

## THE EFFECT OF SHORT TERM WATER STORAGE ON FRACTURE TOUGHNESS AND MICRO HARDNESS OF A LOW-SHRINKAGE SILORANE AND DIMETHACRYLATE BASED NANOHYBRID COMPOSITES

Maha Adly Abdel Motie \*

### **ABSTRACT**

**Objectives:** The purpose of this study was to assess the effect of water storage on the fracture toughness ( $K_{IC}$ ), and micro-hardness of a low shrinkage silorane based and a nanohybrid dimethacrylate composite resin materials.

**Materials and Methods:** Two types of composite resins were selected: nano hybrid methacrylate based (Grandio) and microhybrid silorane based (Filtek P<sub>90</sub>). For fracture toughness test, a total of 40 single edge notched bar-shaped specimens were prepared and stored in distilled water for 24hrs and 6 weeks. The effect of water uptake on fracture toughness following each storage regimen was determined by loading the specimens to failure in a 3-point flexure strength test setup using a universal testing machine. For Vickers hardness test, 40 disc shaped specimens (height 2 mm, diameter 5 mm) were prepared from each composite material and subjected to testing after 24 hours and six weeks of water storage. The fractured surface was examined using scanning electron microscopy (SEM) to determine the failure pattern following both storage periods.

**Results:** Statistical analysis ( $T=8$ ,  $p<0.0001$ ) revealed that the 24hrs fracture toughness of Silorane was significantly higher ( $1.65\pm 0.12$  MPa.m<sup>1/2</sup>) than Grandio ( $1.11\pm 0.12$  MPa.m<sup>1/2</sup>). After six weeks storage in water the two materials showed a significant decrease ( $T=13.5$ ,  $P<0.001$ ) in fracture toughness with Silorane still exhibiting a higher fracture toughness ( $1.22\pm 0.07$  MPa.m<sup>1/2</sup>) compared to Grandio ( $0.56 \pm 0.08$  MPa.m<sup>1/2</sup>).

Silorane showed a highly significant difference in VHN ( $67.18\pm 1.33$ ) compared to Grandio ( $42.37\pm 0.73$ ) at the 24 hrs period. After 6 weeks storage in water, a significant decrease was observed in VHN of Grandio ( $30.55\pm 0.71$ ) while Silorane did not show any decrease in VHN ( $67.44\pm 1.16$ ). SEM imaging findings were consistent with the results

**Conclusions:** Within the limitations of this study, Silorane P<sub>90</sub> exhibited higher fracture toughness and microhardness compared to Grandio nanohybrid composite in both storage periods. Although water storage decreased fracture toughness of Silorane it still remained significantly higher than Grandio. VHN of Silorane was not significantly affected by water storage after six weeks, while, Grandio showed a highly significant decrease in VHN following water storage.

\* Assistant Professor, Dental Biomaterials, Faculty of Dentistry, Alexandria University, Egypt

## INTRODUCTION

The organic base of most modern resin-based composites (RBCs) consists of the Bis-GMA oligomer. However, these composites set by a free radical polymerization reaction involving the carbon double bonds in the dimethacrylate monomers. This contributes to the main short comings of dental composites, that is marginal leakage due to polymerization shrinkage and stress which contribute to clinical problems in the integrity of the restoration margins.<sup>(1)</sup>

Efforts to overcome clinical deficiencies of RBCs have led to the development of new matrix materials, respective to change in the filler amount, shape or surface treatment. Other approaches include the development of liquid crystalline monomers or ring opening systems to develop non or minimally shrinkage dental composites which contain spiro orthocarbonates as additives to dimethacrylates or epoxy-based resins.<sup>(2)</sup>

Some modern developments in dental composite research have focused on the use of ring opening systems like oxirane – based resins, that have shown many desirable properties such as improved depth of cure, lower polymerization shrinkage, higher strength as well as equivalent hardness when compared with conventional methacrylate based dental composites.<sup>(3)</sup>

A low shrink silorane composite was developed to reduce polymerization shrinkage and the related polymerization stress. The name silorane is derived from a combination of the monomers, siloxane and oxirane. The network of silorane is generated by the cationic ring opening of the cyclo aliphatic oxirane which reduce polymerization shrinkage. The cationic ring opening reaction is also insensitive to oxygen.<sup>(1)</sup>

The siloxane chain increased the hydrophobicity of the compound which improves the long term resistance of the restoration. Additionally,

hydrophobic materials tend much less to absorb the dyes of the daily nutrition and are less sensitive towards exogenic staining than hydrophilic materials.<sup>(4,5)</sup> Silorane is more biocompatible as it is free from Bisphenol A which is widely used in methacrylate based composite.<sup>(6,7)</sup> It exhibits mechanical properties that are comparable to methacrylate resin – based composites, it has better marginal integrity, better flexural strength, and lower solubility in water.<sup>(8)</sup>

Several properties of silorane based composite have been previously studied, there remains a need of carrying out studies about the performance analysis between materials with different composites.

Fracture toughness ( $K_{1C}$ ) is an intrinsic property which is related to the ability of the material to resist crack propagation and represents the critical stress intensity at the tip of the flaw which allows crack propagation under plain strain conditions. During stress application, these flaws may lead to the formation of microcracks in the material which enlarge and propagate causing catastrophic failures because filled resins in general are relatively brittle unlike ductile materials, which can accommodate some applied stress in the form of plastic deformation.<sup>(9,10)</sup>

The hardness of a restorative material is an indicator of its malleability and polishing capacity and it is often an indicator to wear.<sup>(11)</sup>

The difficulties that are associated with the maintenance of the properties of restorative materials that undergo constant thermal and mechanical stress in the oral environment necessitates the continuous optimization of these materials. The aim of this study was to investigate the effect of short term water storage on the fracture toughness and microhardness of silorane and methacrylate based composites. The hypotheses to be tested was that aging in water even for short duration would cause a reduction in fracture toughness and microhardness of low shrinkage silorane in comparison to the nanohybrid composite.

## MATERIALS AND METHODS

Two types of composite resin materials were investigated in this study. Silorane P<sub>90</sub> a low shrinkage microhybrid composite, and Grandio a nanohybrid methacrylate based composite.

The composition and manufacturers of the materials are presented in Table I.

TABLE (1): Restorative materials, Composition and Manufacturers.

Material	Composition	Manufacturer
Filtek silorane P90 (microhybrid low shrink composite) (Syringe)	<b>Resin matrix</b> 3, 4- Epoxycyclohexylethyl- cyclopolymethylsiloxane,bis, 3- 4- epoxycyclohexylethyl- phenylmethyl silane. <b>Fillers</b> Silanized quartz, yttrium fluoride 76 wt%. 55% vol	3M, ESPE, ST, Paul, MN, USA.
Grandio (Nano hybrid)	<b>Resin matrix</b> BIS GMA TEGDMA <b>Fillers</b> Silica 20-60 nm Barium alumina borosilicate 87 %wt. 71% vol	Voco GmbH Cuxhaven Germany

A total number of eighty specimens were fabricated from both types of composite resins. For each test forty specimens were prepared and divided into two groups of twenty specimens each according to the type of composite used.

Group I: fabricated from Silorane P<sub>90</sub> microhybrid composite (n=20).

Group II: fabricated from Grandio nanohybrid composite (n=20).

Half of the specimens (n=10) from each group were stored in 37°C distilled water for 24 hours. The other half (n=10) were stored in distilled water

for 6 weeks until testing. All specimens were stored in glass beakers in an incubator (MLWBST 5020, Germany) at 37°C throughout the storage periods.

### Fracture toughness test:

A total of forty bar shaped specimens were fabricated in a plexi glass mold with a razor blade insert to produce a sharp notch at mid span ( $a/w = 0.5$ ).

Specimens were prepared according to the American Society for Testing Materials (ASTM) guidelines for the single edge notched beam specimen (standard E-399).<sup>(12)</sup> The dimensions of the specimens were 5x2.5x20 mm (height x thickness x length) with a 2.5mm notch on one side. Each composite material was inserted into the mold in two increments, each increment covering the entire length of the mold. Photoactivation was done for the first increment in two overlapping exposures of 20 seconds each using LED curing unit (Elipar S10 3M ESPE, USA) of 1200 mw/cm<sup>2</sup> light intensity and 10 mm tip diameter to cover the entire length of the specimens. The second increment was then inserted and the razor blade was put into the composite to produce the centrally placed notch.

The top layer was covered with a celluloid strip on top of which a glass slide was placed to ensure a smooth surface and then light cured. After polymerization, excess resin composite was carefully removed and the edges were smoothed by 400 grit abrasive paper.

After each storage period, each specimen was dried and placed horizontally in the lower table of the universal testing machine (Comten Industries, USA) with the notch facing downwards. The load was applied to the centre of the specimens with a spherical indenter 2mm in diameter at a cross head speed of 0.5 mm/sec till fracture occurred. Visual examination of the fractured parts was performed to ensure that the fracture planes was through the notch and that it was perpendicular to the vertical

and horizontal planes through the centre of the specimens.<sup>(13)</sup>

Fracture toughness ( $K_{IC}$ ) in MPa.  $m^{1/2}$  was calculated according to the equation:<sup>(14)</sup>

$$K_{IC} = (3Pl^{1/2} / 2bw^2) \times f(a/w)$$

$$f(a/w) = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.80(a/w)^4.$$

Where P = load at fracture in Newtons

l = length of specimen

w = height of the specimen

a = length of notch in mm

b = thickness of the specimen

### Vickers Microharness test

A total number of forty disc shaped specimens (height 2mm, diameter 4mm) were prepared for this test. The Vickers microharness test was carried out using a digital microhardness tester (Model LM-100, FM 1159 Leco corporation Michigan, USA). Load of 50 g was applied on the diamond pyramid micro-indentor with 136° angle between the opposing faces for 30 seconds load cycle. Five indentations were made on each sample, for each composite material. The mean Vickers hardness number was calculated for each specimen according to the formula  $VHN = 1.854 F/d^2$  where F is the indentation load, and d is the average of the diagonal length of the indentation. The VHN was measured for both types of composite after the 24 hours and six weeks water storage.

### Scanning electron microscopy (SEM)

Finally, representative specimens of each composite were coated with a 40-nm layer of gold (Denton Vacuum Inc., Moorestown, New Jersey) and imaged with a scanning electron microscope (JEOL 5300 LV, Tokyo, Japan). Each specimen was mounted on an aluminum stub and examined

at different magnifications. SEM images of the fractured surfaces were obtained with an accelerating voltage of 25 KV.

### Statistical analysis

Comparison of fracture toughness and microhardness between specimens made from Silorane and those made from Grandio at the 24 hrs and the six weeks water storage was done. Analysis of variance was used followed by Tukey test for post hoc pairwise comparison.

## RESULTS

The mean fracture toughness values and standard deviations of both composite materials at the two storage periods in MPa are shown in table 2 and graphically presented in figure 1. The mean fracture toughness of Silorane  $P_{90}$  at 24 hrs was significantly higher ( $1.65 \pm 0.12$ ) than Grandio ( $1.11 \pm 0.12$ ) at  $P < 0.0001$ . After six weeks storage in water, the two materials showed a significant decrease in fracture toughness. The above observation is also still valid with silorane exhibiting a higher fracture toughness with mean value of  $1.22 \pm 0.07$  MPa compared to Grandio ( $0.65 \pm 0.08$ ) at  $P < 0.0001$ .

TABLE (2): Comparison between the mean fracture toughness in MPa for Silorane and Grandio at 24 hours and six weeks water storage.

Materials/ storage periods	Group I Silorane Mean±SD	Group II Grandio Mean±SD	T test
After 24 hrs	1.65±0.12	1.11±0.12	8.01 <0.0001*
After 6 weeks	1.22±0.07	0.65±0.08	13.59 <0.0001*
T test P value	7.79 <0.0001*	8.01 <0.0001*	

\*: Statistically significant at  $P \leq 0.05$ .

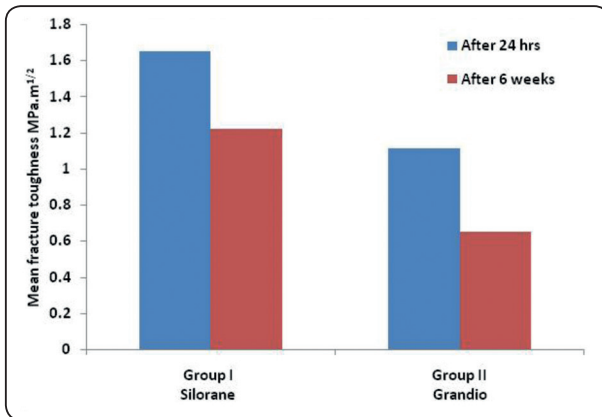


Fig. (1): Showing the mean fracture toughness values of Silorane and Grandio at both storage periods.

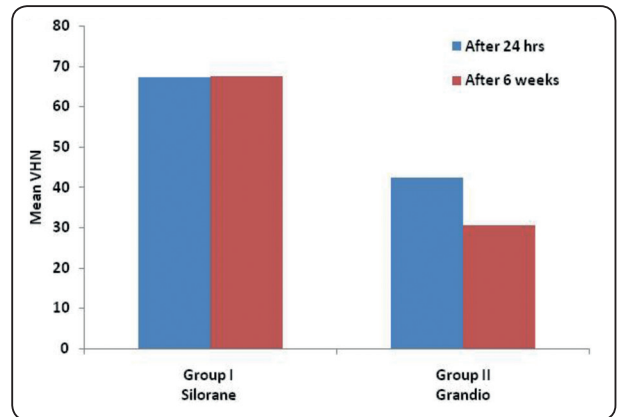


Fig. (2): Showing the VHN mean values of Silorane and Grandio at both storage periods.

The mean values and standard deviations of the Vickers hardness number of both composite resin material at the two storage periods are presented in table 3 and figure 2.

There was a significant difference in the VHN of the two studied groups. Silorane P<sub>90</sub> showed a highly significant difference (67.18±1.33) than Grandio (42.37±0.73) in the 24 hrs period. A significant decrease in VHN was observed in Grandio after 6 weeks storage in water (30.55±0.71), while Silorane P<sub>90</sub> did not show any significant decrease in VHN following 6 weeks water storage.

storage period, fracture occurred through the resin matrix which indicates good filler/ matrix adhesion. While after 6 weeks of water storage some fillers dislodgement occurred with micro cracking along the filler/matrix interface.

SEM micrographs of Grandio nanohybrid composite after water storage for 24 hours showed some fillers dislodgment and interfacial debonding which indicates lesser adhesion between the resin and the fillers. After 6 weeks water storage, multiple fillers dislodgment and presence of internal pores were shown in Grandio nanohybrid composite.

TABLE (3): Comparison of the Vickers hardness number among the study groups.

	Group I Silorane Mean ± SD	Group II Grandio Mean ± SD
after 24 hrs	67.18±1.33 <sup>b</sup>	42.37±0.73 <sup>a</sup>
after six weeks	67.47±1.16 <sup>bd</sup>	30.55±0.71 <sup>c</sup>
ANOVA	1959.96	
P value	<0.0001*	

\*: Statistically significant at P ≤ 0.05.

Different superscript letters denotes significant difference

SEM images of fractured surfaces of the tested composite resin materials are shown in figures 3-6. It is evident that in Silorane P<sub>90</sub>, after the 24 hours

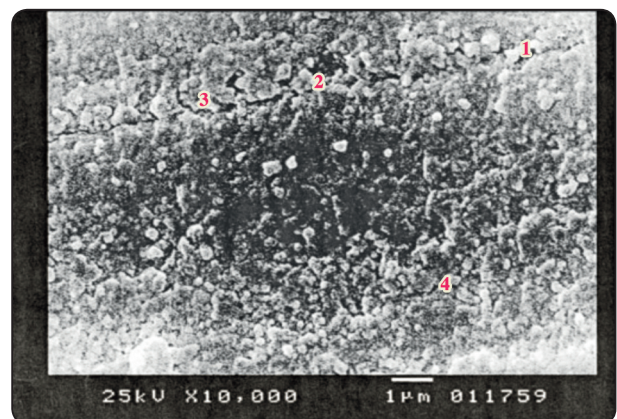


Fig. (3): SEM micrograph of the fractured surface of Silorane P90 after 24 hours water storage showing the filler particles well adhered to and covered by the matrix. Microcrack growth through the resin matrix was also noticed (Sites 1-4).

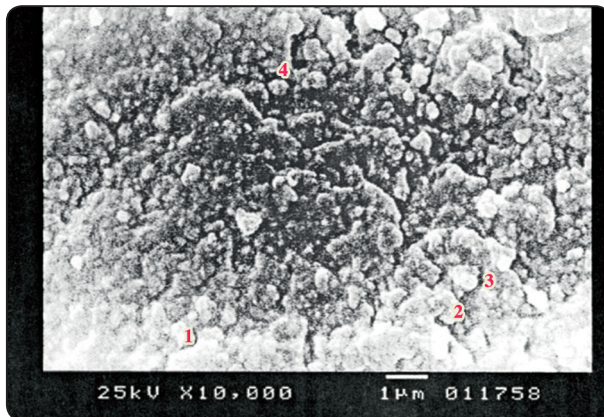


Fig. (4): SEM micrograph of the fractured surface of Grandio after 24 hours water storage showing detached fillers. Presence of interfacial separation between the filler particles and matrix is also present (Sites 1-4).

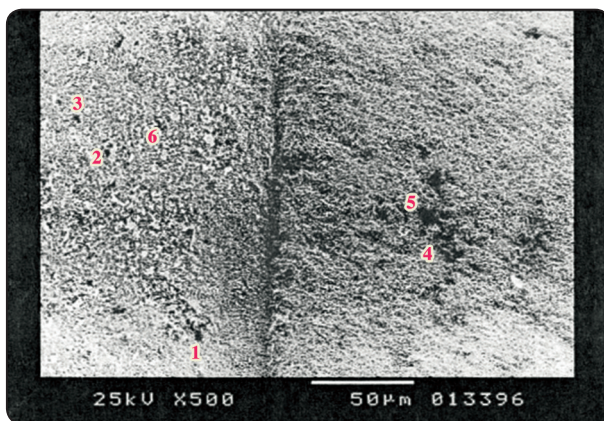


Fig. (5): SEM micrograph of the fractured surface of Silorane P90 after 24 hours water storage showing some fillers dislodgement (Sites 1-3) and microcracking along the filler/ matrix interface (Sites 4-6).



Fig. (6): SEM micrograph of the fractured surface of Grandio after 6 weeks water storage showing multiple filler dislodgement and presence of internal pores (Sites 1-6).

## DISCUSSION

The maintenance of composite's physical and mechanical properties is essential to ensure long term clinical success of the restoration. Composite is a brittle material that is susceptible to microscopic surface flaws as a result of the finishing and polishing procedures, imperfect interfaces between the resin matrix and fillers and residual stresses which occur by resin shrinkage. The clinical longevity of composite resins is affected by the surface flaws which acts as fracture initiation sites and may propagate through the material matrix leading to fracture and subsequent caries.<sup>(15)</sup> Dental materials researchers regard the fracture toughness as a more accurate predictor than traditional compressive and tensile testing of how a material will perform under various occlusal and masticatory stresses. Materials with greater fracture toughness will perform better at high stress levels. Therefore, fracture toughness could help in predicting the clinical performance of dental materials.<sup>(14)</sup>

Fracture toughness testing requires pre-cracking of the specimens to simulate a sharp natural flaw in the interior of a material. Since the stress concentration is highest when the notch or crack is sharpest, it was believed that the most accurate evaluation would be achieved by testing specimens with an extremely sharp flaw i.e one made by propagating crack from a sharp notch. Single edge notched beam (SENB) is one of the most common methods used to study fracture toughness for different materials. In the dental field, this method gained a lot of popularity because of its simplicity regarding specimen preparation and testing as well, recording the most accurate and predictable values.<sup>(16)</sup>

Results of this study showed that Silorane P<sub>90</sub> low shrinkage composite had a significantly higher fracture toughness compared to Grandio nanohybrid composite after 24 hrs water storage. This might be due to the different chemistry of the resin matrix

of silorane, where the monomers does not contain C = C aliphatic groups, therefore polymerization of free radicle and cataionic species should be different. The photopolymerization of Silorane is achieved by opening of cationic rings. This occurs when the reactive centre of a propagating chain is a positively charged carbon atom (carbocation). The epoxy ring is opened after the addition of an oxirane monomer to form a chain. The cationic reaction has been called living polymerization in which two reactive species do not extinguish each other as quickly as free radicles in the methacrylate resin polymerization.<sup>(17,18)</sup> Although the resin matrix has a strong effect on fracture toughness, the filler type, distribution and concentrations may also contribute to fracture toughness of composite resins. Fillers reinforce the matrix and provide additional toughening mechanism such as crack pinning, crack blunting and increased fracture surface area as well as microcrack – induced toughening.<sup>(11,12)</sup> The significantly higher fracture toughness of Silorane P<sub>90</sub> might also be related to the dense spherical filler particles of quartz and yttrium flouride of 0.1-3.5  $\mu\text{m}$  in size which are bound to organic matrix by an epoxy functional silane bonding agent through a silanization process.<sup>(1)</sup>

The results of the fracture toughness after 24 hrs water storage are in consistence with the SEM imaging finding where Silorane showed crack growth through the resin matrix which indicates good filler/ matrix adhesion producing strength and toughness. Also, interparticle crack growth was observed through resin matrix promoting crack deflection which provide extrinsic toughening by shielding crack tip from some of the applied load.<sup>(19)</sup> On the other hand, SEM image of Grandio showed evidence of interfacial separation which indicates lesser adhesion between the resin and fillers in the nano hybrid composite.

Previous studies<sup>(9,19,20)</sup> demonstrated that aging in water can significantly decrease the fracture toughness of composite resins. Resistance to

degradation in an aqueous medium is important for the clinical longevity of the restoration. Absorption of water is believed to produce adverse effects as degradation of silane coupling agent, resin degradation, pull out of the fillers and softening of the resin matrix.

In the current study, six weeks of water storage was selected based on previous studies that revealed that this was the time after which resinous materials reached full water saturation level.<sup>(19,21)</sup> Different types of composite react differently to hydration. The results of this study showed that Silorane exhibited significantly higher fracture toughness after 6 week water storage. This was in consistence with previous studies of Weinman et al<sup>(1)</sup>, Kopperund et al<sup>(9)</sup>, Palin et al<sup>(22)</sup> and Li et al<sup>(23)</sup>. They all found that Siloranes had higher stability after water storage compared to the tested methacrylate based composites. This might be due to the hydrophobic nature of the siloxane groups that are incorporated in the material and that the oxirane polymers are responsible for the greater stability towards many physical forces in aqueous medium. The small initial degree of conversion for Siloranes also suggest a slower polymerization reaction with an increasing tendency that despites its lower values may represent an adequate polymerization which was reflected by its hydrolytic stability.<sup>(24,25)</sup>

On the other hand, the lower fracture toughness of Grandio nanohybrid composite following the 6 weeks water storage, might be related to the chemistry of the resin monomers. Ferracene<sup>(21)</sup> and Indrami et al<sup>(26)</sup> found that dimethacrylate resins contained both polar and non polar groups and that the water sorption of Bis GMA/TEGDMA were higher due to the presence of hydrophilic ether groups in TEGDMA, hydroxyl groups in Bis GMA and the presence of ester groups in all. There is always an incomplete and significant concentration of untreated C=C remaining with the resin. Such incomplete conversion may leave unreacted monomers that might dissolve in a wet environment.<sup>(22)</sup> The result is interface cracking and

stresses that promote mechanical breakdown by easier crack propagation and lower  $K_{IC}$  as revealed in this study. The lower fracture toughness of Grandio might also be explained by the presence of metallic ions i.e barium in the composition of the fillers. Such ions are electropositive and tend to react with water. The charge balance inside the silica network is changed with the penetration of hydrogen ions of the water in the spaces occupied by barium.<sup>(27)</sup> The increased concentrations of hydroxyl ions breaks the siloxane (Si-O-Si) bonds and an autolytic cycle of surface degradation occurs.<sup>(21)</sup> This mechanism would explain the continuity of the superficial softening with storage time.

Fracture toughness results following 6 weeks water storage were in consistence with SEM imaging. Silorane showed only some filler dislodgments and microcracking along the filler matrix interface. While in Grandio plucking of the filler particles from the resin matrix was predominant with apparent porosity and interfacial debonding.

The hardness of composite resin is particularly dependent on the filler type and contents and it correlates with mechanical properties such as abrasion resistance or polishability.<sup>(24)</sup> In the present study silorane exhibited higher Vickers hardness number in comparison to Grandio. This was in contradiction with the results of Hanhel et al<sup>(28)</sup> who found that Silorane showed lower hardness values compared to methacrylate based composites. However, the results of this study was in agreement with Maia et al<sup>(29)</sup> who found no significant difference in hardness between silorane and methacrylate based non flowable composites. There was a reduction in VHN of Grandio after 6 weeks water storage. Water causes the matrix to dilate and it reduces the frictional forces between the polymer chains. This lead to matrix degradation around the filler particles with subsequent loss of particles and reduced surface integrity of the composite. Consequently, the surface hardness may be affected by hydrolytic degradation.<sup>(30)</sup> On the other hand the

VHN of Silorane was not significantly reduced after 6 weeks water storage. This might be explained by the relatively small filler particle size and more stable chemical sturcture of silorane. It might also be linked to difference in composition of the resin matrix and the polymerization process. This was confirmed by other studies which reported that in nanohybrid composite, smaller voids were left on the surface where smaller particles were debonded from the resin as compared to low shrinkage Silorane.<sup>(31-33)</sup> This also suggest that Silorane will not undergo increase in wear as a result of degradation in water of the polymer matrix, fillers and filler matrix interface.

## CONCLUSIONS

Within the limitation of this study it could be concluded that Silorane P<sub>90</sub> exhibited higher fracture toughness and microhardness compared to the nanohybrid composite (Grandio) in both storage periods.

Although storage in water decreased the fracture toughness of silorane composite, it still remained higher than the nanohybrid (Grandio).

The VHN of Silorane was not significantly reduced after storage in water for 6 weeks.

The silorane technology produced a system with higher mechanical properties and better hydrolytic stability compared to the methacrylate based composites.

## REFERENCES

1. Weinmann W, Thalacker C. and Guggenbenger R. Siloranes in dental composite. *Dent Mater*, 2005; 21: 68-74.
2. Moszner N, Slaz U. New developments of polymeric dental composites. *Progress in polymer science* 2001; 26(4): 535-576.
3. Eick JD, Kostoryz EL, Rozzi SM, Jacobs DW, Oxman JD, Cappelow CC. In vitro bio-compatibility of oxirane/ polyol dental composites with promising physical properties. *Dent Mater* 2002; 18: 413-421.



4. Le Prince J, Palin WM, Mullier T, Devaux J, Vreven J, Leloup G. Investigating filler morphology and mechanical properties of new low-shrinkage resin composite types. *Journal of oral rehabilitation* 2010; 37: 364-76.
5. Mustaza TehA, Braden M, Mangala P. Comparison of various properties of a silorane based dental composite with two methacrylate based dental composites. *GSTF International Journal of Advances in Medical Research (JAMR)* 2014; 1: 78-83.
6. Schweickl H, Schmalz G, Weinmann W. The induction of gene mutations and micronuclei by oxiranes and siloranes in mammalian cells in vitro *Journal of Dent Research* 2004; 83: 17-21.
7. Tilbrook DA, Clarke RL, Howle NE, Braden N. Photo curable epoxy-polyol matrices for use in dental composites. *Biomaterials* 2000; 21: 1743-53.
8. Boaro LC, Goncalves F, Guimaraes TC, Ferracane JL, Pfeifer CS, Braga RR. Sorption, solubility, shrinkage and mechanical properties of "low shrinkage" commercial resin composites. *Dental Materials* 2013; 29: 398-404.
9. Kopperud HM, Schdmit M, Kelven S. Elution of substances from a silorane based dental composite. *European Journal of Oral Science* 2010; 118: 100-2.
10. Tyas MJ, Harcourt JK. Fracture toughness of water aged resin composite restorative materials. *Dent Materials* 1995; 11: 201-7.
11. Beun S, Glorieux T, Devaux J, Vreven J, Leloup G. Characterization of nano filled compared to universal and microfilled composite. *Dent Materials* 2007; 23: 51-9.
12. ASTM Designation: E399-90. Standard test method for plane – strain. Fracture toughness of metallic materials, *Annual Book of Standards*; 1997.
13. Bonilla ED, Mardirossian G, Caputo AA. Fracture toughness of posterior resin composite. *Quintessence Int.* 2001; 32: 206-10.
14. Medina Tirado JI, Nagy WW, Dhuru VB, Zienert AJ. The effect of thermocycling on the fracture toughness and hardness of core build up materials. *J. Prosthet. Dent* 2001. 86 474-80.
15. Knobloch LA, Kerby RE, Seghi R, Berlin JS. Fracture toughness of packable and conventional composite materials. *J. Prosthet. Dent* 2002; 88: 307-313.
16. Ilie N, Hickel R, Valceanu AS, Huth KC. Fracture toughness of dental restorative materials. *Clin Oral Investig* 2012; 16: 489-98.
17. Tilbrook DA, Clarke RL, Howle NE, Braden N. Photo curable epoxy-polyol matrices for use in dental composites. *Biomaterials* 2000, 21: 1743-53.
18. Shin MA, Drummond JL. Evaluation of chemical and mechanical properties of dental composite. *J. Bio Med. Mater Res.* 1999, 48: 540-545.
19. Shah MB, Ferracane J.L, Kruzic J.J. R curve behaviour and toughening mechanisms of resin – base dental composite. Effect of hydration and post-cure heat treatment. *Dent Materials* 2009: 1436 1-11.
20. Ferracane J. Resin – based composite performance are there some things we can't predict ? *Dent Mater* 2013; 29: 51-8.
21. Ferracane J.L. Hygroscopic and Hydrolytic effects in dental polymer networks. *Dent Materials* 2006; 22, 211-222.
22. Palin WM, Fleming GJP, Burke FJT, Marquis PM, Randall RC. The influence of short and medium term water storage of the hydrolytic stability of novel low shrink dental composites. *Dent Materials* 2005; 21: 852-63.
23. Ilie N, Hickel R. Macro-micro and nano mechanical investigation on silorane and methacrylate based composites. *Dent Materials* 2009; 25: 810-9.
24. Schneider LJJ, Cavalcante LM, Silikas N, Watts DC. Degradation resistance of silorane, experimental ormocer and dimethacrylate resin based dental composites. *J. Oral Science* 2011; 53: 413-9.
25. De Moraes Porto ICC, De Aguiar FHB, Brandt WC, Liporoni PCS. Mechanical and physical properties of silorane and methacrylate based composite *J. of Dentistry* 2013; 2080 1-8.
26. Indrami DJ, Cook WD, Televantos F, Tyas MJ, Harcourt JK. Fracture toughness of water aged resin composite restorative materials. *Dent Mater* 1995 11: 201-7.
27. Ferracane JL, Berge HX, Condon JR. In vitro aging of dental composites in water-effect of degree of conversion, filler volume and filler/ matrix coupling. *J Biomed Mater Res* 1998; 42: 465-72.
28. Hahnel S, Henrich A, Burgens R, Handel G, Rosentritt M. Investigation of mechanical properties of modern dental composites after artificial aging for one year. *Operative Dentistry* 2010; 35, 412-9.

29. Maia R, Reis RS, Moro AFV, Perez CR, Pessoa BM, Dias KRHC. Properties evaluation of silorane, low shrinkage, non flowable and flowable resin based composites in dentistry Peer J, Dol 2015 864 1-9.
30. Price RB, Felix CA, Anderous P. Knoop hardness of ten resin composites irradiated with high power LED and quartz tungsten – halogen lights. Biomaterials 2005, 26: 2631-41.
31. Marghalani H. Effect of finishing / polishing systems on the surface roughness of novel posterior composites. J Esthet Restor Dent 2010; 22: 127-38.
32. Eick JD, Smith RE, Pinzino CS, Kostoryz EL, Chappelow C. Photopolymerization of developmental monomers for dental cationically initiated matrix resins. Dent Mater 2005; 21: 384-90.
33. Antonson S, Yazici A, Kilinc E, Antonson D, Hardigan P. Comparison of different finishing/ polishing systems on surface roughness and gloss of resin composite. J Dent 2011; 39: 9-17.