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Evaluation of polymerization in fluoride-containing composite resins

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Abstract Fluoride-containing restorative materials are frequently utilized to delay or inhibit caries. The quality of the fluoride-containing composite resins was evaluated by testing their microhardness, polymerization shrinkage, thermal expansion coefficient, and surface morphology. Some of them were evaluated in conjunction with the thermocycling process. The microhardness values of the thermocycled specimens were similar to those of the specimens immersed only in distilled water. Among the specimens, Surefil showed the highest (68.6 ± 1.2 Hv) value. A linear correlation was found between microhardness and the filler content (vol%) of the specimens regardless of their states. Polymerization shrinkage rapidly increased during the light curing, and then it reached a plateau. The shrinkage values increased as the specimens became thicker. In a temperature range of 30 ~ 80 °C, the coefficients of thermal expansion of the control specimens ranged between 43×10^{-6}/°C and 77×10^{-6}/°C. An inverse correlations were observed between the filler content (vol%) and the coefficient of thermal expansion and between microhardness and the coefficient of thermal expansion of the control specimens. Tetric Ceram showed a perforated or ‘‘Swiss-cheese’’ morphology after thermocycling. It was unique and occurred only in this product.

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Introduction

Dental caries is one of the most commonly and widely occurring oral diseases. The process of dental caries initiates from the dental plaque on the tooth surface. A film of oral bacteria on the tooth surface produces acids when they metabolize carbohydrates. These acids diffuse into the underlying enamel or dentin and then dissolve the mineral in the subsurface. The dissolved calcium and phosphate ions then diffuse out of the tooth, leading to subsurface demineralization. Caries can develop adjacent to dental restorations in the presence of a microgap and can cause clinical problems and restoration replacement [1, 2]. To delay or inhibit the development of secondary caries near a restored lesion, fluoride-containing restorative materials are frequently utilized. Fluoride released by the fluoride-containing restorative materials plays an important role in preventing caries in microgaps between restorations and the root subsurface. The fluoride released inhibits bacterial metabolism by forming hydrogen fluoride (HF) molecules when the plaque is acidified [3]. Fluoride inhibits demineralization when present at the crystal surface and enhances remineralization by forming a fluorapatite-like veneer on the surface [4]. The amount of fluoride released by dental material is affected by the physico-chemical properties of the materials and is related to their cariostatic effect. Conventional glass-ionomer cement releases the greatest amount of fluoride, compomers and resin-modified glass-ionomers are placed in the middle, and composite resins release the least fluoride [5–7].

Polymerization is a process in which monomer molecules convert into a polymer network by activating photoinitiators using a blue light, which has emission spectrum between 400 nm and 500 nm. During the polymerization process, the intermolecular distance reduces as conversion has achieved. Bis-GMA is one of the basic monomers of high viscosity and has been reported to have a volumetric shrinkage of 5% [8]. To reduce high viscosity, monomers of lower weight molecules have been mixed with Bis-GMA. Such dilution allowed the level of filler to be increased and, as a result, mechanical properties were improved and polymerization shrinkage in most composite resins reached to 2 ~ 3% [9, 10]. Shrinkage during the polymerization process and expansion caused by external temperatures have been reported to be associated with margin microleakage [11, 12]. The process of contraction and expansion as a result of external temperature has been reported to influence the bonding ability of dental restoratives, possibly leading to secondary caries and postoperative sensitivity [13–15]. Microleakage has also been reported to have a correlation with the coefficient of thermal expansion [16]. Thus far, many investigators have reported the coefficient of thermal expansion of composites and teeth under diverse experimental conditions [11, 12, 17–20]. However, the reported coefficients generally lacked consistency.

The purpose of the current study was to investigate the quality of polymerization of the fluoride-containing composite resins by evaluating some of their mechanical properties and surface morphology in conjunction with the thermocycling process.

Materials and methods

Materials

Fluoride-containing composite resins were used, whose characteristics are listed in Table 1. The specimens were polymerized using a light-curing machine (CuringLight XL3000, 3M, St. Paul, USA) and some of their physical properties were explored in conjunction with the thermocycling process.

Experimental procedure

To measure the surface microhardness of the specimens, a Vickers hardness tester (FM-7, FUTURE-TEC Inc., Japan) was utilized before and after the thermocycling process. The thermocycling process was utilized to apply hot and cold stimuli repeatedly. Fourteen (seven for the thermocycling process (Group 1) and the other seven for the distilled water storage process (Group 2)) specimens from each product were prepared by placing the resin into an acrylic ring mold (7 mm in diameter and 1 mm in depth) and covering it with a thin slide glass. The slide glass was pressed firmly to ensure a flat surface. The specimen was light polymerized with a 700 mW/cm^2 light intensity for 40 s. The polymerized samples were kept in a dark container for 24 h prior to taking the measurements. After 24 h, the microhardness of the surface was measured before the thermocycling process using a hardness tester. Two indentations were made on the surface under conditions of a 200-g load and a 15-s dwell time. After that, the measured specimens were divided into two groups. Specimens in Group 1 were immersed in a water bath and repeatedly thermocycled between 4 °C and 60 °C with a dwell time of 30 s in each bath. The repeated measurement was performed after 2,000, 5,000, and 10,000 cycles. Specimens in Group 2 were immersed in distilled water without thermocycling until the termination of the thermocycling process of Group 1. The same measurements were performed after 2,000, 5,000, and 10,000 cycles. Each additional measurement was performed near the previously measured position to maintain consistency.

For polymerization shrinkage measurements ($n = 5$) during the light curing process, a linometer (RB 404, R&B Inc., Daejon, Korea) was utilized. This system is composed of a sample holder, a curing light, a shrinkage sensing part, software, and a computer. The specimen resin is located between the covering slide glass and aluminum disc on the specimen holder. A teflon (polytetrafluoroethylene, PTFE) mold (1.50, 2.50, and 3.50 mm thickness with an inner diameter of 4 mm) was placed over the aluminum disc and the teflon mold was filled with the specimen resin. To facilitate the measuring process, the disc was coated slightly with Vaseline. After being filled completely with resin, the teflon mold was removed. A slide glass was then secured over the resin. The probe of the light-curing unit

Table 1 Characteristics of the resins tested in this study

Material	Composition	Filler type	Filler content (vol%)*	Batch	Manufacturer
Surefil	Urethane modified Bis-GMA, TEGDMA	Ba-Al-F-borosilicate glass, silica	66	020227	Dentsply/ Detrey
Solitaire2	Bis-GMA, UDMA, TEGDMA	Ba-Al-F-borosilicate glass, porous silica	58	310697	Heraus Kulzer
Heliomolar	Bis-GMA, UDMA	Aluminosilicate, YbF_3	41	D51604	Vivadent
Tetric Ceram	Bis-GMA, UDMA, TEGDMA	Ba-Al-F-borosilicate glass, Ba glass, YbF_3	53.4	MF542	Vivadent

* According to the manufacturers

was in contact with the slide glass. Before light curing, the initial position of the aluminum disc was set to zero. The light was irradiated from the unit with a 700 mW/cm^2 light intensity for 40 s. As the resin polymerized, it shrunk toward the light source. The aluminum disc under the resin also moved toward the light source. The amount of disc displacement that occurred due to polymerization shrinkage was automatically measured by the non-contacting inductive gauge for 300 s. The utilized shrinkage sensor in this study was a non-contacting type whose resolution was 0.1 μm with a 100-μm measuring range.

In order to evaluate the coefficient of thermal expansion of the products before and after the thermocycling process, fifteen specimens (1.5 × 2 × 12 mm) per product were prepared in a metal die. Each specimen was polymerized using the same light-curing unit and polymerization conditions previously described. The resin in the metal die was covered with a thin (200 μm) transparent cover glass. The end of the light guide was in contact with the cover glass during the light-polymerization process. After removing each specimen from the metal die, the unexposed rear side was light polymerized for 40 s to ensure complete polymerization. All light-polymerized specimens were then stored in a dark container prior to making measurements.

Five specimens from each product were randomly selected. The coefficient of thermal expansion was evaluated using a thermomechanical analyzer (TMA) (TMA120, Seiko, Tokyo, Japan). The linear thermal expansion of each specimen was recorded in a temperature range between 30 °C and 80 °C through the probe that was in contact with the specimens. Each specimen was heated at a rate of 5 °C/min in order to obtain uniform heat distribution in the specimen. In order to reduce additional polymerization shrinkage due to the elevated temperature during measuring, only one measurement per specimen was recorded. After each measurement, the machine was cooled to below 30 °C. The coefficient of thermal expansion was evaluated using internal software from the TMA in a temperature range between 30 °C and 80 °C. The rest of the specimens were repeatedly thermocycled 5,000 and 10,000 times between 4 °C and 60 °C with a dwell time of 30 s in each bath. After 5,000 thermocycles, five specimens were removed, and the remaining five specimens were removed after 10,000 thermocycles. The coefficient of thermal expansion of the removed specimens was also evaluated as were the control specimens under the same measurement conditions.

To observe surface morphology, specimens from each product were prepared by placing the resin into an acrylic ring mold (7 mm in diameter and 1 mm in depth) and covering them with a thin slide glass. The slide glass was firmly pressed to ensure a flat surface. The specimens were light polymerized with a 700 mW/cm^2 light intensity for 40 s, and then were kept in a dark container for 24 h prior to taking the measurements. After 24 h, the polymerized specimens were polished using SiC paper (#2000) and then alumina paste (1 μm) in order to expose fillers. Then, specimens were sonicated in distilled water for 3 min. The prepared specimens were immersed in a water bath and repeatedly thermocycled between 4 °C and 60 °C, with a dwell time of 30 s in each bath. After 10,000 themocycles, specimens were removed from the water bath and surface observation was performed using a scanning electron microscope (SEM) (S-4200, Hitachi Co., Tokyo, Japan) after coating surface with gold.

Statistical analysis

The acquired data for the maximum polymerization shrinkage and the coefficient of thermal expansion among specimens were analyzed by two-way ANOVA at the 0.05 level of significance.

Results

Table 2 shows the microhardness of specimens for different numbers of thermocycles in a water bath and the equivalent period of immersion in distilled water. Surefil and Heliomolar showed the highest (68.6 ± 1.2 Hv) and lowest (28.4 ± 0.8 Hv) values, respectively. After 10,000 thermocycles, Surefil and Heliomolar still showed the highest and lowest microhardness values. However,

Table 2 Microhardness (Hv) for different number of thermocycles

		0	2,000	5,000	10,000
Surefil	Th	68.6 ± 1.2	65.2 ± 1.1	64.4 ± 1.6	62.2 ± 1.0
	Dw	68.7 ± 1.0	63.5 ± 1.6	65.3 ± 1.3	64.6 ± 0.8
Solitaire 2	Th	50.6 ± 1.2	37.8 ± 1.0	37.6 ± 0.7	35.5 ± 1.3
	Dw	50.9 ± 1.5	37.2 ± 0.6	39.7 ± 0.9	37.0 ± 0.5
Heliomolar	Th	28.4 ± 0.8	23.2 ± 0.8	23.2 ± 0.5	23.7 ± 0.2
	Dw	28.6 ± 0.6	24.1 ± 0.7	24.3 ± 0.8	23.9 ± 0.5
Tetric Cerim	Th	49.4 ± 1.5	41.7 ± 1.1	39.8 ± 1.1	41.1 ± 0.5
	Dw	48.5 ± 0.5	37.8 ± 1.3	39.1 ± 1.0	39.0 ± 0.5

Th, thermocycled; Dw, immersed in distilled water for same time as thermocycled specimens

Solitaire 2 showed the greatest decrease (~30%) compared to the control (non-thermocycled) group. On the other hand, Surefil showed the least amount of decrease (~9%) among them. The microhardness values of the thermocycled specimens and specimens immersed in distilled water showed a similar decreasing pattern. The major decrease of microhardness occurred before 2,000 thermocycles. A linear correlation was found between microhardness and the filler content (vol%) among the specimens whether they were control, thermocycled, or immersed only in distilled water. For the control specimens, the correlation coefficient was over 0.99 (Fig. 1).

Figures. 2 and 3 show the polymerization shrinkage profiles of specimens during a 300-second period with different specimen thicknesses. The amount of shrinkage rapidly increased during the first 40-s period, the time required for light curing, and then it reached a plateau. Solitaire 2 and Surefil showed the greatest and the least amount of shrinkage for all tested thicknesses, respectively.

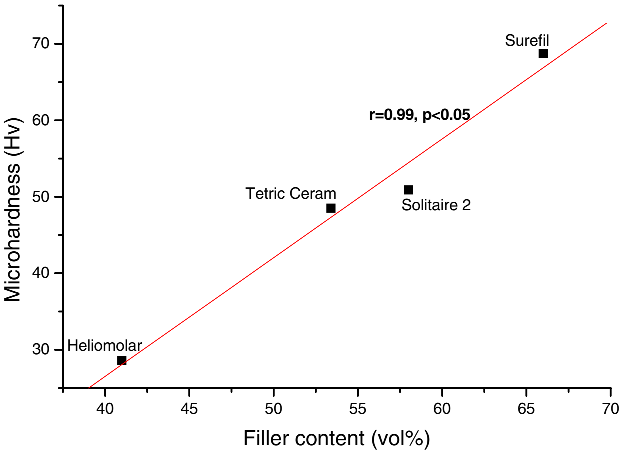

Fig. 1 The correlation between microhardness and the filler content (vol%) of the control specimens

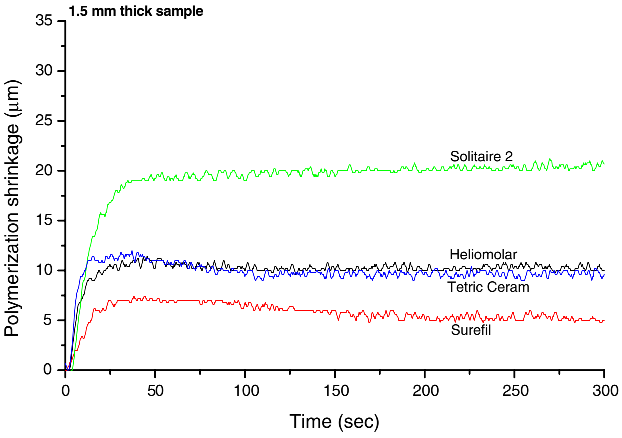

Fig. 2 Polymerization shrinkage of specimens at the thickness of 1.5 mm

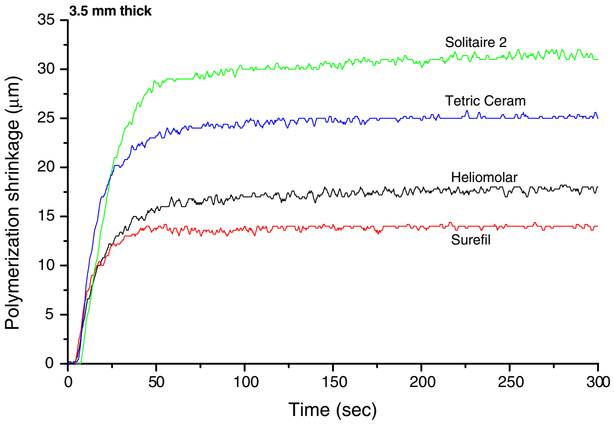

Fig. 3 Polymerization shrinkage of specimens at the thickness of 3.5 mm

Table 3 shows the maximum polymerization shrinkage (μm) of specimens of different thicknesses. At a thickness of 1.5 mm, Solitaire 2 showed 2 ~ 3 times greater shrinkage than the other specimens. As the specimens became thicker, the shrinkage values increased regardless of the product.

Table 4 shows the coefficient of thermal expansion $(\times 10^{-6}/^\circ\mathrm{C})$ in a temperature range of 30 ~ 80 °C for various thermocycles. For control (non-thermocycled) specimens, Heliomolar and Surefil showed the greatest $(76.7 \pm 2.6 \times 10^{-6}/^\circ\mathrm{C})$ and least $(43.2 \pm 1.4 \times 10^{-6}/^\circ\mathrm{C})$ coefficient value, respectively. After 10,000 thermocycles, specimens showed a 5.6 ~ 15.0% reduction of coefficient value compared to the non-thermocycled state. Solitaire 2 and Tetric Ceram showed statistically similar ($p < 0.05$) coefficient values regardless of the thermocycling process.

Figure 4 shows the relationship between the filler content (vol%) and the coefficient of thermal expansion of the tested control specimens. An inverse correlation was observed between them. The correlation coefficient for the

Table 3 Maximum polymerization shrinkage (μm) of specimens through the polymerization process

	Specimen A	Specimen B	Specimen C
Surefil	6.0 ± 0.8^{A1}	12.0 ± 1.4^{A2}	14.0 ± 0.3^{A3}
Solitaire 2	21.2 ± 1.7^{B1}	24.2 ± 1.2^{B2}	32.0 ± 0.8^{B3}
Heliomolar	11.2 ± 0.9^{C1}	13.5 ± 1.3^{A2}	17.5 ± 1.0^{C3}
Tetric ceram	10.5 ± 1.2^{C1}	20.0 ± 1.4^{C2}	25.0 ± 1.4^{D3}

Specimen A, 1.5 mm thick; Specimen B, 2.5 mm thick; Specimen C, 3.5 mm thick

Statistically significant difference within columns is shown by superscript letters$^{A, B, C, D}$, within rows by superscript numbers$^{1, 2, 3}$. Same letters or numbers are not significantly different ($p < 0.05$)

Table 4 The coefficient of thermal expansion ($\times 10^{-6}$/°C) for different number of thermocycles

	0	5,000	10,000
Surefil	43.2 ± 1.4^{A1}	37.8 ± 2.8^{A2}	38.4 ± 0.9^{A2}
Solitaire 2	63.8 ± 2.0^{B1}	55.9 ± 1.1^{B2}	55.1 ± 0.7^{B2}
Heliomolar	76.7 ± 2.6^{C1}	70.1 ± 0.9^{C2}	72.4 ± 3.3^{C2}
Tetric Ceram	63.2 ± 3.1^{B1}	53.4 ± 3.8^{B2}	53.7 ± 0.6^{B2}

Statistically significant difference within columns is shown by superscript letters$^{A,\ B,\ C}$, within rows by superscript numbers$^{1,\ 2,\ 3}$. Same letters or numbers are not significantly different ($p < 0.05$)

non-thermocycled or thermocycled specimens was greater than –0.94.

Figure 5 shows the relationship between the coefficient of thermal expansion and the microhardness of the control specimens. A strong inverse correlation was observed between them.

Figure 6 shows the surface morphology of specimens before and after the thermocycling process. The filler morphology of Heliomolar (a and b) was not clearly identified. Solitaire 2 and Surefil showed a similar filler morphology. Many large fillers among the small fillers were observed. After 10,000 thermocycles, large fillers in Solitaire 2 and Surefil were detached and partially extruded from the interfacing matrix (d and f). Tetric Ceram showed an apparent disintegration of fillers. Some disintegrated fillers showed a perforated or ''Swiss-cheese'' morphology. This morphology was observed only in Tetric Ceram after thermocycling (h).

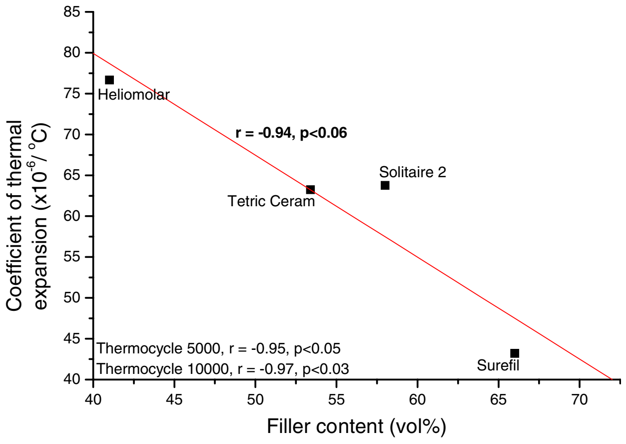

Fig. 4 The correlation between the coefficient of thermal expansion ($\times 10^{-6}$/°C) and the filler content (vol%) of the control specimens

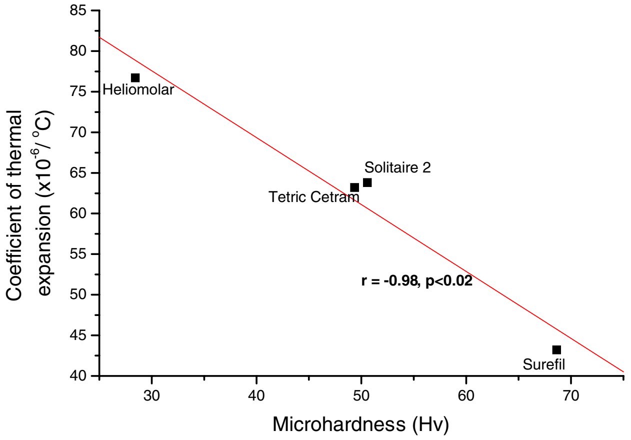

Fig. 5 The correlation between the coefficient of thermal expansion and microhardness of the control specimens

Discussion

Polymerization of light-curing dental composite resins is a complex interaction between the curing light and restorative materials. The degree of polymerization can indirectly be determined by the measurement of microhardness. Microhardness is the resistance of solids against local deformation such as a permanent indentation or penetration [21]. In general, a positive correlation has been established between microhardness and the filler content (vol%) of the composite resins [22, 23]. In the current study, the same linear positive correlation was found among the tested specimens. The tested specimens contained similar filler elements such as Ba, Al, F, Yb, and Si with different filler content (vol%). The filler content varied between 41% and 66%. The filler volume of Surefil (66%) was approximately 1.6 times greater than that of Heliomolar (41%). In case of the control specimens, on the other hand, the microhardness of Surefil (68.6 ± 1.2 Hv) was approximately 2.4 times greater than that of Heliomolar (28.4 ± 0.8 Hv). Besides the filler content, the content of each element, the filler distribution, and the filler size may affect the resultant microhardness. The decrease in the level of microhardness may be related to the combination of the chemical softening of water and aging. Water sorption results in a swelling of the resin matrix and it introduces tensile stress at the filler-resin interfaces. Among the monomers, TEGDMA has exhibited the highest water sorption [24]. Additionally, it strains the Si–O–Si bond in the inorganic fillers. The high energy arising from the strained Si–O–Si bonds makes the fillers more susceptible to stress and weakens the microhardness level of the surface [25]. A difference of water sorption (difference of monomers combination) or porosity of silica and glass may affect the decrease of microhardness. Fluoride release may also decrease the level of surface microhardness. Dissolution of fillers will leach ions, Ba, Al, F, Yb, and Si, into water and may create vacancies on the surface. External water will then fill the vacancies. Since osmotic pressure can reach high values, these

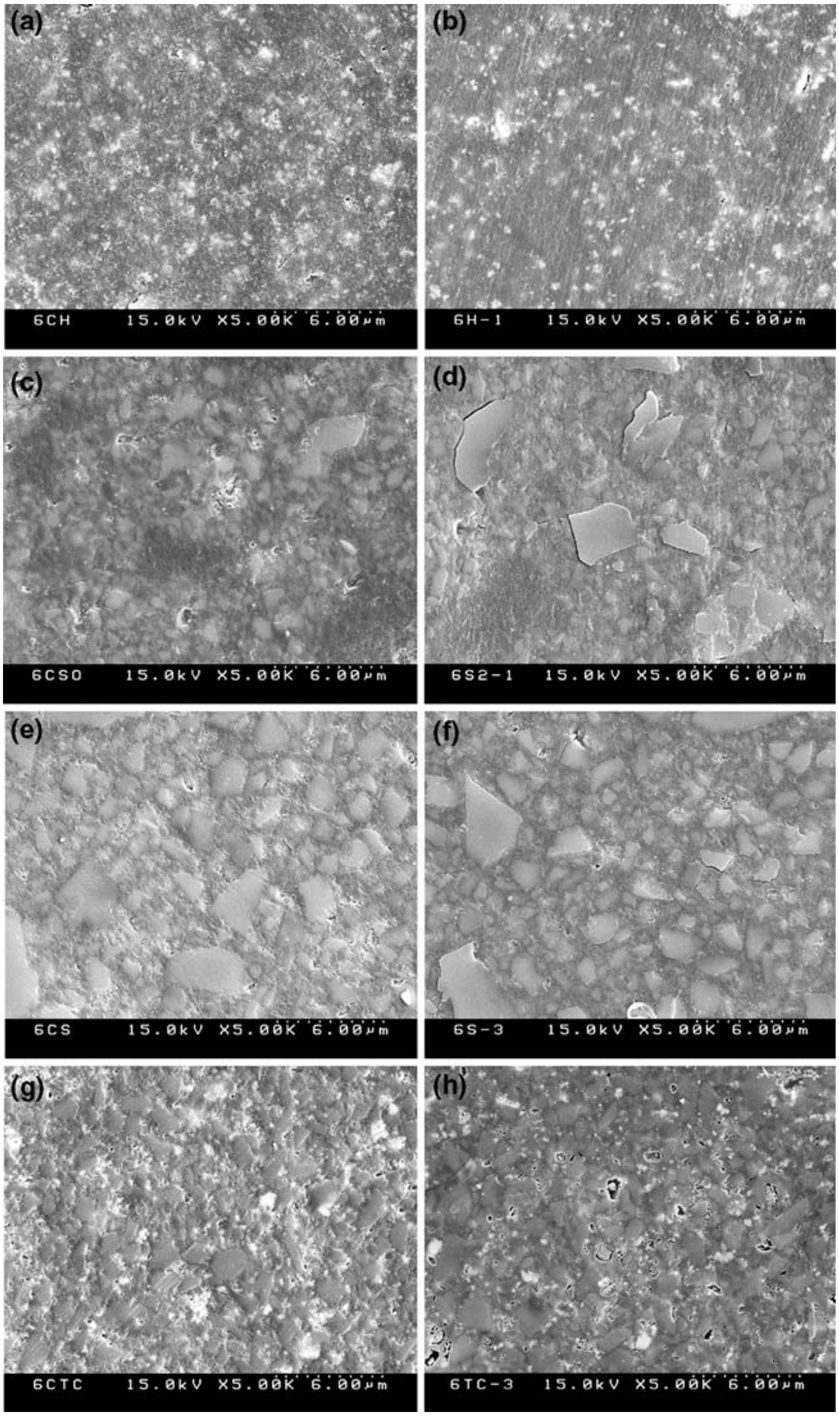

Fig. 6 The surface morphology of specimens before and after the thermocycling process (**a**, **c**, **e**, **g)** non-thermocycled surface morphology of Heliomolar, Solitaire 2, Surefil, and Tetric Ceram; (**b**, **d**, **f**, **h)** 10,000 thermocycled)

vacancies may expand and grow [18]. In the course of this process, the surface becomes soft and sometimes visible holes develop. Post-curing is the exposure of previously polymerized composite to elevated temperatures which produce further polymerization reactions. Free radical half-life of the light-polymerized composite resins can be greatly reduced by aging, temperature rise, and by the amount of filler particles present [26]. However, unlike normal post-curing by heat, repeated cooling and heating by cold and hot water during the thermocycling process may not affect the free radical half-life. The similar microhardness decrease of the specimens stored only in distilled water compared to those of the thermocycled may be attributed to this property.

Thermocycling is a simplified process that imitates temperature variation in the oral cavity. In most cases, the temperature in the mouth remains constant if there is no eating and/or drinking. When ice or hot water between

60 °C and 70 °C is placed in the mouth, a sudden thermal shock can occur, thereby damaging the dental pulp [27]. To test the effect of repeated temperature variation, 60 °C and 4 °C were chosen as the upper and lower temperatures, respectively. These temperatures have been commonly employed in other studies that investigated the effect of thermocycling on the physical properties of restorative materials [28]. Some products exhibited an apparent surface modification under the thermocycling process. Large fillers in Solitaire 2 and Surefil were detached and partially extruded from the matrix. Such modifications may arise from the thermal expansion difference between resin matrix and fillers. Under repeated thermocycling, this difference can be more extensive. The Swiss-cheese like morphology in Tetric Ceram after thermocycling is a common feature in the thermocycled compomers [23]. Dissolved fluoride including many other metallic elements may affect this modification. Since fluoride is contained in the tested specimens as compounds or fluoride-containing filler, it is not easy to determine what type of filler(s) is (are) responsible for this disintegration. The reason why this modification is not found in other products is unclear. Technical differences of the filler manufacturing are suspected as a probable reason of the observed difference.

Polymerization is the process of converting monomer molecules into a polymer network. Molecules placed equidistantly by a van der Waals' force change their position through covalent bonding. Through this process, the intermolecular distance is reduced. Each monomer has a different degree of shrinkage as a result of a different degree of conversion and monomer size [29]. Polymerization shrinkage increases when the molecular weight decreases. Among the most commonly utilized monomers, UDMA and TEGDMA exhibit a much higher degree of monomer to polymer conversion than Bis-GMA and Bis-EMA [24]. Since the quantity and combination of these monomers are different for each product, the spectrum of the degree of polymerization shrinkage will be broad. In addition to these organic monomers, inorganic fillers are also known to influence polymerization shrinkage [30–32]. In general, higher filler content is better for better mechanical properties of composite resin. Higher filler content implies less possible shrinkage due to lower resin volume. To increase the filler content, the higher viscosity of Bis-GMA was lowered by mixing Bis-GMA with lower molecular weight monomers such as TEGDMA and UDMA. Such dilution of Bis-GMA can increase polymerization shrinkage. In many cases, the exact ratios of fillers and monomers are unknown, because of the proprietary nature of the materials. The estimation of each factor on the final polymerization shrinkage is a complicated task. In the present study, the specimens did not show any specific correlation between the maximum polymerization shrinkage and the filler or resin content (vol%).

In the current study, the tested specimens had an inverse correlation ($r = -0.94$ for non-thermocycled specimens; –0.97 for 10,000 thermocycled specimens) between the filler content (vol%) and the coefficient of thermal expansion. Lower thermal expansion for a higher filler loading resin can be expected because of less resin volume. The same inverse correlation was found between microhardness and the coefficient of thermal expansion ($r = -0.98$ for control specimens). One interesting finding is the reduction of the coefficient of thermal expansion through the thermocycling process. The reduction of the coefficient is primarily related to the reduction of displacement against external heating. Since the coefficient of thermal expansion is related to the slope between the temperature and displacement values, the reduced displacement is probably related to additional polymerization by aging. In general, the reported coefficient for the dental composites ranged between 20×10^{-6}/°C and 80×10^{-6}/°C [17, 20]. These values, including our data, are significantly different from those of enamel and dentin. The reported coefficient of thermal expansion of enamel and dentin is approximately 11×10^{-6}/°C and 17×10^{-6}/°C, respectively [19]. The difference of the coefficient of thermal expansion between the composite resins and host teeth may increase the amount of microleakage under the complicated thermal environment in the oral cavity. On the basis of the above correlations, a composite resin with high filler content would appear to be a good choice for dental restorations because of low thermal expansion and high microhardness value.

Conclusions

Fluoride-releasing composite resins were polymerized using a light-curing unit. Their microhardness, polymerization shrinkage, thermal expansion coefficient, and surface morphology were evaluated under the thermocycling process to test the quality of polymerization. Surefil and Heliomolar showed the highest and lowest microhardness values, respectively, through the whole thermocycling process. Specimens showed similar microhardness values whether they were thermocycled or immersed only in distilled water. Microhardness and the filler content (vol%) were linearly correlated regardless of the specimen states. The polymerization shrinkage rapidly increased only during the first 40-s period, the time required for light curing. As the specimens became thicker, the shrinkage values increased regardless of the product. Among the specimens, Solitaire 2 showed the greatest shrinkage for all thicknesses. In a temperature range of 30 ~ 80 °C, the coefficient of thermal expansion of specimens ranged between 43×10^{-6}/°C and 77×10^{-6}/°C. These values are several times greater than that of enamel and dentin. Thermocycling process made the fillers of Tetric Ceram to be perforated. A ''Swiss-cheese'' morphology was observed only in Tetric Ceram.

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