Abstract: This study evaluated the microhardness of four types of low-shrinkage composite resins and two types of universal composite resins with either 12 or 16 J/cm² light power energy. Three disks were made for each group \((n = 3)\) for a total of 36 specimens. The specimens were prepared by condensing the composite resin into a circular copper mold (diameter: 6 mm; height: 2 mm) and polymerizing with 700 mW/cm² light power density. The microhardness values of the resin specimens were measured using a Vickers hardness tester after different storage durations. Z250 and Clearfil Majesty Posterior composites showed softer subsurfaces when comparing the 24 h samples for all six types. Conversely, Kalore GC and Admira (AD) composites showed harder subsurfaces during the 24 h samples. All the composite resins showed significant differences \((P < 0.05)\) in microhardness values at one of the aging times when they were polymerized with either 12 or 16 J/cm² light power energy. Composite resin AD had a higher microhardness value after polymerization with 12 J/cm² than with 16 J/cm². The results indicated that low-shrinkage composite resins have better subsurface characteristics, and the light power energy of 16 J/cm² is better for the polymerization of most composites.

Keywords: water aging; surface hardness; low shrinkage; composite resin.

Introduction

With advantages such as convenient operation, good aesthetic appearance, acceptable physical properties, and instant polymerizing behavior, light-cured composite resins have been widely used in dentistry. However, changes of spacing distance among molecules caused by the conversion from Van der Waals bond distances to covalent bonds leads to the shrinkage of composite resins during polymerization (1,2). Minimizing interfacial stress is critical because of the shrinkage of the restorative material, which may result in debonding at the adhesive interface, marginal discoloration, postoperative pain, secondary caries in the tooth-restoration interface, and ultimate failure of the restoration (3,4). The major methods of reducing polymerization shrinkage are decreasing monomer percentages by increasing inorganic fillers, using prepolymerized filler particles, synthesizing and using low-shrinkage monomers, and reducing the amount of covalent bonds formed during polymerization (5). More and more low-shrinkage composite resins are synthesized by manufacturers in different ways. Extensive research on the mechanical properties of low-shrinkage composite resins has been performed. These investigations mainly evaluate immediate mechanical properties and are carried out after short-term storage in water. However, little information is available regarding the surface hardness of low-shrinkage composite resins after long-term storage in water.

Physical properties significantly affect the clinical lifespan of restorations, and clinicians must take these into consideration when choosing the appropriate material for patients (6). The surface hardness of material is one such property and is well correlated with degree of conversion, abrasion resistance, and compressive...
strength (7). Poor wear resistance (8) and susceptibility to toothbrush abrasion (9) are related to low hardness values, resulting in decreasing fatigue strength and even failure of the restoration. The degree of deformation of composite resins is determined by their hardness, which is also a widely evaluated property and an important parameter to compare with the hardness of tooth structure (10). The capacity of a material to resist the penetration of a diamond indenter is used to evaluate hardness, and the Vickers hardness test is usually performed (11). In clinical practice, composite resins are exposed to the oral environment, so their resistance to degradation is of great importance for the durability of a restoration (12).

Issues resulting from insufficient polymerization and residual monomers have been reported to compromise the mechanical properties of polymers (13). Adequate polymerization is necessary for the durability of composite resin restorations. This procedure requires sufficient light power energy. Therefore, the effect of 12 months of aging in water and radiant exposure on the subsurface hardness of six commercially available composite resins, including four low-shrinkage resins, was assessed in this study.

### Materials and Methods

#### Preparation of specimens

Six commercially available light-polymerized composite resins were evaluated in this study (Table 1). Clearfil Majesty Posterior (CM), Kalore GC (KA), Filtek LS (LS), Admira (AD), Z250 (Z2), and Solitaire2 (S2) were selected to represent a range of commonly used products. Z250 and S2 are considered universal composite resins. The other four resins are recommended as low-shrinkage composites by their respective manufacturers. The other four resins are recommended as low-shrinkage composites by their respective manufacturers.

A polyester film was positioned between a glass plate and a circular copper mold to avoid air entrapment and oxygen inhibition. The composite resins were then condensed into the mold (diameter: 6 mm; height: 2 mm), and another polyester film and glass plate were placed on the uncured composite material. It was pressed to the thickness of the mold for a period of 60 s with a static load of 500 g. The thickness of the composite samples was set to 2 mm, which is the thickness that composite resins can be adequately polymerized in clinical practice. A flat and smooth surface from the glass plate was used for the test specimens to produce fewer variations in the microhardness measurements. All composite resin specimens were polymerized with a Rainbow LED Curing Light (Liang Ya Dental Equipment Corporation, Guang-
zhou City, P. R. China). The tip of the light curing unit (LCU) was vertically placed on the composite surface and 1 mm away from the surface of the composite resins. The light power density of the LCU was measured with a hand-held LED radiometer (model 644726, Dentsply International, York, PA, USA). The curing time was recommended by the manufacturer, and light power density was used to calculate light power energy to ensure adequate polymerization of the composite resins. The light power energy values were 12 or 16 J/cm². The light power density of the LCU was 700 mW/cm². To deliver light power energy of 12 J/cm², the curing time was set to 17 s for the Rainbow LED Curing Light (700 mW/cm² × 17 s, Liang Ya Dental Equipment Corporation). For light power energy of 16 J/cm², the curing time was set to 23 s (700 mW/cm² × 23 s). Thirty-sixty specimens were made and divided into 12 groups (identified factors: composite resin and light power energy value) with three specimens each. Each specimen was removed from the mold after photocuring and stored in distilled water, which was changed weekly in a light-proof container at 37°C.

**Microhardness test**

Twenty-four hours after polymerization, the Vickers hardness tester (HMV-G21ST, Shimadzu Corporation, Kyoto, Japan) was used to test the surface and sub-surface microhardness values of specimens at room temperature (23°C) under a load of 980.7 mN, with a dwell time of 5 s. The diamond pyramid micro-indenter of the Vickers hardness tester penetrated the specimens, and an indentation could be seen on the surface or subsurface of the specimens through the optical microscope under 40× magnification. The microhardness value was then calculated by measuring the length of the x-axis and y-axis of the indentation. To reduce the variation, the measurement was repeated three times to make different indentations, which were separated by at least 1 mm and averaged to obtain a mean microhardness value.

The samples were again immersed in distilled water at 37°C. A series of microhardness values were measured after 1, 3, 6, 9, and 12 months. The subsurface/surface Vickers hardness of each composite resin for each group was calculated after each measurement. The hardness percentage value = (average subsurface Vickers hardness of each group at a certain point of time)/(maximum surface Vickers hardness of each group at the same time) × 100%. If the value was over 80%, the resin was considered fully polymerized.

**Statistical analysis**

Statistical analysis of normality was conducted. Because of non-parametric distribution, data were submitted to the Kruskal-Wallis H test and Mann-Whitney nonparametric U test. The Kruskal-Wallis H test was used to evaluate the effect of the water aging duration on the microhardness of each group. Mann-Whitney nonparametric U test was used to analyze differences in the microhardness of the same composite resin polymerized with light power energy values of 12 or of 16 J/cm² at different aging times. The significance level α = 0.05 was used for all tests. All statistical analyses were performed using SPSS software (Version 16.0, SPSS Inc., Chicago, IL, USA).

**Results**

The results showed that the ratio of the subsurface/surface Vickers hardness of each composite resin was over 80%, indicating that all the composite resins had been fully polymerized. Consequently, only the subsurface Vickers hardness of each group was analyzed. The measured microhardness values of the six composite resins are summarized in Tables 2 and 3. For most composite resins, except LS polymerized with 12 J/cm² light power energy, significant differences (P < 0.05) in microhardness values were demonstrated when the effect of the water aging duration on the microhardness of each group was evaluated by the Kruskal-Wallis H test. After the 12 month immersion, both the Z2 and CM resins showed

| Table 2 Mean subsurface microhardness values of six types of composite resins polymerized with 12 J/cm² light power energy at different water aging durations |
|-----------------------------------------------|
| Resin  | 24 h | 1 mon | 3 mon | 6 mon | 9 mon | 12 mon |
| Z2     | 80.5 | 77.2  | 77.3  | 76.9  | 75.3  | 75.3   |
| S2     | 40.2 | 39.9  | 40.2  | 41.5  | 41.1  | 40.6   |
| CM     | 107.6| 102.4 | 99.8  | 97.6  | 96.4  | 95.2   |
| KA     | 32.2 | 35.9  | 41.5  | 39.9  | 40.4  | 39.1   |
| AD     | 42.1 | 43.2  | 46.8  | 46.5  | 45.3  | 45.1   |
| LS     | 49.4 | 49.8  | 48.8  | 48.5  | 48.7  | 48.3   |

| Table 3 Mean subsurface microhardness values of six types of composite resins polymerized with 16 J/cm² light power energy at different water aging durations |
|-----------------------------------------------|
| Resin  | 24 h | 1 mon | 3 mon | 6 mon | 9 mon | 12 mon |
| Z2     | 81.0 | 76.2  | 76.0  | 76.8  | 75.0  | 74.4   |
| S2     | 44.0 | 42.0  | 43.0  | 44.2  | 43.4  | 42.1   |
| CM     | 110.8| 103.8 | 98.4  | 99.5  | 99.0  | 99.4   |
| KA     | 34.2 | 39.7  | 42.3  | 41.5  | 41.8  | 39.7   |
| AD     | 41.4 | 44.7  | 45.5  | 44.7  | 44.1  | 44.9   |
| LS     | 49.3 | 52.1  | 49.5  | 48.8  | 49.0  | 48.8   |
lower subsurface microhardness when compared with the 24 h specimens. Conversely, KA and AD composites showed harder values for the same period. For S2 and LS composites, evaluation of the microhardness values was different for 12 and 16 J/cm² when 24 h specimens were compared with the aged ones. Table 4 shows the results of Mann-Whitney U test for pairwise comparisons of subsurface Vickers hardness of each composite resin polymerized with light power energy values of 12 or of 16 J/cm² at different aging times.

### Discussion

The primary focus of this study was to investigate changes in subsurface hardness characteristics over time for different composites and light power energy combinations. The tested composite resins were mainly selected to represent available low-shrinkage resins.

CM shows the greatest reduction in microhardness over time among the six composites. Water inside the composite resins plasticizes the molecules, resulting in lower subsurface microhardness values (14). Apparently, water absorption during immersion in water is a major factor in the debonding of the filler and matrix, dislodging of filler particles, propagation of matrix cracking, and resin superficial flaws (14-16). In fact, the physical or chemical degradation of the polymer matrix is not the only reason for the decrease in microhardness values. The dissolving of the filler and filler-matrix interface is also confirmed by other relevant studies (15,16). The mechanism of the overall hydrolysis degradation is a water diffusion process that is affected by the type of polymer, filler load, and filler particle surface management (17). The friction forces may decrease among the polymer matrix chains, as swelling of the matrix occurs after resins have been stored in distilled water. CM is a nanocomposite with small particle fillers that are silanized to establish an excellent bond with the matrix. Therefore, the total surface area of the polymer is increased, leading to a greater sorption of water (18,19). Moreover, the tensile stresses increase at the matrix-filler interfaces, promoting the pulling out of fillers (15).

KA specimens increase in microhardness by around 20% and 30% from 24 h to 3 months, whereas AD specimens increase by around 10% over the same period. As for KA, the rising hardness values after water aging may result from increased monomer conversion and extra postcuring reactions. Nearly 75% of the polymerization takes place during the first 10 min (20,21), followed by the postcuring polymerization reaction (22). The postcuring reaction can provide between 19% and 26% of the monomer conversion in this dark cure process (23). Furthermore, KA contains less triethylene glycol dimethacrylate (TEGDMA), which shows more hydrophilicity compared with bisphenol A-glycidyl methacrylate (Bis-GMA) and urethane dimethacrylate (UDMA) (17). As for AD, it is a new kind of composite resin from organically modified ceramics (ORMOCERS). ORMOCERS can be described as inorganic-organic hybrid copolymers composed of inorganic network polymers and organic networks. They exhibit excellent mechanical properties, low shrinkage, and high microhardness because of the strong covalent bonds between inorganic and organic sections (24).

Silorane-based composites (SBC) are synthesized by oxirane and siloxane molecules. The two benefits of SBC are the low polymerization shrinkage because of the ring-opening reaction (25,26) of the oxirane and the hydrophobicity resulting from the insolubility of

| Resin | Light power energy (J/cm²) | 24 h | 1 mon | 3 mon | 6 mon | 9 mon | 12 mon |
|-------|----------------------------|------|-------|-------|-------|-------|--------|
| Z2    | 12                        | a    | a     | a     | a     | a     | a      |
|       | 16                        | a    | a     | b     | a     | a     | a      |
| S2    | 12                        | a    | a     | a     | a     | a     | a      |
|       | 16                        | b    | b     | b     | b     | b     | b      |
| CM    | 12                        | a    | a     | a     | a     | a     | a      |
|       | 16                        | a    | a     | a     | a     | a     | b      |
| KA    | 12                        | a    | a     | a     | a     | a     | a      |
|       | 16                        | b    | b     | a     | b     | a     | a      |
| AD    | 12                        | a    | a     | a     | a     | a     | a      |
|       | 16                        | a    | b     | b     | b     | a     | a      |
| LS    | 12                        | a    | a     | a     | a     | a     | a      |
|       | 16                        | a    | b     | a     | a     | a     | a      |

Different lowercase letters in the same column are significantly different ($P < 0.05$) for each composite resin.
siloxane in the oral environment (27). LS is an SBC with hydrophobicity and low polymerization shrinkage. The microhardness increases from 24 h to 1 month of storage time, which can be explained by self- or dark polymerization. At 12 months, subsurface microhardness has a small decrease when compared with the microhardness at 24 h, because of the high chemical stability and hydrophobicity of the silorane matrix.

Solution and absorption are two main reasons for the reduction in microhardness of Z2 and S2. Immersing specimens in water will lead to the occurrence of a rapid residual monomer elution and water absorption. The residual monomers are mostly eluted within a few days, leaving spaces among the polymer chains, which are occupied by the absorbed water molecules. This process requires between 1 and 4 weeks. The residual monomers left inside the composite resins adversely influence the mechanical properties because of the plasticizing effects, which significantly decrease interchain forces. Water absorption reduces the microhardness values of composite resins in the same way. The water molecules appear to have a greater impact than monomers on the plasticizing effect, reducing the mechanical properties because of the smaller volume (28). The matrix component of composite resins may offer another explanation. A higher amount of TEGDMA in composite resin will lead to more water absorption. Additionally, Bis-GMA-based composite resins were confirmed by Braden and Davy to have greater water sorption than others (29).

In summary, the results show the better subsurface characteristics of low-shrinkage composite resins, and a light power energy of 16 J/cm² is better for polymerization of most composites. However, a light power energy of 12 J/cm² is enough to polymerize AD, and the clinical operative time can be shortened. This study presents the problem that water aging can affect the surface or subsurface microhardness values of composite resins. However, oral conditions may be complicated by factors such as the pH value, amount and type of the saliva enzymes, and food and beverages. Abrasion, fatigue, and bite force can also influence the hydrolytic process. Future studies are needed on clinical and in vitro property changes of composite resins.

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Conflict of interest
The authors have no conflict of interest to declare.

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