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Light-curing Time and Aging Effects on the Nanomechanical Properties of Methacrylate- and Silorane-based Restorations

A Catelan • T Pollard • AK Bedran-Russo
PH dos Santos • GMB Ambrosano • FHB Aguiar

Clinical Relevance

The methacrylate-based restorative system showed higher nanomechanical properties over a silorane-based system, predicting better clinical longevity.

SUMMARY

The aim of this study was to assess the influence of light-curing time on the nanohardness (H) and reduced elastic modulus (E_r) of components (underlying dentin, hybrid layer, adhesive, and composite) of methacrylate- and silorane-based restorations after 24 hours and six months of storage. Class II slot preparations were carried out in human molars (n=3) and restored with methacrylate (Clearfil SE Bond [Kuraray] + Filtek Z250 [3M ESPE]) or silorane (LS restorative system [3M ESPE]) restorative systems and light-cured using light-emitting diode at 1390 mW/cm^2 for the recommended manufacturers' time or double time. Restorations were sectioned, and bonded dentin-resin interfaces were embedded in epoxy resin and polished for evaluation with a Berkovich fluid cell tip (TI 700 Ubi-1 nanoindenter, Hysitron). Data were statistically analyzed by analysis of variance and Tukey's test (alpha=0.05). Overall, the H and E_r values

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*Anderson Catelan, DDS, MS, PhD, Department of Restorative Dentistry, Piracicaba Dental School, University of Campinas, Piracicaba, Brazil

Timothy Pollard, MS, Department of Mechanical and Industrial Engineering, College of Engineering, University of Illinois, Chicago, IL, USA

Ana Karina Bedran-Russo, DDS, MS, PhD, Department of Restorative Dentistry, College of Dentistry, University of Illinois, Chicago, IL, USA

Paulo Henrique dos Santos, DDS, MS, PhD, Department of Dental Materials and Prosthodontics, Araçatuba School of Dentistry, São Paulo State University, Araçatuba, Brazil

Gláucia Maria Bovi Ambrosano, DDS, MS, PhD, Department of Social Dentistry/Statistics, Piracicaba Dental School, University of Campinas, Piracicaba, Brazil

Flávio Henrique Baggio Aguiar, DDS, MS, PhD, Department of Restorative Dentistry, Piracicaba Dental School, University of Campinas, Piracicaba, Brazil

*Corresponding author: UNICAMP, Av. Limeira, 901 Areião P.O. Box 52, 13414-903 Piracicaba, SP, Brazil; e-mail: catelan@estadao.com.br

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were higher for methacrylate-based restorations than for silorane materials ($p \leq 0.05$), an increase in curing time did not improve the H and E_r of the bonded interface components of either material ($p > 0.05$), and aging significantly decreased the mechanical properties of interface components of both resin-based restorative systems ($p \leq 0.05$). In general, nanomechanical properties decreased after six months of storage, the methacrylate restorative system exhibited higher H and E_r than silorane, and light-curing time did not influence the properties tested.

INTRODUCTION

Most current dental composite resins are methacrylate-based monomers, such as bisphenol-A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA), with well-known high volumetric shrinkage[1] ranging from 1.9 to 3.5 vol%.[2] Light-cured restorative materials exhibit a significant percentage of unreacted methacrylate groups due to incomplete conversion of the C=C bonds.[3] However, a higher monomer conversion rate results in greater shrinkage strain.[4] Polymerization stress can result in many adverse effects, such as cuspal deflection,[5] debonding at the adhesive interface, postoperative sensitivity,[6,7] microleakage,[6] secondary caries, marginal discoloration, and restoration and dental fractures.[7]

A low-shrinkage monomer, silorane, was developed from the reaction of oxirane and siloxane molecules.[5,8,9] Methacrylate polymerizes by the free-radical cure, while silorane chemistry presents a cationic ring-opening polymerization mechanism,[5,8] and more light-curing time is needed to initiate the polymerization reaction by cation formation.[1,5,10] Silorane exhibits low polymerization shrinkage,[5,8,11] less than 1 vol%,[2] and the mechanical properties are comparable to those of conventional methacrylate dental composites.[9] Silorane composite is used with a dedicated two-step self-etch adhesive system; both primer and bond agents are light-cured, creating distinct layers.[1]

During restorative procedures, the distance between the guide tip of the light-curing unit and the resinous material surface in deep cavities reduces the irradiance that reaches the restorative material and decreases the monomer conversion and physical properties.[12] The increase in curing time improves monomer conversion into polymers, thereby improving the physical properties of the material.[4,13,14]

Nanoindentation is a reliable technique to obtain site specific nanohardness (H) and reduced elastic modulus (*Er*) of the resin-dentin interface components.[15] This technique would allow users to determine how extended light-curing time affects the properties of individual components of the resin-dentin bonded interface of different resin-based dental restorative materials.

The objective of this study was to evaluate the influence of different monomers and curing time on the H and *Er* of resin-dentin bonded interface components after 24 hours and six months of water storage. The null hypotheses tested were that (1) there would be no difference between the two distinct resin-based materials, (2) there would be no difference in how the light-curing times affect H and E_r, and (3) the aging would not affect the mechanical properties tested.

METHODS AND MATERIALS

The local Institutional Review Board approved the study protocol (#031/2010) for use of extracted human molars. Twelve freshly noncarious, unrestored human molars were collected and stored in 0.1% thymol solution at 4°C. The teeth were cleaned, stored in distilled water at 4°C, and used within three months after extraction.

The roots were embedded in polystyrene resin (Piraglass, Piracicaba, Brazil), and the occlusal surfaces were ground with 320-grit silicon carbide (SiC) grinding paper (CarbiMet 2 Abrasive Discs, Buehler Inc, Lake Bluff, IL, USA) under running water (APL-4, Arotec, São Paulo, SP, Brazil) until the distance between the occlusal surface and the cementum-enamel junction was 5 mm. Standardized Class II slot preparations with cervical margins in root dentin/cementum were performed in one of the interproximal surfaces of each molar using a high-speed diamond bur (No. 3100, KG Sorensen, Barueri, SP, Brazil) under water spray to final dimensions of 4 mm width, 6 mm height (1 mm below the cementum-enamel junction), and 2 mm axial depth. A custom-made preparation device allowed the standardization of the cavity dimensions. Each bur was used to cut three preparations.

The composition of the restorative materials is shown in Table 1. Two composite resins (Filtek Z250 and Filtek LS) and two self-etching adhesive systems (Clearfil SE Bond and Filtek LS Adhesive) were used to restore the cavities.

Table 1: *Materials Used*

Material	Batch Number	Composition (According to Manufacturer)
Clearfil SE Bond (Kuraray Medical Inc, Okayama, Japan)	Lot 00955A Primer	MDP, HEMA, water, CQ, hydrophilic dimethacrylate.
	Lot 01416A Bond	MDP, Bis-GMA, HEMA, CQ, hydrophobic dimethacrylate, N,N-diethanol p-toluidine, colloidal silica.
Filtek LS adhesive (3M ESPE, Seefeld, Germany)	Lot 9BN Primer	Bis-GMA, HEMA, water, ethanol, silica treated silica filler, CQ, phosphoric acid-methacryloxy-hexylesters mixture, phosphorylated methacrylates, copolymer of acryl and itaconic acid, phosphine oxide.
	Lot 9BK Bond	Hydrophobic dimethacrylate, phosphorylated methacrylates, TEGDMA, silane treated silica, CQ, stabilizers.
Filtek Z250 (A2 shade; 3M ESPE, St Paul)	Lot N144001BR	Filler: 60 vol%, aluminum oxide, silica, and zirconium oxide (0.01-3.5 μm).
		Resin: Bis-GMA, Bis-EMA, and UDMA.
Filtek LS composite (A2 shade; 3M ESPE, St Paul)	Lot N183458	Filler: 55 vol%, silica, and yttrium trifluoride (0.04-1.7 μm).
		Resin: Bis-3,4-Epoxycyclohexylethyl-Phenyl-Methylsilane and 3,4-Epoxycyclohexylcyclopolymethylsiloxane.

Abbreviations: Bis-EMA, ethoxylated bisphenol-A dimethacrylate; Bis-GMA: bisphenol-A glycidyl dimethacrylate; CQ, camphorquinone; HEMA, 2-hydroxyethylmethacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.

The preparations were randomized into four treatments, and nanoindentation measurements were performed after 24 hours and six months of storage on the same specimen, for a total of eight experimental groups (n=3) (Table 2). Restoration procedures were carried out using the following protocols. For the methacrylate groups, Clearfil SE Bond primer (bottle A) was first vigorously scrubbed with applicator brushes for 20 seconds; a mild air stream was applied for solvent volatilization; then a coat of adhesive resin (bottle B) was applied, followed by a gentle air stream, and light-curing for 10 seconds (G1 and G5) or 20 seconds (G2 and G6). For the silorane groups, Filtek LS Adhesive primer (bottle 1) was actively applied for 15 seconds, a mild air stream was applied, and then it was cured for 10 seconds (G3 and G7) or 20 seconds (G4 and G8). Afterward, adhesive resin (bottle 2) was applied, followed by a gentle air stream, and light-curing for 10 seconds or 20 seconds. The composite resins were incrementally placed using three horizontal layers (each approximately 2 mm) and light-cured for 20 seconds or 40 seconds, according to experimental groups (Table 2).

Resin-based materials were light-cured from the occlusal surface using a second-generation light-emitting diode (LED) unit (Bluephase 16i, Vivadent, Bürs, Austria) at 1390 mW/cm^2 of irradiance (at 0 mm). The output light power (mW) was measured with a power meter (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel). The tip diameter was measured with a digital caliper (Mitutoyo Sul Americana, Suzano, SP, Brazil) and recorded as 7 mm; the tip area was determined in centimeters squared. Irradiance (mW/cm^2) was calculated by dividing the output light power by the tip area. Irradiance was also calculated by positioning a spacer device (with heights of 4 mm and 6 mm) between the light guide tip of the curing unit and the surface of the power meter as well as beneath the resin disks for both composites (2 mm thick, simulating the first increment) and 4 mm from the top surface of the resin disk. The distance between the tip of the light-curing unit and the bottom of the cavity was 6 mm, resulting in 610 mW/cm^2 of irradiance. The increments of composite were approximately 2 mm thick, the total irradiance of the top surface of the first composite increment was 990 mW/cm^2 (4 mm distance between the tip of the light-curing device and the top surface of the first composite increment). The irradiance at the bottom surface at 6 mm (beneath the composite resin at 2 mm thickness) was 380 ± 5 mW/cm^2.

The restoration was cut in half, and one of the halves was embedded in epoxy resin (Buehler Inc) and polished manually with 800-, 1000-, and 1200-grit SiC grinding paper (CarbiMet 2 Abrasive Discs, Buehler Inc) under running water. A standardized metallographic polishing technique was used, the specimens were polished to a mirrorlike finish with polycrystalline diamond suspensions of grades 9, 6, 3, and 1 μm (MetaDi Supreme, Buehler Inc), and 0.05 μm alumina suspension polish (MasterPrep, Buehler Inc) on soft polishing pads (MicroCloth, Buehler Inc). Between each polishing stage, specimens were cleaned using an ultrasonic cleaner (CD-

Table 2: *Experimental Groups*

Group	Restorative System	Light-curing Time[a]	Water Storage
G1	Methacrylate	As recommended by the manufacturers	24 h
G2	Methacrylate	Double time	24 h
G3	Silorane	As recommended by the manufacturer	24 h
G4	Silorane	Double time	24 h
G5	Methacrylate	As recommended by the manufacturers	6 mo
G6	Methacrylate	Double time	6 mo
G7	Silorane	As recommended by the manufacturer	6 mo
G8	Silorane	Double time	6 mo

[a] *Double time was 10 s or 20 s for the adhesive system and 20 s or 40 s for the composite resin.*

4800, Practical Systems Inc., Odessa, FL, USA) with distilled water for five minutes.

Nanoindentation measurements were performed in the restoration components with a Berkovich fluid tip attached to a TI 700 Ubi-1 nanoindenter (Hysitron Inc, Minneapolis, MN, USA). The bottom of the block of epoxy resin was fixed on a metal disc and stabilized on the equipment platform with magnets. Wax was placed around the boundaries of the block and filled with Hanks' balanced salt solution (BioWhittaker, Lonza Walkersville Inc, Walkersville, MD, USA) to keep the specimen hydrated throughout the testing procedure.

Three regions were selected visually using an optical microscope coupled to the equipment. A three-axis piezo scanner (TriboScan, Hysitron Inc) was attached to the microscope to control the tip positioning and the *in situ* scanning probe imaging; the load-displacement transducer with a probe attached was used to indent the specimen while collecting the load-displacement data. Figure 1 shows the four aggregated images, two topography forward images of the silorane and two gradient forward imaging modes of the methacrylate restorative system. The specimens were stored in Hank's solution for six months at 37°C, changed weekly,[16] and remeasured.

An elongated pyramidal Berkovich fluid diamond tip (curvature radius $\approx$ 100 nm, Hysitron Inc) was used for imaging and testing on the hydrated samples. At each of the three regions previously selected with the optical microscope, three indentations were made with maximum load values of 100 μN for the hybrid layer and 1200 μN for the other components of the restoration (dentin, layer of the adhesive, and composite) under a standard trapezoidal load function of 10-40-10 seconds. Nine indentations were made in each component per specimen (n=3). The indentation load-displacement data collected were used to calculate the H and E_r by the TriboScope software (version 8.2.0.14, Hysitron Inc), using the Oliver-Pharr method.[17] The H and E_r averages of the nine measurements were used to determine the individual properties of the dentin, hybrid layer, adhesive, and composite resin of each specimen.

Nanomechanical properties readings after 24 hours and six months were performed in the same specimen, and proc-mixed analysis of variance (ANOVA) was used for repeated measures. The H and E_r data for dentin, hybrid layer, adhesive, and composite were analyzed by three-way ANOVA (factors were material, curing time, and aging) and Tukey's test (alpha=0.05). The H and E_r of the bond layer of the Filtek LS System Adhesive were subjected to two-way ANOVA (factors were curing time and aging) and Tukey's test at a preset alpha of 0.05; because this layer was only for the silorane adhesive system, silorane- and methacrylate-based materials were not compared.

RESULTS

ANOVA showed no interaction for any factor studied ($p>0.05$). The H and *Er* data are exhibited in Tables 3 and 4, respectively.

The H and E_r values of the methacrylate resin systems were higher than those for the silorane-based materials ($p\leq0.05$), except for the *Er* of the adhesive at 24 hours for both curing times ($p>0.05$). Mechanical properties of the underlying intertubular dentin were not influenced by the material or curing time ($p>0.05$), and it decreased over time ($p\leq0.05$).

The greater light-curing time did not improve the H and E_r of the materials ($p>0.05$). The six months of storage aging decreased the H and E_r values of all dentin-resin interface components ($p\leq0.05$), except for the E_r of the adhesive ($p>0.05$). The H and E_r of

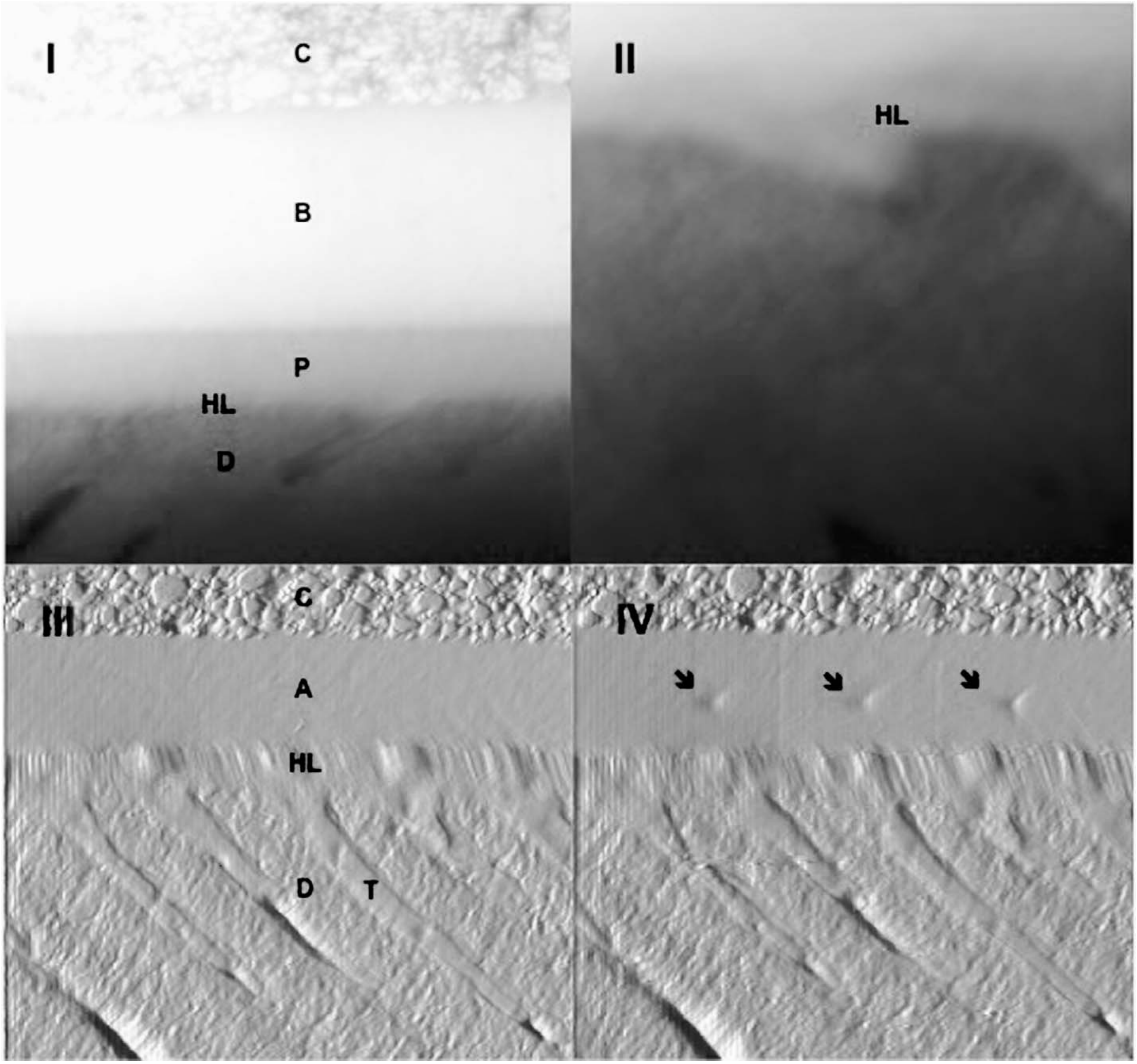

Figure 1. *Representative scanning probe microscopy images obtained by the TriboScanner. (C) Composite resin, (B) Layer of bond agent of the silorane adhesive, (P) Layer of primer of the silorane adhesive, (A) Layer of adhesive of the Clearfil SE Bond, (HL) Hybrid layer, (D) Dentin, (T) Resin tag. (I) Silorane group: topography image mode, scan size 40 × 40 μm. (II) Scan size 20 × 20 μm. (III) Methacrylate group: gradient image mode, scan size 40 × 40 μm. (IV) Indentations performed at the layer of adhesive (arrows).*

the resin composites were not affected by the aging factor ($p>0.05$).

DISCUSSION

Longevity of adhesive restorations is dependent on adequate and stable adhesion of the restorative materials to dental hard tissues over time. The first null hypothesis tested was rejected; the methacrylate restorative system showed higher nanomechanical properties than the silorane system, except for the E_r of the adhesive at 24 hours. Self-etch adhesives are less technique sensitive because there are no rinsing and drying steps; this maintains the ideal dentin humidity and reduces the risk of inaccuracies during application.[18] Two-step self-etch

Table 3: *Nanohardness (H [MPa]) of the Restoration Components According to Light-curing Time, Restorative System, and Aging*

Restoration Component	Light-curing Time	Restorative System	Aging[a]	
			24 h	6 mo
Dentin	Recommended	Methacrylate	1289.63 (125.56) A	959.96 (48.78) B
		Silorane	1390.26 (122.44) A	1002.69 (51.63) B
	Double time	Methacrylate	1301.85 (104.63) A	1030.12 (138.79) B
		Silorane	1290.56 (112.23) A	993.80 (100.44) B
Hybrid layer	Recommended	Methacrylate	379.18 (106.38) Aa	126.56 (47.62) Ba
		Silorane	252.94 (97.36) Ab	89.02 (13.71) Bb
	Double time	Methacrylate	383.15 (40.25) Aa	292.96 (33.23) Ba
		Silorane	327.26 (124.05) Ab	97.75 (23.67) Bb
Adhesive	Recommended	Methacrylate	258.41 (82.29) Aa	186.74 (19.12) Ba
		Silorane	191.62 (34.85) Ab	108.38 (14.32) Bb
	Double time	Methacrylate	282.55 (43.85) Aa	211.21 (26.91) Ba
		Silorane	204.95 (32.06) Ab	137.65 (10.67) Bb
Bond agent	Recommended	Silorane	338.25 (27.41) A	270.45 (4.21) B
	Double time	Silorane	332.23 (25.41) A	296.73 (19.17) B
Composite resin	Recommended	Methacrylate	1108.90 (231.02) a	977.41 (23.95) a
		Silorane	777.16 (62.87) b	638.25 (65.45) b
	Double time	Methacrylate	1123.62 (155.86) a	1089.33 (31.00) a
		Silorane	793.06 (50.74) b	750.52 (74.76) b

[a] *Distinct letters (capital in the row and lowercase in the column) for each restoration component are statistically different at* $p \leq 0.05$.

adhesive contains an acid primer that demineralizes and penetrates monomers into the dentin subsurface simultaneously; this is followed by application of a solvent-free hydrophobic resin to improve the mechanical properties.[19] One-step self-etch adhesives contain a mixture of acid, organic solvents, water, and hydrophilic and hydrophobic monomers in a single bottle.[19]

Clearfil SE Bond consists of a weakly acidic and hydrophilic self-etch primer and a solvent-free viscous hydrophobic resin coating layer that can increase the mechanical properties due to highly cross-linking monomers.[19] A specific two-step self-etch adhesive (Filtek LS System Adhesive) was formulated for silorane low-shrinkage composite. The hydrophilic and solvated self-etch LS primer is applied and light-cured, creating the hybrid layer (Fig. 1-II).[1,20] Then, LS bond is applied as a low-viscosity bifunctional hydrophobic monomer (phosphorylated methacrylate) and also light-cured, creating distinct layers (primer and bond, Fig. 1-I). It reacts with methacrylate by the acrylate groups and with oxirane by the phosphate groups.[11] So LS primer represents a one-step self-etch adhesive.[1,20] The solvated adhesives, such as silorane adhesive primer, have been related to poor mechanical properties, despite the improvement in degree of conversion (DC) from the increased mobility of the molecules over solvent-free adhesives.[21] Thus, the resin bond component of the methacrylate adhesive applied after the primer may exhibit better mechanical behavior, as demonstrated by the higher H and E_r of the hybrid layer and adhesive, compared with the silorane bonding system.

Sufficient cations are necessary to initiate the cationic ring-opening polymerization of the silorane composite; the onset of this reaction is slow, and additional light-curing is required compared with the free-radical cure of the methacrylate monomers into a polymer network.[1,5,10] Higher DC, Knoop microhardness, and depth of cure were found for methacrylate compared with the silorane composite.[22] Thus, the superior physical properties of the methacrylate-based composite probably resulted in higher H and E_r values than silorane.

The second null hypothesis was accepted as the light-curing time did not influence the H and E_r values of the restorative systems. Improvements in the physical properties of resin-based materials have been related to increased curing times because of the higher DC.[4,13,14,18] Light intensity is reduced approximately 10% by interposing 1 mm of air between the guide tip of the light-curing unit and the

Table 4: *Reduced Elastic Modulus (E_r [GPa]) of the Restoration Components According to Light-curing Time, Restorative System, and Aging*

Restoration Component	Light-curing Time	Restorative System	Aging[a]	
			24 h	6 mo
Dentin	Recommended	Methacrylate	23.73 (2.86) A	20.28 (1.61) B
		Silorane	23.83 (1.71) A	20.70 (0.82) B
	Double time	Methacrylate	24.37 (1.88) A	20.34 (2.67) B
		Silorane	24.11 (1.54) A	20.78 (0.90) B
Hybrid layer	Recommended	Methacrylate	6.12 (1.49) Aa	2.40 (0.72) Ba
		Silorane	5.01 (1.51) Ab	1.54 (0.15) Bb
	Double time	Methacrylate	6.08 (0.19) Aa	4.90 (0.67) Ba
		Silorane	5.33 (1.57) Ab	1.90 (0.48) Bb
Adhesive	Recommended	Methacrylate	5.65 (2.07) a	6.18 (0.91) a
		Silorane	4.21 (0.65) a	2.36 (0.20) b
	Double time	Methacrylate	5.89 (0.92) a	5.35 (0.58) a
		Silorane	3.90 (0.70) a	2.80 (0.14) b
Bond agent	Recommended	Silorane	5.29 (0.36) A	4.55 (0.04) B
	Double time	Silorane	5.56 (0.19) A	4.89 (0.30) B
Composite resin	Recommended	Methacrylate	16.79 (2.93) a	15.59 (0.80) a
		Silorane	13.16 (1.33) b	12.53 (1.41) b
	Double time	Methacrylate	16.63 (1.67) a	17.72 (0.98) a
		Silorane	13.80 (0.95) b	12.45 (1.48) b

[a] *Distinct letters (capital in the row and lowercase in the column) for each restoration component are statistically different at $p \leq 0.05$.*

material surface irradiated.[23] Special care should be taken in deep cavities and when the curing unit is at low light power during the polymerization of resinous materials. A light-curing time of 40 seconds is recommended for silorane composite resin using quartz-tungsten-halogen with irradiance between 500 and 1400 mW/cm^2 and for LEDs with output between 500 and 1000 mW/cm^2. For LEDs with irradiance between 1000 and 1500 mW/cm^2, a light-curing time of 20 seconds is recommended. An irradiation of 10 seconds is recommended to cure the primer and bond of silorane system adhesive, without a specific recommendation of minimum irradiance. In this study, a high light power LED of 1390 mW/cm^2 was used, indicating 20 seconds and 10 seconds of light polymerization for composite and adhesive, respectively. However, the irradiance achieved on the surface of the first composite increment was 990 mW/cm^2 at 4 mm from the guide tip and 610 mW/cm^2 at 6 mm for the adhesive system.

The second-generation LED unit used exhibits a narrow spectrum (between 410 and 530 nm, with a peak on the curve at 454 nm), which includes the maximum energy absorption peak of camphorquinone at 468 nm, which absorbs wavelengths from 360 to 510 nm.[24] However, the extended curing time available for light polymerization did not improve the H and E_r of the materials, perhaps because the high light power was sufficient to form more cross-linked polymers, which are less susceptible to degradation than linear polymers,[3] but results in the deceleration of the polymerization reaction and in limits on the conversion rate.[25]

The third null hypothesis was rejected because the long-term storage decreased the mechanical properties of most resin-dentin interface components. Bonding interface components can be degraded by hydrolysis; the water sorption results in polymer plasticization by swelling and reducing the frictional forces between the polymer chains, thereby decreasing the mechanical properties.[18]

The 10-methacryloyloxydecyl dihydrogen phosphate (MDP) monomer contained in the methacrylate adhesive tested in contact with the dental tissues form the MDP-calcium salt hardly dissolved in water; therefore the bond between MDP and hydroxyapatite should be stable.[26] Thus, the chemical interaction improves the resistance to hydrolytic breakdown and debonding stress, keeping the restoration margins sealed for a longer period.[27] Moreover, application of the hydrophobic bonding agent after the hydrophilic primer improves the mechanical properties by the presence of the cross-linking monomers,[19] which may contribute to reducing the adhesive interface degradation over time.

All-in-one adhesives, such as the one-step self-etch silorane adhesive primer, act as permeable membranes and can be more susceptible to aging.[28] These adhesives are strongly influenced by the light intensity of the curing unit.[19] The bond of the silorane adhesive is also solvent-free and contains more monomers with more cross-linking ability.[19,21] The nanomechanical properties of the components of the adhesive interface (hybrid layer, adhesive, and bond layer of the silorane adhesive) were reduced after storage, except for the E_r of the adhesive. Although the solvated silorane adhesive primer showed similar E_r as the methacrylate adhesive at 24 hours, after aging it exhibited significant lower properties, likely because of greater susceptibility to plasticization by the greater amount of hydrophilic monomers[28] and possible residual solvent.

Siloxane species present in the silorane composite exhibit high hydrophobicity,[8,9] and the H and E_r of this material was not affected after six months of storage, probably because of the hydrophobic nature of the siloxane species.[8,9] The higher conversion rate of the methacrylate composite compared with silorane[22] may have compensated for its lower hydrophobicity and increased the plasticization resistance of the Filtek Z250, for which properties also did not decrease with aging. The mechanical properties of the underlying intertubular dentin decreased over time regardless of the restorative material. Dentin tissue contains collagenolytic enzymes, such as matrix metalloproteinases and cysteine cathepsins, which are responsible for the hydrolytic degradation of the collagen matrix.[29]

The conversion of the monomers into structured polymers is related to the increase of the physical properties of the resinous material; this polymerization reaction is dependent on various factors, such as design and size of the tip guide, distance of the light guide tip from the material surface, power density, exposure duration, shade and opacity of the composite, increment thickness, and composition of the materials, resulting in clinical performance improvement of light-cured materials and more durability of the adhesive restorations.[12]

CONCLUSIONS

Overall, methacrylate restorative systems exhibited higher H and E_r than silorane; increased light-curing time did not influence the nanomechanical properties, which were significantly reduced after long-term storage.

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Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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REFERENCES

1. Van Ende A, De Munck J, Mine A, Lambrechts P, & Van Meerbeek B (2010) Does a low-shrinking composite induce less stress at the adhesive interface? *Dental Materials* **26(3)** 215-222.
2. Weinmann W, Thalacker C, & Guggenberger R (2005) Siloranes in dental composites *Dental Materials* **21(1)** 68-74.
3. Asmussen E, & Peutzfeldt A (2001) Influence of selected components on crosslink density in polymer structures *European Journal of Oral Sciences* **109(4)** 282-285.
4. Yap AU, & Seneviratne C (2001) Influence of light density on effectiveness of composite cure *Operative Dentistry* **26(5)** 460-466.
5. Palin WM, Fleming GJ, Nathwani H, Burke FJ, & Randall RC (2005) In vitro cuspal deflection and microleakage of maxillary premolars restored with novel low-shrink dental composites *Dental Materials* **21(4)** 324-335.
6. Duarte S Jr, Phark JH, Varjão FM, & Sadan A (2009) Nanoleakage, ultramorphological characteristics, and microtensile bond strengths of a new low-shrinkage composite to dentin after artificial aging *Dental Materials* **25(5)** 589-600.
7. Mine A, De Munck J, Van Ende A, Cardoso MV, Kuboki T, Yoshida Y, & Van Meerbeek B (2010) TEM characterization of a silorane composite bonded to enamel/dentin *Dental Materials* **26(5)** 524-532.
8. Guggenberger R, & Weinmann W (2000) Exploring beyond methacrylates *American Journal of Dentistry* **13(Special No)** 82D-84D.
9. Ilie N, & Hickel R (2006) Silorane-based dental composite: behavior and abilities *Dental Materials Journal* **25(3)** 445-454.
10. Bouillaguet S, Gamba J, Forchelet J, Krejci I, & Wataha JC (2006) Dynamics of composite polymerization mediates the development of cuspal strain *Dental Materials* **22(10)** 896-902.
11. Tezvergil-Mutluay A, Lassila LV, & Vallittu PK (2008) Incremental layers bonding of silorane composite: the initial bonding properties *Journal of Dentistry* **36(7)** 560-563.

12. Aguiar FH, Lazzari CR, Lima DA, Ambrosano GM, & Lovadino JR (2005) Effect of light curing tip distance and resin shade on microhardness of a hybrid resin composite *Brazilian Oral Research* **19(4)** 302-306.

13. Aguiar FH, Braceiro A, Lima DA, Ambrosano GM, & Lovadino JR (2007) Effect of light curing modes and light curing time on the microhardness of a hybrid composite resin *Journal of Contemporary and Dental Practice* **8(6)** 1-8.

14. Borges BC, Souza-Junior EJ, Catelan A, Ambrosano GM, Paulillo LA, & Aguiar FH (2011) Impact of extended radiant exposure time on polymerization depth of fluoride-containing fissure sealer materials *Acta Odontoloǵgica Latinoamericana* **24(1)** 47-51.

15. Higashi C, Michel MD, Reis A, Loguercio AD, Gomes OM, & Gomes JC (2009) Impact of the adhesive application and moisture on the mechanical properties of the adhesive interface determined by the nano-indentation technique *Operative Dentistry* **34(1)** 51-57.

16. Habelitz S, Marshall GW Jr, Balooch M, & Marshall SJ (2002) Nanoindentation and storage of teeth *Journal of Biomechanics* **35(7)** 995-998.

17. Oliver WC, & Pharr GM (1992) Improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments *Journal of Materials Research* **7(6)** 1564-1583.

18. De Munck J, Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M, & Van Meerbeek B (2005) A critical review of the durability of adhesion to tooth tissue: methods and results *Journal of Dental Research* **84(2)** 118-132.

19. Seki N, Nakajima M, Kishikawa R, Hosaka K, Foxton RM, & Tagami J (2011) The influence of light intensities irradiated directly and indirectly through resin composite to self-etch adhesives on dentin bonding *Dental Materials Journal* **30(3)** 315-322.

20. Santini A, & Miletic V (2008) Comparison of the hybrid layer formed by silorane adhesive, one-step self-etch and etch and rinse systems using confocal micro-Raman spectroscopy and SEM *Journal of Dentistry* **36(9)** 683-691.

21. Gaglianone LA, Lima AF, Gonçalves LS, Cavalcanti AN, Aguiar FH, & Marchi GM (2012) Mechanical properties and degree of conversion of etch-and-rinse and self-etch adhesive systems cured by quartz-tungsten halogen lamp and light-emitting diode *Journal of the Mechanical Behavior of Biomedical Materials* **12** 139-143.

22. Kusgoz A, Ülker M, Yesilyurt C, Yoldas OH, Ozil M, & Tanriver M (2011) Silorane-based composite: depth of cure, surface hardness, degree of conversion, and cervical microleakage in Class II cavities *Journal of Esthetic and Restorative Dentistry* **23(5)** 324-335.

23. Prati C, Chersoni S, Montebugnoli L, & Montanari G (1999) Effect of air, dentin and resin-based composite thickness on light intensity reduction *American Journal of Dentistry* **12(5)** 231-234.

24. Faria-e-Silva AL, Lima AF, Moraes RR, Piva E, & Martins LR (2010) Degree of conversion of etch-and-rinse and self-etch adhesives light-cured using QTH or LED *Operative Dentistry* **35(6)** 649-654.

25. Bae JH, Cho BH, Kim JS, Kim MS, Lee IB, Son HH, Um CM, Kim CK, & Kim OY (2005) Adhesive layer properties as a determinant of dentin bond strength *Journal of Biomedical Materials Research Part B: Applied Biomaterials* **74(2)** 822-828.

26. Yoshida Y, Nagakane K, Fukuda R, Nakayama Y, Okazaki M, Shintani H, Inoue S, Tagawa Y, Suzuki K, De Munck J, & Van Meerbeek B (2004) Comparative study on adhesive performance of functional monomers *Journal of Dental Research* **83(6)** 454-458.

27. Sarr M, Kane AW, Vreven J, Mine A, Van Landuyt KL, Peumans M, Lambrechts P, Van Meerbeek B, & De Munck J (2010) Microtensile bond strength and interfacial characterization of 11 contemporary adhesives bonded to bur-cut dentin. *Operative Dentistry* **35(1)** 94-104.

28. Tay FR, Pashley DH, & Peters MC (2003) Adhesive permeability affects composite coupling to dentin treated with a self-etch adhesive *Operative Dentistry* **28(5)** 610-621.

29. Tjäderhane L, Nascimento FD, Breschi L, Mazzoni A, Tersariol IL, Geraldeli S, Tezvergil-Mutluay A, Carrilho MR, Carvalho RM, Tay FR, & Pashley DH (2013) Optimizing dentin bond durability: control of collagen degradation by matrix metalloproteinases and cysteine cathepsins *Dental Materials* **29(1)** 116-135.