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Effects of resin formulation and nanofiller surface treatment on the properties of experimental hybrid resin composite

Lawrence Musanje*, Jack L. Ferracane

Department of Biomaterials and Biomechanics, Oregon Health and Science University, 611 SW Campus Dr., Portland, OR 97239, USA

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Abstract

This study evaluated the effects of nanofiller surface treatment and resin viscosity on the early and long-term properties of experimental hybrid composites. Three resin formulations (low, medium and high viscosity) were prepared by varying the ratio of TEGDMA:UDMA:bis-GMA (47:33:16 wt%; 30:33:33 wt%; 12:33:51 wt%). Composites contained 71.3 wt% silanated strontium glass (1–3 μm) and 12.6 wt% of either silanated or unsilanated silica (OX-50; 0.04 μm). Specimens ($n = 10$) for flexural strength, flexural modulus, fracture toughness and Knoop hardness were tested after 24 h, 1 and 6 months exposure to water at 37°C. Degree of conversion (DC) was determined 24 h after photoinitiation using FTIR. Resin viscosity only had a marginal influence on the mechanical response of composites but it can be adjusted to achieve a balance between DC and mechanical properties. Adding non-bonded nanofiller to hybrid composites had no systematic effect on DC. Non-bonded nanofillers had no significant effect on the long-term properties of hybrid composites.

Keywords: Composite; Viscosity; Nanofiller; Silane; Properties

1. Introduction

Both the addition of unsilanated (non-bonded) nanofiller [1,2] and lowering the viscosity of the resin in composites are viable means of reducing polymerization contraction stress [3], but their long-term effects on the properties of composites are unknown. Contraction stress that develops within the composite during polymerization can cause failure of the bond between the composite and tooth structures [4] causing microleakage and recurrent decay. Hence, measures to lower contraction stresses in composites have been adopted, e.g., the inlay technique [5], incremental placement (5) and soft-start polymerization [6]. Nevertheless, significant leakage around composites still occurs [7,8], and there are continued efforts to reduce contraction stresses.

More recently, adding non-bonded nanofiller to hybrid composites has shown success in reducing contraction stress [1,2]. A study that examined the effects of various levels of non-bonded nanofiller on reducing polymerization contraction stress in hybrid composites showed that ~12.6 wt% was most effective [2]. In addition, lowering the viscosity of the composite resin can enhance its capacity to flow and relieve stress, subsequently reducing contraction stress [3,9]. While these two approaches may reduce contraction stresses, their long-term effect on the properties of composites requires investigation. This information is critical to predicting their effect on the durability of composites.

Our aim therefore was to study the effects of resin viscosity and non-bonded nanofillers on both the initial and long-term mechanical properties of experimental hybrid composites. Two null hypotheses were tested. First, the incorporation of non-bonded nanofillers would not have a detrimental effect on the initial or long-term properties of resin composites. Second, the properties of the composites would be independent of resin viscosity at either time period.

2. Materials and methods

2.1. Materials

Three resin formulations of varying viscosity were prepared by adjusting the ratio of TEGDMA:UDMA:

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*Corresponding author. Tel.: +1-503-494-8696; fax: +1-503-494-8260.

E-mail address: musanjel@ohsu.edu (L. Musanje).

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bis-GMA (47:33:16; 30:33:33; 12:33:51 wt%) to produce low-, medium- and high-viscosity resins, respectively. To these resin formulations were added silanated (methacryloxypropyltrimethoxysilane) strontium glass (Sr; 1–3 μm; Bisco Inc., Schaumburg, IL, USA) and either silanated or unsilanated colloidal silica (OX-50, Degussa, Germany; 0.04 μm). Thus two groups of composites per resin formulation were produced, i.e., one containing the silanated (bonded) and the other containing an equivalent amount of unsilanated (non-bonded) silica. These groups were identified as low-viscosity-silanated (LS), low-viscosity-unsilanated (LU), medium-viscosity-silanated (MS), medium-viscosity-unsilanated (MU), high-viscosity-silanated (HS) and high-viscosity-unsilanated (HU). The final wt% of the filler and resin in the composites were 71.3 wt% Sr, 12.6 wt% OX-50 silica and 16.1 wt% resin. The final wt% of initiator (camphoroquinone), accelerator (Ethyl-4-dimethylaminobenzoate) and inhibitor (4-methoxy phenol) were 0.7, 3.0 and 0.05 wt%, respectively. The viscosity of each of the six composites was measured using a parallel plate geometry (750 μm gap) at a constant shear rate of $1\,s^{-1}$ on a commercial rheometer (AR1000, TA Instruments, New Castle, DE, USA), to verify the differences (Table 1).

2.2. Specimen preparation

Single-edge notch fracture toughness (K_{Ic}) specimens ($25 \times 5 \times 2.5$ mm; $n = 10$) were prepared in a steel mold with a razor blade insert to produce a sharp notch at mid-span ($a/w = 0.5$). The specimens were cured in the Triad II unit (Dentsply, York, PA, USA) for 40 s from both the top and bottom surfaces.

Specimens for flexural strength (FS) and flexural modulus (E) testing ($n = 10$) were made by packing composite in rectangular glass tubes with inside dimensions of $25 \times 2 \times 2\,mm^3$ (VitroCom Inc., Mountain Lakes, NJ), and were also cured in the Triad II unit for 80 s (40 s from the top and bottom).

Three series of specimens ($n = 10$) were prepared from each of the six formulations of composite. Specimens were aged in deionized water at 37°C. Degree of conversion (DC) was determined 24 h after photoinitiation using FTIR. Mechanical testing for FS, E, K_{Ic} and Knoop hardness (KHN) was done in ambient air (dry conditions) at room temperature (~24°C) at 24 h, 1 and 6 months after storage. Deionized water was replaced every 7 days.

2.3. Testing methods

Fracture toughness (K_{Ic}, MPa/m^2; $a/w = 0.5$) was determined in three-point bend (span = 20 mm), on a universal testing machine (Model TT-B, Instron Corp., Canton, MA, USA) at a cross-head speed of 0.127 mm/min and was calculated according to the equation:

$$K_{Ic} = [\mathrm{PHS}/(\mathrm{BHW}^{1.5})]f(a/w), \qquad (1)$$

where P is the peak load (N), S the span (m), B the specimen thickness (m), W the specimen width (m) and $f(a/w)$ was calculated according to the equation provided in the ASTM standard E399.

KHN testing ($n = 6$) was performed on some of the fracture toughness specimens retrieved after testing (Kentron Hardness Tester, Torsion Balance Co., Clifton NJ). Specimens were tested with a 100 g load and a 15 s dwell time using a 136° diamond pyramid indenter. Three indents were made per specimen. The same specimens ($n = 6$; 24 h aging time) were used for the DC analysis. Thin chips (10–15 μm) were removed from samples, placed on a KCl crystal and were scanned in transmission using micro-FTIR (DS-20/XAD, Analect Instruments, Irvine, CA, USA) at an $8\,cm^{-1}$ resolution. The pastes of the uncured composites were similarly tested. DC was calculated from the ratio of the C=C peak from the methacrylate group to that of the unchanging C···C peak from the aromatic ring for the cured and uncured specimens using standard baseline techniques [10].

Table 1
Composition and viscosity of the six experimental composites used in this study

Composite	Resin (T/U/B)[a]	Filler[b]	Nanofiller surface treatment	Viscosity (mPa s at $1\,s^{-1}$)[c]
Low-viscosity-silantated (LS)	47:33:16	Sr glass + silica nanofiller	Silane	1936 ± 131
Low-viscosity-unsilanated (LU)	47:33:16	Sr glass + silica nanofiller	None	1790 ± 126
Medium-viscosity-silanated (MS)	30:33:33	Sr glass + silica nanofiller	Silane	6175 ± 117
Medium-viscosity-unsilanated (MU)	30:33:33	Sr glass + silica nanofiller	None	7663 ± 186
High-viscosity-silanated (HS)	12:33:51	Sr glass + silica nanofiller	Silane	31,987 ± 1319
High-viscosity-unsilanated (HU)	12:33:51	Sr glass + silica nanofiller	None	34,587 ± 588

[a] T/U/B = wt% TEGDMA/UDMA/bis-GMA (total resin content = 16.1 wt%).

[b] Total filler content = 83.9% (71.3 wt% silane-treated Sr glass + 12.6 wt% OX-50 silica nanofiller).

[c] Average of three runs.

FS (MPa) and modulus (E, GPa) were determined in three-point bend ($25 \times 2 \times 2\,\text{mm}^3$; span 20 mm) using the universal testing machine at a cross-head speed of 0.127 mm/min, according to ISO 4049. FS and E were calculated using the following equations:

$$\text{FS} = \frac{3PL}{2bd^2}, \tag{2}$$

$$E = \left(\frac{\Delta P}{\Delta y}\right)\frac{L^3}{4bd^3}, \tag{3}$$

where P is the peak load, L the support span, d and b are specimen depth and breadth, and $\Delta P/\Delta y$ the gradient of the (steepest) linear portion of the deflection curve [11]. Cross-head motion was used to estimate beam deflection.

2.4. Statistical analysis

A two-way ANOVA and Tukey's test ($p \leqslant 0.05$) were used to test the effects of resin viscosity and nanofiller surface treatment on DC of the materials. A three-way ANOVA and Tukey's test ($p \leqslant 0.05$) were applied to test for the effects of nanofiller surface treatment, resin viscosity and aging time on the properties of the materials.

3. Results and analysis

Composites made from resins with the lowest viscosity had higher DC values than those made with the medium- and high-viscosity resins when tested 24 h after specimen preparation (Fig. 1). A two-way ANOVA and Tukey's test showed that both nanofiller surface treatment and resin viscosity had significant effects on DC ($p = 0.02$ and $p < 0.005$, respectively), but that there was a significant interaction between the two factors ($p < 0.005$). Thus multiple comparisons analysis of individual cell means was performed. In general, the DC was higher for composites made from resin mixtures of lower viscosity, except for the HU composite that had a higher DC than the MU composite ($p = 0.29$). The effects of nanofiller surface treatment on DC were quite equivocal and were only significant for the medium- and high-viscosity composites (medium silanated > medium unsilanated, $p = 0.03$; high unsilanted > high silanated, $p < 0.005$).

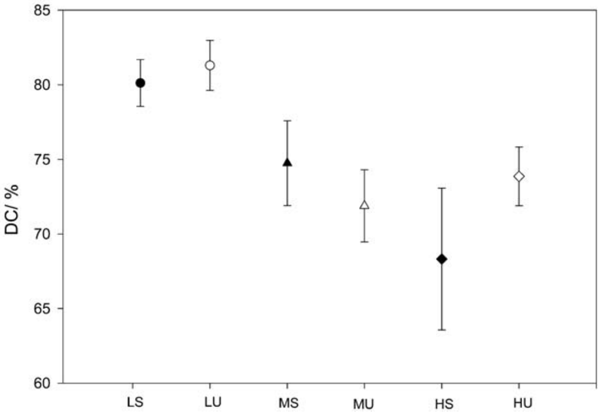

Fig. 1. DC values (mean ± standard deviation for $n = 6$, determined 24 h after irradiation) vs. the corresponding resin composite (LS, LU, MS, MU, HS and HU arbitrary x-axis).

A three-way ANOVA showed that nanofiller surface treatment (Table 2), resin viscosity (Table 3), and aging time (Table 4) had significant effects on FS, E, K_{Ic} and KHN ($p < 0.05$) and that there was no significant interaction among the three factors for all properties; FS ($p = 0.63$), E ($p = 0.9$), K_{Ic} ($p = 0.17$) and KHN ($p = 0.16$).

Incorporating silanated nanofiller particles significantly increased the FS of the high-viscosity composites at all three time periods (24 h, 1 and 6 months) and that of the medium-viscosity composites at 1 month, by 13–18% (Table 2). It also significantly improved KHN of the high-viscosity composites by 13% at 1 month, and of the medium-viscosity composite by 8% at 24 h. Fracture toughness of only the high-viscosity composites was significantly affected by incorporating silanated nanofillers, with an increase of ~20% at 1 and 6 months. Elastic modulus was minimally affected by adding silanated nanofillers, the only difference being a 6% increase for the medium-viscosity composite at 24 h (Table 2).

The properties of the low-viscosity and high-viscosity composites with silanated nanofillers were similar at the three test periods, except for FS and elastic modulus, which were about 10% higher in the high-viscosity composite at 1 month (Table 3). There was more variability in the properties of low-viscosity and high-viscosity composites with unsilanated nanofillers: FS was higher in the low-viscosity composite by 15% at 24 h, fracture toughness was also higher in the low-viscosity composite by 13% at 24 h and 21% at 6 months, but elastic modulus was about 8% higher in the high-viscosity composite at 1 and 6 months.

The mechanical properties of the medium- and high-viscosity composites with similar nanofiller treatment were indistinguishable, except KHN at 24 h was 12% higher in the medium than high-viscosity composite with silanated nanofillers. Fracture toughness at 6 months was 18% higher in the medium than high-viscosity composite with unsilanated nanofillers (Table 3).

An initial decline in properties at 1 month followed by a recovery at 6 months to values similar to those at 24 h was a general trend observed (Table 4).

Table 2
Surface treatment effect—statistical comparison of the effect of nanofiller surface treatment on the properties of composites made with resins of three different viscosities and after aging in water

Time	Visc	Sil	FS (MPa)	E (GPa)	K_{Ic} (MPa/m^2)	KHN (kg/mm^2)
24 h	L	S	129.0 (20.4)	15.33 (0.40)	1.66 (0.11)	70.6 (3.5)
		U	130.8 (17.8)	15.78 (0.36)	1.64 (0.12)	70.7 (5.5)
	M	S	137.8 (7.6)	15.64 (0.58)*	1.62 (0.21)	80.1 (3.4)*
		U	125.1 (13.9)	16.56 (0.47)*	1.54 (0.08)	73.3 (2.0)*
	H	S	129.5 (7.9)*	15.77 (0.67)	1.51 (0.11)	71.3 (4.6)
		U	111.7 (7.1)*	16.39 (0.42)	1.42 (0.10)	68.8 (1.5)
1 month	L	S	109.5 (10.7)	15.08 (0.47)	1.53 (0.12)	69.8 (4.2)
		U	106.2 (13.5)	15.28 (0.47)	1.47 (0.12)	65.4 (1.6)
	M	S	133.3 (9.9)*	16.36 (0.31)	1.53 (0.0)	68.6 (3.3)
		U	109.0 (4.6)*	16.03 (0.41)	1.38 (0.14)	64.8 (4.5)
	H	S	127.4 (15.4)*	16.54 (0.52)	1.60 (0.14)*	71.2 (1.7)*
		U	107.4 (7.0)*	16.53 (0.78)	1.28 (0.20)*	61.7 (2.4)*
6 months	L	S	135.8 (13.7)	16.21 (0.48)	1.66 (0.08)	68.3 (5.8)
		U	130.2 (19.7)	15.92 (0.48)	1.60 (0.18)	65.7 (3.7)
	M	S	142.8 (19.1)	16.77 (0.51)	1.52 (0.13)	68.7 (2.7)
		U	133.5 (11.6)	16.86 (0.33)	1.49 (0.10)	66.4 (0.7)
	H	S	139.8 (14.1)*	16.94 (0.55)	1.59 (0.19)*	63.7 (0.3)
		U	122.0 (11.3)*	17.19 (0.49)	1.26 (0.17)*	65.4 (5.0)

Means (1 standard deviation) within a series having asterisks in the same column are significantly different from one another ($p<0.05$).

Table 3
Resin viscosity effect—statistical comparison of the effect of resin viscosity on the properties of composites made with two different nanofiller surface treatments and after aging in water

Time	Sil	Visc	FS (MPa)	E (GPa)	K_{Ic} (MPa/m^2)	KHN (kg/mm^2)
24 h	S	L	129.0 (20.3)	15.33 (0.40)	1.66 (0.11)	70.6 (3.5)*
		M	137.8 (7.6)	15.64 (0.58)	1.62 (0.21)	80.1 (3.4)
		H	129.5 (7.9)	15.77 (0.67)	1.51 (0.11)	71.3 (4.6)*
	U	L	130.8 (17.8)*	15.78 (0.36)	1.64 (0.12)*	70.7 (5.5)
		M	125.1 (13.9)	16.56 (0.47)	1.54 (0.08)	73.3 (2.0)
		H	111.7 (7.1)*	16.39 (.42)	1.42 (0.10)*	68.8 (1.5)
1 month	S	L	109.5 (10.7)	15.08 (0.47)	1.53 (0.12)	69.8 (4.2)
		M	133.3 (9.9)*	16.36 (0.31)*	1.53 (0.0)	68.6 (3.3)
		H	127.4 (15.4)*	16.54 (0.52)*	1.60 (0.14)	71.2 (1.7)
	U	L	106.2 (13.5)	15.28 (0.47)	1.47 (0.12)	65.4 (1.6)
		M	109.0 (4.6)	16.03 (0.41)*	1.38 (0.14)	64.8 (4.5)
		H	107.4 (7.0)	16.53 (0.78)*	1.28 (0.20)	61.7 (2.4)
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		M	142.8 (19.1)	16.77 (0.51)	1.52 (0.13)	68.7 (2.7)
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		H	122.0 (11.3)	17.19 (0.49)*	1.26 (0.17)*	65.4 (5.0)

Means (1 standard deviation) within a series having asterisks in the same column are significantly different from one another ($p<0.05$).

4. Discussion

4.1. *Effect of unsilanated nanofiller on the properties of composites*

The higher DC for the high-viscosity unsilanated composite compared to the silanated composite ($p<0.005$) was presumably due to reduced constraints on the mobility of the polymerizing resin when there is less adhesion to filler particles, but this was contradicted by the lower DC for the medium-viscosity unsilanated composite compared to the silanated composite ($p = 0.03$). This comparison of DC values is complex, because silane molecules contribute to the DC in

Table 4
Aging time effect—statistical comparison of the effect of aging time in water on the properties of composites made with three resin viscosities and two different nanofiller surface treatments

Visc	Sil	Time	FS (MPa)	E (GPa)	K_{Ic} (MPa/m^2)	KHN (kg/mm^2)
L	S	24 h	129.0 (20.3)*	15.33 (0.40)*	1.66 (0.11)*	70.6 (3.5)
		1 month	109.5 (10.7)	15.08 (0.47)*	1.53 (0.12)	69.8 (4.2)
		6 months	135.8 (13.7)*	16.21 (0.48)	1.66 (0.08)*	68.3 (5.8)
	U	24 h	130.8 (17.8)*	15.78 (0.36)	1.64 (0.12)*	70.7 (5.5)
		1 month	106.2 (13.5)	15.28 (0.47)*	1.47 (0.12)	65.4 (1.6)
		6 months	130.2 (19.7)*	15.92 (0.48)*	1.60 (0.18)*	65.7 (3.7)
M	S	24 h	137.8 (7.6)	15.64 (0.58)	1.62 (0.21)	80.1 (3.4)
		1 month	133.3 (9.9)	16.36 (0.31)*	1.53 (0.0)	68.6 (3.3)*
		6 months	142.8 (19.1)	16.77 (0.51)*	1.52 (0.13)	68.7 (2.7)*
	U	24 h	125.1 (13.9)*	16.56 (0.47)	1.54 (0.08)	73.3 (2.0)
		1 month	109.0 (4.6)	16.03 (0.41)*	1.38 (0.14)	64.8 (4.5)*
		6 months	133.5 (11.6)*	16.86 (0.33)*	1.49 (0.10)	66.4 (0.70*
H	S	24 h	129.5 (7.9)	15.77 (0.67)	1.51 (0.11)	71.3 (4.6)*
		1 month	127.4 (15.4)	16.54 (0.52)*	1.60 (0.14)	71.2 (1.7)
		6 months	139.8 (14.1)	16.94 (0.55)*	1.59 (0.19)	63.7 (0.3)*
	U	24 h	111.7 (7.1)	16.39 (0.42)*	1.42 (0.10)	68.8 (1.5)
		1 month	107.4 (7.0)*	16.53 (0.78)*	1.28 (0.20)	61.7 (2.4)
		6 months	122.0 (11.3)*	17.19 (0.49)	1.26 (0.17)	65.4 (5.0)

Means (1 standard deviation) within a series having asterisks in the same column are significantly different from one another ($p < 0.05$).

composites with silanated nanofillers, but not in those with untreated fillers, and it is not possible to distinguish this effect. Therefore, DC values only reflect an overall DC, and no systematic differences could be associated with the nanofiller surface treatment.

Lower properties for composites containing untreated fillers may be expected because the fillers that are not chemically bonded to the resin do not effectively transfer stress to the matrix and thus provide minimal reinforcement. However, except for the high-viscosity composites, filler surface treatment had little effect on mechanical properties. This apparent contradiction is possibly due to the fact that silanated strontium glass that was chemically bonded to resin matrix constituted a large proportion of the total filler content (~85%), and therefore predominantly determined the mechanical properties of the composites. Only the high-viscosity composite showed sensitivity to surface treatment of the nanofillers. It is likely that increased viscosity due to the poorer wetting of the untreated fillers by the resin monomers and the originally higher viscosity of the resin resulted in the high-viscosity composites with non-bonded nanofillers being less homogeneous, thus containing more flaws. If so, then a negative effect on strength properties, e.g., FS and K_{Ic} but not on E would be expected; as was the case.

In a previous study, the contraction stress of composites with untreated nanofillers was reduced [1]. Because the contraction stress is a function of volumetric shrinkage, elastic modulus and the flow capacity of the composite, it is possible to obtain a reduction in contraction stress without a reduction in modulus or shrinkage if the flow capacity of the composite is enhanced. Untreated nanofillers, by not being bonded to the polymer matrix, may allow enhanced freedom of movement of the forming polymer network, thereby enhancing flow and subsequently relieving stresses produced by polymerization contraction. Thus overall, the addition of approximately 12.6 wt% of non-bonded nanofillers may reduce internal stress without negatively affecting the initial or long-term properties of hybrid dental composites.

4.2. *Effect of resin viscosity on the properties of composites*

The decrease in DC with increasing viscosity of the resin composite due to the increase in bis-GMA content (Fig. 1) was expected and agrees with other studies [12–15]. The enhanced polymerization and higher DC for the less viscous resin composite is likely due to the enhanced diffusion of the reactive species and to the fact that the T_g of the material is closer to its curing temperature than for the more viscous materials. However, high DC values did not necessary translate into superior properties.

All composites in this study had similar filler content, but the viscosity of their resin was varied by changing the concentration of bis-GMA. The bulky aromatic rings of bis-GMA and the hydrogen bonding that occurs between the molecules hinders the mobility of monomers and polymer chains, thereby enhancing the three-dimensional microstructure of the composite and increasing its mechanical strength. While the rigid structure of bis-GMA can enhance mechanical strength, it also increases the viscosity of the resin base and raises its T_g, therefore impeding diffusion of the reactive species and causing a reduction in DC of the polymerizing composite. These two opposing effects may explain why there was no systematic difference in properties among composites of different resin viscosities. This was in agreement with the results from another study that evaluated resins having the same corresponding range of resin viscosities [16]. While resin viscosity only had marginal effects on the mechanical properties, its adjustment still needs consideration so as to achieve a balance between DC and the mechanical properties. A relatively high DC is preferable to produce a material with good mechanical properties and a minimum of unreacted, leachable components that may affect its biocompatibility. However, maximizing conversion may require the use of low-viscosity diluents that produce composites with reduced properties and higher polymerization shrinkage. Overall, the medium-viscosity composites containing an equal mixture of bis-GMA/TEGDMA/UDMA provided optimum mechanical properties.

4.3. Effect of aging on mechanical properties

The changes in mechanical properties of resin composites with time are essential to predicting durability. Previous studies on the effects of water storage on the properties of composites reveal conflicting information. For example, while some studies have shown an increase in K_{Ic} [17,18], others have reported a decrease [10,19] for composites exposed to a solvent. A significant reduction in some properties (e.g., K_{Ic} and FS) after water storage for ~3 months, with minimal change thereafter [10,19,20], is apparently a general trend for dental composites. This trend was not observed in this study, which showed an initial reduction followed by a recovery of properties at 6 months to values similar to those at 1 day.

These initial declines in properties upon aging in water might be attributed to leaching of components from the composite and to water plasticization of the resin matrix [21–23]. The tendency for the low- and medium-viscosity resins to be more susceptible to the initial water degradation was surprising, because they had a higher DC and contained less of the more hydrophilic bis-GMA molecules, both of which would minimize water plasticization. The increase in properties from 1 to 6 months is difficult to explain, but several factors may be considered. There is the potential for post-irradiation polymerization, but this is unlikely to continue for months at a relatively low temperature (37°C). It is also possible that molecular relaxations within the polymer occurred over time thus leaving the material in a less internally strained condition, as previously hypothesized for the enhanced in vitro wear of composites [24]. Some recent studies on commercial composites have shown that FS after 180 days of water storage was not significantly different from that at 1 day [25,26], which agrees with the present study. The resin matrix has previously been shown to play a predominant role in water sorption [27–29], with a subsequent decline in the mechanical properties of resin composites [30,31]. It is likely that the effects of water aging are dependent upon the composition of the resin monomer in the composites, which may account for the differences reported by the different authors.

While it is tempting to develop different hypotheses about the individual effects, it should be noted that the reductions in properties that occurred in this study upon aging of the composites in water for up to 6 months were generally $<15\%$. In only three cases were the properties of any composites significantly lower at 6 months than at 24 h (i.e., KHN of MS, medium-viscosity unsilanated and HS composites). Therefore, one must conclude that these composites were relatively stable for up to 6 months of aging in water.

5. Conclusions

This study showed resin viscosity to be an important determinant of the properties of resin composites. The addition of approximately 12.5 wt% of non-bonded nanofiller does not negatively affect the initial or long-term properties of hybrid dental composites.

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