 – micro-processor control system, 2 – control valves, 3 – chewing simulator, 4 – peristaltic pomp, 5 – cooling thermostat, 6 – heating ultra-thermostat

Time of the subsequent procedures performance within each thermal shocks cycle was programmed and repeatable. Retention time of the cooled and heated liquid was 30 seconds, time pumping in and out of operating liquid was 10 seconds (fig. 4).

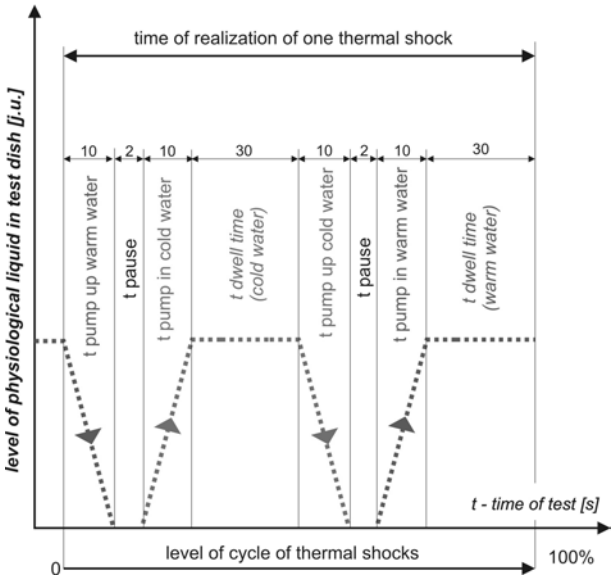

Fig. 4. Thermal shock algorithm with a single pumping of the operating liquid

Microhardness studies were conducted according to Vicker's method using Futertech FM 700 (Future-tech Corp. Japan), with load of 50g. A specified penetration time of the indenter was 15 seconds. The measurements were taken at ten points of the samples' surfaces. Measuring coordinates were determined in order to include possibly a whole sample surface. They were identical for all samples. The studies were conducted both at the exposed (lc) and non-exposed (nlc) samples surface.

Microscopic analyses of the composites structure were carried out in the Laboratory of Electron Microscopy of the Catholic University in Lublin. Microscopic observations were conducted by means scanning electron microscope (SEM) by Zeiss.

Ageing studies were also performed (for 6 months period), based on micro-hardness evaluation of composites as a function of exposure time in saline. One of the objectives of the studies was to obtain a reference sample for the comparison with the results obtained in thermal fatigue test.

3. Studies results

Results of the performed fatigue tests with the use of thermal shocks simulator are shown in fig. 5 and table 3. The results of ageing studies are presented as a box plot in figure 6.

4. Discussion

The effect of the thermal influence on the decrease of microhardness methacrylate-based composites Venus and Ice. The highest drop of microhardness after 4000 thermal cycles (4kTC) for Venus material was noticed, which can be seen in the graph (fig. 5c) and was confirmed by the t-Student test results (tab. 4). T parameter values for this material were the highest in the most comparisons. The influence of the thermal fatigue on the faster weakening of non-exposed surface (nlc) than the exposed one (lc) of Venus material has been demonstrated.

Investigations of Ice material confirmed the influence of thermal shocks on the micro-hardness decrease. It was not as high as in case of Venus material, however it was visible. This relationship was confirmed by t-Student test. The highest values of t parameter were obtained in comparison of the results before and after thermal fatigue test performance.

In case of FSi (Filtek Silorane) material a decline in average microhardness values after 4000 TC cycles was not shown. However, a slight increase was noticed. Statistically significant increase of micro-hardness at the exposed surface was also confirmed by t-Student test results. However, in case of this material impact of 4000 thermal cycles was the least visible and it resulted in different consequences that the observed for the two other materials.

That fact is connected with different phase composition Filtek Silorane, a new silorane-based composite. Similar observation was presented in the literature [14].

Analysing the results of ageing studies it can be concluded that despite a slight micro-hardness fluctuations during the test

Table 3. Results of microhardness. Descriptive statistics. TC – thermal cycles, lc – expose surface, nlc – non-exposed surface

Group	Valid N	Mean	Median	Minimum	Maximum	Std.Dev.	Coef.Var.
Filtek Silorane 0TC lc	40	51,97275	52,20000	48,80000	57,00000	1,791623	3,447235
Filtek Silorane 0TC nlc	40	49,38750	49,71000	42,76000	55,48000	2,742934	5,553903
Filtek Silorane 4kTC lc	40	54,80075	55,24500	47,42000	61,31000	3,102902	5,662153
Filtek Silorane 4kTC nlc	40	50,15750	50,02500	42,09000	56,24000	3,091503	6,163590
Ice 0TC lc	40	51,95350	51,86500	45,53000	57,71000	2,736424	5,267064
Ice 0TC nlc	40	49,96100	49,84000	45,18000	54,28000	2,700346	5,404909
Ice 4kTC lc	40	47,23800	47,22500	41,92000	51,75000	2,737509	5,795141
Ice 4kTC nlc	40	44,58550	44,99500	35,28000	52,56000	4,141693	9,289327
Venus 0TC lc	40	48,60775	48,39500	43,94000	55,73000	2,613053	5,375794
Venus 0TC nlc	40	48,88650	49,11000	42,90000	54,27000	2,974151	6,083787
Venus 4kTC lc	40	37,78125	37,88000	33,82000	41,77000	1,973859	5,224440
Venus 4kTC nlc	40	35,14625	34,96000	30,37000	41,45000	2,322400	6,607817

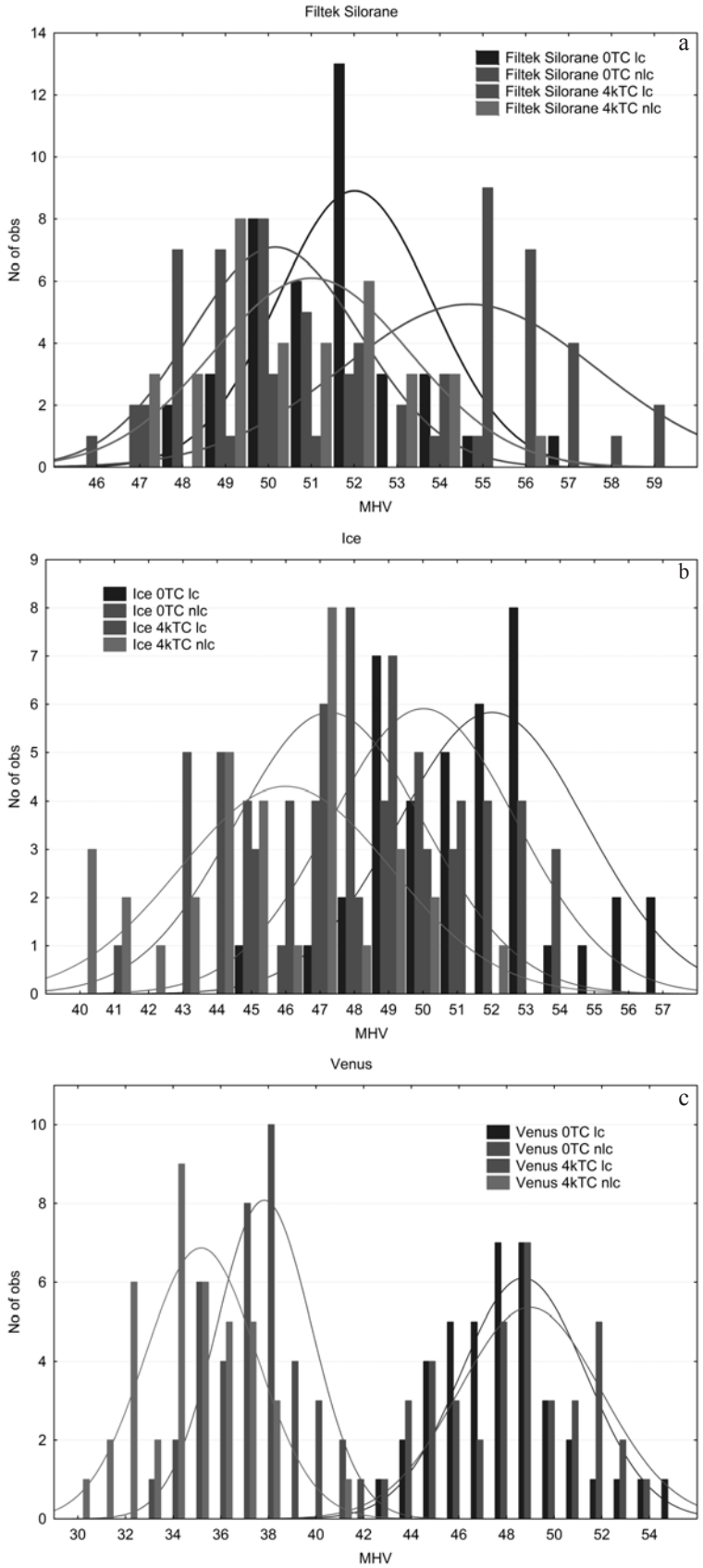

Fig. 5. Stemplot of micro-hardness of the studied materials after fatigue tests: a) Filtek Siloran, b) Ice, c) Venus

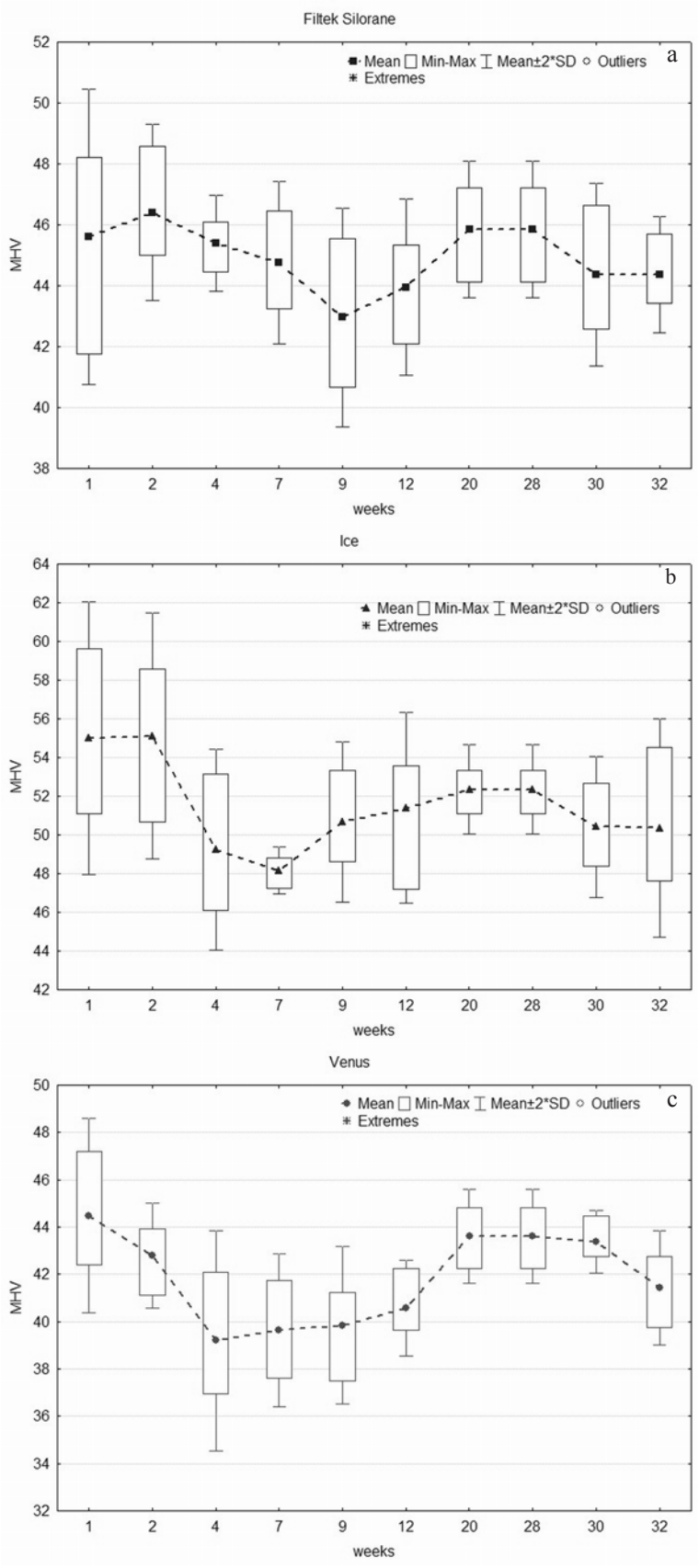

Fig. 6. Relationship of micro-hardness of the studied materials and ageing time in saline: a) Filtek Siloran, b) Ice, c) Venus

Table 4. T-Student test results of microhardness. TC – thermal cycles, lc – exposed surfaces, nlc – non-exposed surfaces

No	Gr. 1 vs Gr. 2	T	df	p
1	FSi 0TC lc vs. Fsi 0TC nlc	4,99	78	0,000004
2	FSi 0TC lc vs. Fsi 4kTC nlc	3,21	78	0,00191
3	FSi 4kTC lc vs. Fsi 0TC lc	4,99	78	0,000004
4	FSi 4kTC lc vs. Fsi 0TC nlc	8,27	78	0
5	FSi 4kTC lc vs. Fsi 4kTC nlc	6,7	78	0
6	FSi 4kTC nlc vs. Fsi 0TC nlc	1,18	78	0,242252
7	Ice 0TC lc vs. Ice 0TC nlc	3,28	78	0,001563
8	Ice 0TC lc vs. Ice 4kTC lc	7,71	78	0
9	Ice 0TC lc vs. Ice 4kTC nlc	9,39	78	0
10	Ice 0TC nlc vs. Ice 4kTC lc	4,48	78	0,000025
11	Ice 0TC nlc vs. Ice 4kTC nlc	6,88	78	0
12	Ice 4kTC lc vs. Ice 4kTC nlc	3,38	78	0,001138
13	Venus 0TC lc vs. Venus 4kTC lc	20,91	78	0
14	Venus 0TC lc vs. Venus 4kTC nlc	24,35	78	0
15	Venus 0TC nlc vs. Venus 0TC lc	0,45	78	0,657331
16	Venus 0TC nlc vs. Venus 4kTC lc	19,68	78	0
17	Venus 0TC nlc vs. Venus 4kTC nlc	23,03	78	0
18	Venus 4kTC lc vs. Venus 4kTC nlc	5,47	78	0,000001

period (fig. 6), an unequivocal impact of the exposure in saline on the changes in micro-hardness have not been demonstrated.

5. Conclusions:

1. Changes of microhardness for FSi (Filtek Silorane) material due to thermal shocks were insignificant.
2. The impact of thermal fatigue on the microhardness decrease of the methacrylate-based composites Venus and Ice has been demonstrated.
3. No impact of ageing in humid environment on the microhardness of the studied materials has been noticed.
4. It has been concluded that the applied method of the studies can be useful for the preliminary qualification of the operational usability of the dental composite materials.

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