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Research Article

A Study of the Micro-Hardness of Silorane-Based and Methacrylate-Based Composites after One-Month Water Storage

Nafiseh Elm Amooz[1], Mohammad Pirouzan[2*]
and Zahra Pirouzan[3]

[1] Assistant Professor, Oral and Dental Diseases Research Center and Kerman Social Determinants on Oral Health Research Center and Department of Operative Dentistry, School of Dentistry, Kerman University of Medical Sciences, Kerman, Iran.
[2]Student Research Committee, Alborz University of Medical Sciences, Alborz, Iran.
[3]Dentistry Student, ShahidSadooughi dental school,
ShahidSadooughi University of Medical Science,
Yazd, Iran.
*corresponding Author: Mohammad Pirouzan, Email: mohammadpirouzan@gmail.com

ABSTRACT

Background and purpose: In order to overcome the issue of polymerizationshrinkage in methacrylate-based dental composites, a new type of composite has been presented recently which are silorane-based and have been claimed to be of significantly lower shrinkage in comparison with methacrylic types. The purpose of this study is to evaluate the micro-hardness of methacrylic and silorane composites subsequent to a one-month period of being stored in water.

Method of study: A number of 20 disk-shaped samples (10mmx2mm) were made with each of the three composites of Z350, Z250, and LS (a total number of 60 samples). After being stored in 37^0C-water for 24 hours, the samples underwent finishing and polishing processes. Subsequently, the samples were randomly assigned to two groups; namely test group and control group (10 samples in each group). The control group was stored in a dry environment and in room temperature (25^0C). The test group was stored in 37^0C distilled water for one month. After a period of one month the samples were placed in a micro-hardness tester machine and their Vickers hardness numbers were obtained. The obtained data was analyzed using SPSS statistical software and compared using two-way ANOVA test and post-hoc Tukey test. The level of significance (P value) was 5%.

Findings: The mean micro-hardness of Z350 and Z250 composites was higher than LS composite in case of the two storage environments. The mean micro-hardness of all composites were lower in water than the room temperature though of none significance in case of LS composite.

Conclusion: Silorane-based composites sustained their micro-hardness better than methacrylic composites after a one-month period of storage in water.

Keywords: Micro-hardness, Dental composites, Silorane, Storage in water

INTRODUCTION

Composites are widely applied in dentistry which is to some extent due to their aesthetic appearance, ease of use, and their ability to bond to tooth structure. These materials ought to be of high long-term strength as to be of desirable clinical application (1, 2, 3). The long-term strength of these materials is affected by not only their intrinsic characteristics, but also by the environment they are placed in (1, 2, 3). The oral area is humid, warm, and affected by thermal cycles. It has also been illustrated that water is able to destruct composites through hydrolysis of filler particles, weakening polymeric matrixes, and separating filler-matrix adhesion. This process has an destructive impact both in long-term and short-term on polymeric networks and alters their structure both physically and mechanically (4, 5, 6).The physical characteristics present their importance at the time of proper material selection since they strongly affect the clinical strength of restorations. One of the main characteristics of these materials is their hardness which is associated with the clinical strength of restorations, abrasion, and composites' degree of conversion (3, 7).As the abrasive resistance of dental materials has a significant impact on the efficiency of clinical restorations, hardness measuring tests are applied to predict the resistance of dental materials (8).

Lower figures of hardness are commonly connected with low abrasive resistance and vulnerability to scratches which might affect the fatigue strength and result in fractures in restorations. Moreover, damages to the resin surface and separation of filer from the surface can form microscopic changes and alters the smoothness of the materials in the course of time and thus interfere with the aesthetic appearance of the restoration and the health of soft and hard tissues (3, 9). Common composites are generally composed of a methacrylate-based resin matrix (25-30% of volume) and fillers of glass or ceramic materials (70-75% of volume) and a matrix-filler adhesive agent. Oligomers including BISGMA, UDMA, and TEGDMA are commonly applied in resin matrixes. Monomeric matrixes strongly impact polymerization, reactivity, mechanical features, and composites' water absorption (8).

Weinmann has recently reported the synthesis of a new monomeric system names siloranewhich is obtained from the reaction of oxirane and siloxane molecules. Silorane-based composites are of low polymerization shrinkage due to the ring-opening of oxirane monomer and their hydrophobicity is higher due to the presence of siloxane derivatives (10). It has also been suggested that silorane composites are stable and insoluble in bio-fluids simulated through water solutions containing epoxide hydrolase, porcine liver esterase, and diluted HCL (11).

Additionally, previous studies indicated contradictory results regarding the impact of aging on composites (3 and 5). Thus, more investigations on the impact of aging on the stability of silorane and methacrylic composites' mechanical characteristics deem to be of necessity.The purpose of the present study is to evaluate and compare the effect of storage in water on the hardness of silorane and methacrylic composites in controlled laboratory environment.

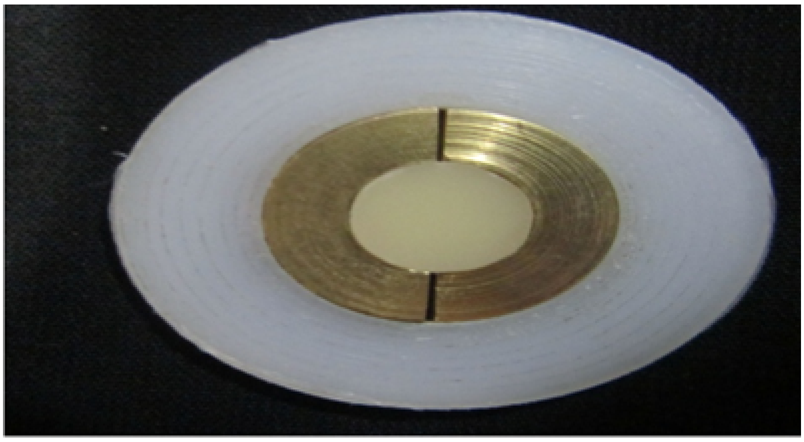
METHOD OF STUDY

2 types of methacrylic composite of Filtek Z350 (Figure3-1) and Filtek Z250 (3M ESPE and USA) (Figure 3-2) and 1 type of silorane composite, Filtek LS (3M ESPE and USA) (Figure 3-3) were applied in this in vitro study.

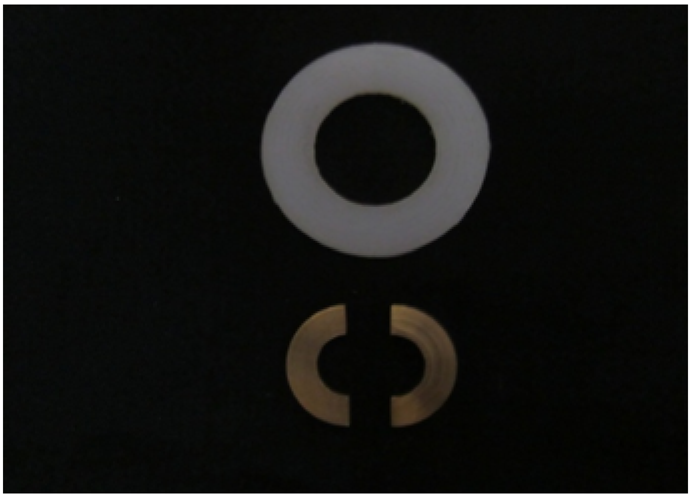
All the composites were selected from the A_2 color. The combination of the applied composites is provided in Table1.

Material	Type	Composition	Manufacturer	Lot No
Filtek Z250	Microhybride	Bis-GMA, Bis-EMA, UDMA, TEGDMA, zirconia/silica (0.01–3.5 μm, 60 vol%)	3M ESPE USA	N386458
Filtek Z350	Nanofill	Bis-GMA, Bis-EMA, UDMA, TEGDMA, Nanofillers of silica(5-20nm) and Nanoclusters of zirconia/silica (0.06 and 1.4 μm ,63.3 vol%)	3M ESPE USA	N261323
Filtek LS	Microhybride	Bis-3,4-EpoxycyclohexylethylPhenylMethylsilane 3,4Epoxycyclohexylcyclopolymethylsiloxane Silanized, Quartz,Yttrium fluoride (0.1-2 μm, 55 vo%l)	3M ESPE USA	N355866

20 samples of each composite (a total number of 60 composites) were fabricated using a two-part, cylinder-shaped brass mold (inner diameter 10mm and thickness 2mm) (Figure1).



During the fabrication process the mold was placed on a slide under microscope and then the composite was placed in the mold with a second slide covering the mold and, subsequently, a 5kg pressure was applied for a period of 3 minutes to ensure the consistency of the molds and eliminate air bubbles. The samples then were exposed to cure for a period of 40 seconds from each dimension (80 seconds in total) with an overlap method. The equipment used in curing was Demetron LC quartz tungsten halogen device with an approximate power of 600-650 mw/cm^2, manufactured by Sds Kerr Co., US. (The device power was checked periodically using a radiometer). The upper slide was exposed to the end of the light guide during polymerization. Thus, the distance between the light source and the sample was standardized using the glass slide (Figure2).

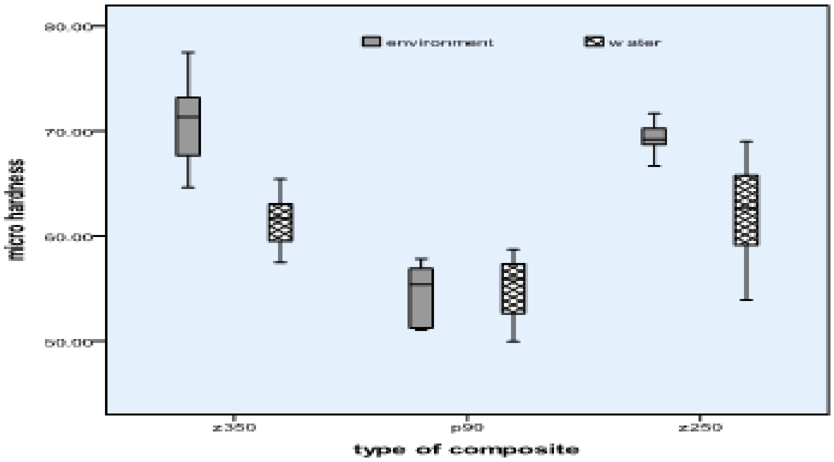


After the light curing process, the samples were stored in 37^{0}C distilled water for24 hours. In order to homogenize the clinical state of the samples as well as removing the o2-inhibited surface layer, the samples were polished using silicon carbide paper 600 and 1200 grit. This procedure was conducted using a mechanical polisher device (Struers, Denmark) through which the respective paper was installed in the device and the sample was placed under consistent finger pressure on the spinning disc for 3 minutes.

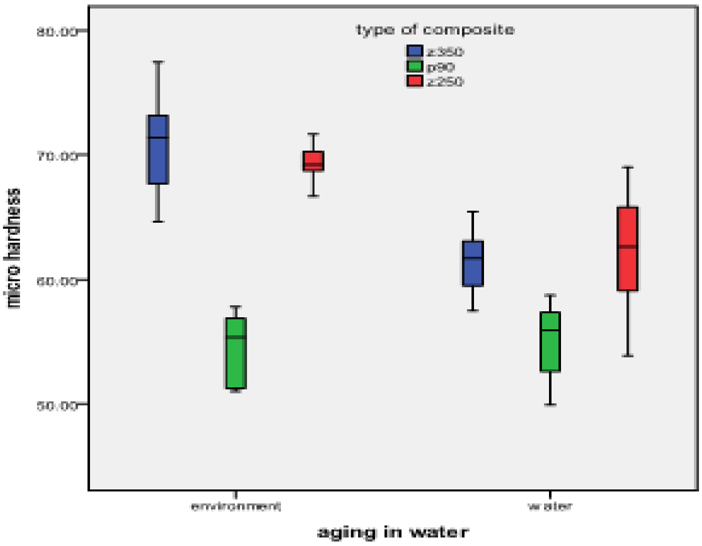
Subsequently, the samples were randomly assigned to the two groups of control and test (10 samples per group):

1- The control group was stored for a period of 1 month in a dry environment and in room temperature (25^{0}C).
2- The test group was stored in 37^{0}C distilled water for one month.

To maintain the temperature of the samples during the abovementioned period, an incubator (Gallen KAMP-Japan) was employed. After one month, the samples were removed from their storage and placed under a micro-hardness tester device (Duramin 20- Denmark-Struers-2000) to measure their micro-hardness with a 100gf pressure through the indenter for a period of 10s with an accuracy of 0.01 μm (Figure3).



The micro-hardness of the samples was measured on 3 different spots on each sample. The distance between the measured spots was at least 3 times of the indenter and was at least 1mm from the edges of the samples. The mean micro-hardness was obtained through the average of the hardness of these 3 spots. The measured hardness was of Vickers type. In Vickers hardness measurement a 136-degree diamond pyramid is employed to apply pressure on a surface and the formed surface is in the shape of a square (Figure4).



The obtained data was analyzed by SPSS18 statistical software and compared using two-way ANOVA test and post-hoc Tukey test. The level of significance (P value) was 5%.

FINDINGS

The results regarding the mean micro-hardness obtained from the two storage conditions are provided in Table1 concerning the composites under study.

The results indicated that the extent of micro-hardness differed in different groups, in other words, the composite type has impacted the mean micro-hardness ($p<0.05$). The mean micro-hardness of Z250 and Z350 composites was significantly higher than LS composite. In regards with the variable of storage condition, a significant difference was observed among the different groups regarding the extent of micro-hardness ($p<0.05$), to elaborate on the issue, storage in water resulted in a reduction of the mean micro-hardness of methacrylic composites (Z250, Z350) which was of statistical significance. Regarding LS silorane composite, the mean micro-hardness slightly increased after being stored in water which was not statistically significant. Moreover, as illustrated in Table4-2, between the two variables of composite type and storage in water a reaction was noticed. In other words, the impact of composite type on the mean micro-hardness differed in different storage conditions (water and room temperature).

Based on the results of two-way variance analysis test, composite type is an effective variable regarding the extent of micro-hardness. In a one-on-one comparison of the groups under study, the mean micro-hardness was higher in the Z350 composite than the LS type. Regarding Z250 and LS composites, a similar correlation was observed meaning that the mean micro-hardness of the Z250 composite as higher than the LS type which was significantly different ($p<0.05$). The findings indicate that the difference of mean micro-harness between the two composite types of Z250 and Z350 is not significant and is of random origins since the observed difference has been of none statistical significance.

Table2: Mean and standard deviation of micro-hardness results of the composites under study

Aging in Water	Composite	Mean of Micro Hardness	*SD
-	Z 350	70.8	3.88
	LS	54.7	2.62
	Z 250	69.5	1.61
+	Z 350	61.5	2.75
	LS	55.1	3.15
	Z 250	62.3	5.19

Table3: Comparison of mean micro-hardness in different storage conditions through Tukey test

Total	Df		Pvalue	F	
	2		<0.001	72.23	
Composites	Mean Difference		Pavalue	CI*	
Z 350 –LS	11.23		<0.001	(8.66 ,13.81)	
Z 350 – Z 250	0.26		0.97	(-2.31 , 2.83)	
Z 250 – LS	10.98		<0.001	(8.40 ,13.55)	

DISCUSSION

The present study was conducted so as to measure the micro-hardness of 2 methacrylate-based composites and 1 silorane-based composite. The applied distilled water has simulated the salivary oral environment.

Filtek LS has been introduced as a posterior composite. Posterior composites are expected to illustrate a higher abrasive resistance which has a significant impact on the clinical application of restorations. Therefore, the micro-hardness test is employed to predict the abrasive resistance of dental materials (12).

A definite chemical softening of methacrylate-based composites (Z350 and Z250) was detected in the present study subsequent to one-month storage in water in comparison with the control groups. This reduction in the hardness of methacrylate-based composites has been reported after different intervals in various studies (3, 8, 20).

Water enters the polymeric network through pores and intermolecular spaces. The absorption of water leads to the expansion of composites and reduction of frictional forces, release of elements such as unreacted monomers, polymerization catalysts, and filler components (5, 6, 12, 13, 14).

Hardness reduction occurs due to the separation of polymeric chains where a water molecule, without creating a chemical connection with a chain, occupies the space between the chains (plastification). Therefore, the main impact is from reducing connections between chains through forming secondary links or occupying the spaces. The other probability is a chemical destruction caused by hydrolysis. Hydrolysis is a complicated process. Following the entry of water to the polymeric mass, the polymeric network is dismantled and oligomers as well monomers are released.As destruction progresses, the microstructure of the composite mass alters due to the formation of pores through the release of oligomers, remaining monomers, and the products of destruction (14). This process causes a reduction in hardness and probably other mechanical properties of the composites under study. Methacrylic composites are generally composed of a resin matrix, glass or ceramic fillers, and an adhesive agent between the filler and matrix. Previous studies have evaluated the effect of water on the hardness reduction of methacrylate-based composites. The phenomena of water absorption and composite materials solubility depend on a series of factors including chemistry of resin monomers, polymerization volume of polymeric matrixes, size, shape, and distribution of filler particles, and interfacial properties between filler particles and resin matrixes (4, 6, 8, 15, 16, 17).

The present study indicated a higher hardness of Z350 composite compared to Z250 composite.

Z350 and Z250 composites have a similar matrix combination including Bis GMA, Bis EMA, UDMA, and TEGDMA, however, the combination of their mineral particle (amount and size of the filler particles) vary. Thus, the difference in their hardness can be attributed to the differences in size, shape, and amount of filler particles present in the combination of these materials (Table3-1). Regarding the effect of monomers on the absorption of composites, it has been reported that the increase of TEGDMA amount in a resin matrixes results in an increase in water absorption (15). Also Bardem and Dury illustrated that resins with Bis GMA cause more water absorption than the types contacting UDMA (18). A study by Watts et al. indicated that a composite with optimized BisGMA and UDMA is of higher physical stability in water and low water absorption (19).

The methacrylic composites under study (Z350 and Z250) have a similar monomeric structure though their monomer/filler ratios vary. Therefore, their varied hardness could be attributed to these different monomer/filler ratios. The hardness of the Filtek LS composite was lower than methacrylic compositions in this study which confirms the results obtained from studies by Bechtold and Perlati (20, 21).

Since the previous studies have indicated that variables such as size, shape, distribution and volumetric as well as weight content of the filer existing in the matrix, strength properties, hardness, and index of elasticity affect the composites, the varied hardness of Filteksilorane and methacrylic composites can be attributed to lower contents of the filler (approximately 55% of volume) of the silorane composite compared to methacrylic composites of Z350 and Z250 (60% and 63.3% of volume respectively).

Moreover, the filler present in Z250 and Z350 composites are of zirconia/silica while the fillers of Filtek LS consist of a combination of quartz and yttrium fluoride. The Knoop hardness number (KHN) of quartz is 820 and the KHN of zirconia is 1160 which justifies the higher hardness of methacrylic composites compared to silorane ones to some extent (20, 21).

Filtek LS composites sustained the level of their hardness in their storage condition to a more agreeable extent than methacrylic composites which has also been confirmed by Kusgoz and Yesilyurt study (8, 13). This issue is due to the water absorption on the polymers' side. Methacrylate-based composites have a matrix which contains Bis GMA, Bis EMA, UDMA, and TEGDMA. Excluding Bis EMA which is a version of BisGMAethoxylated, other molecules (Bis GMA, UDMA, and TEGDMA) contain hydroxyl groups which leading to the continuation of water absorption while Filtek LS composite contains Cyclopolymethylsiloxane – Epoxy cyclohexyl-4 and 3. Cyclosiloxane scaffold leads to the occurrence of hydrophobicity and reduces the absorption of water (10).A second probable reason for the LS composite ability to sustain hardness compared with Z250 and Z350 is due to the existing filler combination in this composite. Composites containing zinc and barium glass fillers are more receptive of hydrolysis compared to quartz fillers (22). Moreover, Yap et al. reported that zirconia glass fillers are more vulnerable regarding hydrolysis (2). The methacrylic composites in the present study contain Zr/Si fillers while the silorane composite contain mineral fillers of quarz and yttrium fluoride. Therefore, varied filler combination can also be a reason for different hardness alterations of composites in their storage conditions.

CONCLUSION

1- The micro-hardness of the methacrylic composites of Z250 and Z350 in both storage environments of water and room temperature was significantly higher than the silorane LS composite.
2- The micro-hardness of the methacrylic composites of Z250 and Z350 in both water and room temperature was higher than the silorane LS composite.
3- The silorane LS-based composite sustained its micro-hardness after being store in water for a period of one month better than its methacrylic peers; in other words, storage in

water had none considerable impact on the micro-hardness of the mentioned composite.

SUGGESTIONS

Considering that the silorane LS composite has been recently released to the dental materials market, it is essential that further clinical and laboratorial studies be conducted to detect the various properties of the mentioned composite and its advantages and disadvantages in comparison with methacrylic composites.

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