



Microhardness, Degree of Conversion, and Water Sorption/Solubility of Non-expired and Expired (Two and Three Years) Dental Composites

Son Kullanma Tarihi Geçmiş (İki ve Üç Yıl) ve Geçmemiş Dental Kompozitlerin Mikrosertliği, Dönüşüm Oranı ve Su Emilimi/Çözünürlüğü

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ABSTRACT

Objective: The aim of this study was to compare the microhardness, degree of conversion, and water sorption/solubility of two- and three-year expired dental composites (Filtek Ultimate Universal) with the non-expired equivalent.

Methods: The prepared specimens (diameter =8 mm; thickness =2 mm) were subjected to Vickers hardness testing on the top and the bottom surfaces, and the degree of conversion was calculated based on the bottom/top hardness ratio. Further, water sorption and solubility were measured after immersion in distilled water for 1, 7, and 28 d. For statistical analysis, Shapiro-Wilk test, one-way analysis of variance, Kruskal-Wallis test, repeated analysis of variance and Friedman test were used ($p<0.05$).

Results: No significant changes in microhardness, degree of conversion, or water solubility were observed between any of the groups. However, the water sorption of the non-expired dental composite was higher than that of the three-year expired group after 28 d. Further, the water sorption/solubility of all of the expired and non-expired materials changed over time between 1 and 28 d.

Conclusion: Thus, the non-expired, two-year expired, and three-year expired dental composites exhibited similar microhardness, conversion degree, and water solubility characteristics. However, the degradation of dental composites is a complex process, and dentists are advised to adhere to expiration dates.

Keywords: Aging, composite resin, dental restoration, dentistry, hardness

ÖZ

Amaç: Bu çalışmanın amacı, iki ve üç yıllık son kullanma tarihi geçmiş dental kompozitlerin (Filtek Ultimate Universal) tarihi geçmemiş kompozitlere göre mikrosertliği, dönüşüm oranı ve su Emilimi/çözünürlüğünü karşılaştırmaktır.

Yöntemler: Hazırlanan örneklerin (çap =8 mm; kalınlık =2 mm) alt ve üst yüzeylerine Vickers sertlik testi uygulandı ve alt/üst sertlik oranına göre dönüşüm oranı hesaplandı. Ayrıca, 1, 7 ve 28 gün distile su içinde bekletildikten sonra su Emilimi ve çözünürlüğü ölçüldü. İstatistiksel analiz için Shapiro-Wilk testi, tek yönlü varyans analizi, Kruskal-Wallis, tekrarlayan varyans analizi ve Friedman testi kullanıldı ($p<0,05$).

Bulgular: Mikrosertlik, dönüşüm oranı veya suda çözünürlük açısından gruplar arasında anlamlı fark bulunamadı. Fakat, son kullanma tarihi geçmemiş dental kompozitlerin üç yıllık dental kompozitlere göre 28. gündeki suda Emilimi daha yüksekti. Ayrıca, tüm son kullanma tarihi geçmiş ve geçmemiş materyallerin su Emilimi/çözünürlükleri 1 ve 28. gün arasında zamanla değişti.

Sonuç: Son kullanma tarihi iki ve üç yıl geçmiş ve geçmemiş dental kompozitler mikrosertlik, dönüşüm oranı ve suda çözünürlük açısından benzer karakteristikler sergiledi. Fakat, dental kompozitlerin degradasyonu karmaşık bir süreçtir ve diş hekimlerine son kullanma tarihlerine uymaları tavsiye edilir.

Anahtar Sözcükler: Yıllanma, kompozit rezin, dental restorasyon, diş hekimliği, sertlik

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Introduction

Dental composites are common materials in dentistry, where the clinical behavior and properties thereof are determined by the material structure, degradation rate, and age (1,2). Once a composite material is applied in a dental cavity, it is difficult to prevent degradation (3,4). This degradation is a complex process and can be classified as either intraoral degradation due to mechanical, chemical and physical effects, or extraoral degradation due to storage conditions and aging (2).

An expiration date is based on the time period that a dental composite can maintain its stability, and is determined by the manufacturer (5). A small amount of dental composite is often used in dental practice, after which the remaining material may be stored until its expiration date (6). However, the use of expired dental composites can lead to fracturing, wear, and discoloration (2). Despite these issues, some dentists continue to use expired dental composites to avoid wasting excess materials (6). Thus, it is important to evaluate the characteristics of expired dental composites and predict their clinical performance.

Hardness, strength, modulus, and water sorption are important composite properties that are directly related to the degree of monomer to polymer conversion within the composite (7). Specifically, insufficient conversion can compromise the mechanical properties of the material, especially hardness (8,9). As the degree of conversion decreases, the free space in the polymeric network increases, which facilitates water diffusion across the network (9).

This study aimed to broadly evaluate and compare the microhardness, conversion degree, water sorption, and solubility of two- and three-year expired dental composites with the non-expired equivalent. The null hypothesis was that expiration date had no effect on the microhardness, degree of conversion, and water sorption-solubility of dental composites.

Methods

Preparation of Specimens

Non-expired, two-year expired, and three-year expired universal dental composites (Filtek Ultimate Universal, 3M ESPE, Saint Paul, USA) were compared. All of the dental composites were kept in the refrigerator before the study. The details of the composite are given (Table 1). Nine cylindrical specimens (diameter =8 mm; thickness =2 mm) for each experimental group (non-expired, two-year expired, and three-year expired) were prepared in a Teflon mold with a glass slide covering the surface of the

polyester matrix. A single layer of the composite material was transferred into the mold and light cured using a polymerization unit (Elipar Free Light 2, 3M ESPE, Saint Paul, USA) according to the manufacturer's instructions. The top surface of each specimen was marked using a waterproof pen. The specimens were removed from the mold and stored in distilled water at 37 °C for 24 h to facilitate maximum polymerization before testing.

Vickers Microhardness and Degree of Conversion

Vickers microhardness testing was conducted using a microhardness tester (Struers Duramin 5, Struers A/S, Ballerup, Denmark). Five indentations were conducted at different locations on the top and bottom surfaces of each specimen under a load of 1.96 N for 10 s. The mean value of the five indentations were used to determine the hardness of the top and bottom surfaces. The degree of conversion was evaluated based on the ratio of bottom hardness to top hardness.

Water Sorption and Solubility

Water sorption and solubility were evaluated using the same specimens after microhardness testing. The procedures given in the ISO 4049:2000 standard were used. However, the specimen dimensions did differ from the standard procedure. The constant mass of the specimens was determined by placing the specimens in a desiccator containing calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Edukim, Turkey) at 37 ± 1 °C for 24 h, followed by weighing using an electronic analytical balance (Kern & Sohn GmnH, ABJ 220-4M, Germany) with 0.0001 g accuracy. The procedure was repeated until each specimen reached constant mass ($M1$; μg), where the mass did not fluctuate by more than ± 0.1 mg over 24 h (10). Thereafter, the dimensions of the specimens were measured using a digital caliper to calculate the volume (V ; mm^3), where the diameter was taken as the mean of two diameter measurements at right angles, and the thickness was taken as the mean of the thickness at the center and at four equally spaced points on the circumference.

All specimens were placed in 2 mL distilled water in an incubator at 37 ± 1 °C for 1 d. The specimens were removed, carefully dried with absorbent paper, and weighed using the analytical balance ($M2a$). The specimens were placed back in the desiccator, and the constant mass procedure was repeated until a constant mass was achieved for 24 h ($M3a$). The specimens were incubated in distilled water for 7 and 28 d, where the distilled water was refreshed every day. The specimens were removed from the water after the respective periods, weighed using the analytical balance to determine $M2b$ and $M2c$, respectively, and placed

Table 1. The composition of the dental composite used in the present study

Name	Manufacturer	Main components	Type	Application procedure	Shade
Filtek Ultimate Universal (FUU)	3M ESPE, St.Paul, MN, USA ®	Bis-EMA, Bis-GMA, UDMA, TEGDMA, PEGDMA, silica, zirconia filler, zirconia/silica cluster filler	Nanofill composite	Curing time is 20 s for 2 mm enamel composite layer	A1 Enamel

back in the desiccator to achieve constant masses M3b and M3c, respectively. Water sorption (W_{sp}) and solubility (W_{sl}) ($\mu\text{g}/\text{mm}^3$) were determined based on M1 for the initial state, M2a and M3a for 1 d, M2b and M3b for 7 d, and M2c and M3c for 28 d as follows:

$$W_{sp} = \frac{M2(a, b, c) - M3(a, b, c)}{V}$$

$$W_{sl} = \frac{M1 - M3(a, b, c)}{V}$$

Scanning Electron Microscope (SEM) Analysis

One specimen from each group was selected to observe surface morphology. The selected specimens were dried in a dehumidifier with silica gel for 72 hours. They were coated with gold, and observed with a scanning electron microscope [EVO LS 10, Zeiss, Germany] under x3,500 magnifications for qualitative analysis of the surface.

Statistical Analysis

Statistical analysis was performed using SPSS 23V software. The compliance to normal distribution was analyzed using the Shapiro-Wilk test. The normally distributed data were analyzed using one-way analysis of variance. The Kruskal-Wallis test was used for the comparison of non-normally distributed data in terms of groups. Repeated analysis of variance was used to compare three or more normally distributed datapoints within the group, while the Friedman test was used to compare non-normally distributed data. The results were presented as mean

± standard deviation and median (minimum-maximum). The significance level was set at $p < 0.050$.

Results

There was no statistically significant difference between the nonexpired ($p=0.162$), two-year expired ($p=0.827$), or three-year expired groups ($p=0.225$) in terms of bottom and top microhardness values and degrees of conversion (Figure 1, Table 2).

The inter- and intragroup comparisons of water sorption and solubility indicated that there were some statistically significant differences in the water sorption and solubility behavior of the composites (Figure 2, Table 3). Specifically, the median water sorption of the non-expired group was significantly higher ($p=0.017$) than that of the three-year expired group after 28 d. Further, there was a statistically significant difference in the median water sorption over time in the non-expired ($p=0.002$), two-year expired ($p < 0.001$), and three-year expired groups ($p=0.001$), where the median water sorption after 28 d water was significantly higher than after 1 d for each group. In addition, the median value of the three-year expired group was higher after 28 d than the median values after both 1 and 7 d.

The mean water solubility did not differ between the groups at any time point ($p > 0.050$). However, there was a statistically significant difference in the mean water solubility over time in the nonexpired ($p < 0.001$), two-year expired ($p < 0.001$), and three-year expired groups ($p < 0.001$). Specifically, the mean water solubility of the nonexpired and two-year expired groups was significantly higher after 28 d compared to 1 and 7 d, while

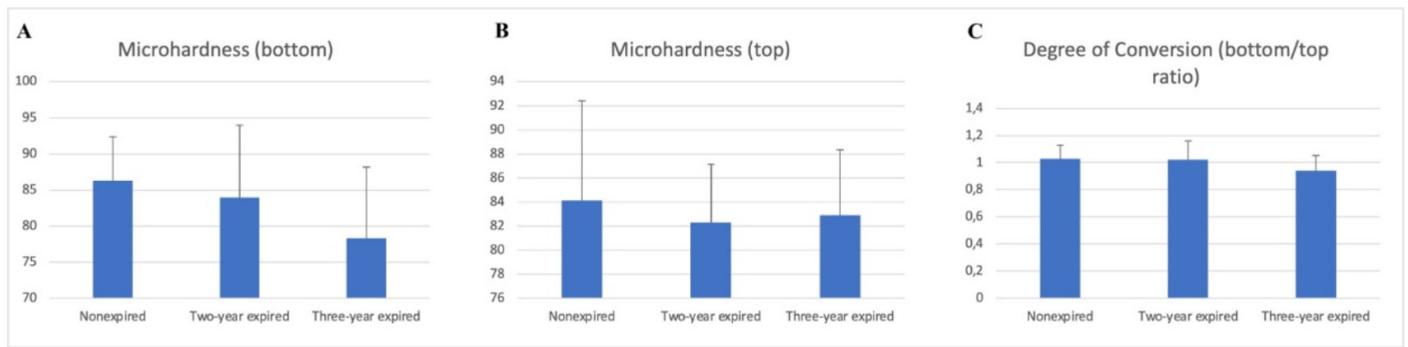


Figure 1. Mean and standard deviations graphics for bottom microhardness (A), top microhardness (B) and degree of conversion (C)

Table 2. Comparison of three groups in terms of bottom and top microhardness and degree of conversion values

		Non-expired	Two-year expired	Three-year expired	p*
Microhardness (bottom)	Mean ± SD	86.31±6.07	83.94±9.98	78.28±9.86	0.162
	Median (min.-max.)	85.46 (78.38-96.68)	81.12 (74.00-105.94)	81.48 (61.52-94.80)	
Microhardness (top)	Mean ± SD	84.10±8.32	82.27±4.84	82.92±5.39	0.827
	Median (min.-max.)	82.68 (73.04-101.98)	83.36 (76.68-90.10)	83.78 (73.64-90.02)	
Degree of conversion (bottom/top ratio)	Mean ± SD	1.03±0.10	1.02±0.14	0.94±0.11	0.225
	Median (min.-max.)	1.00 (0.91-1.23)	1.00 (0.86- 1.23)	0.96 (0.73- 1.09)	

*Analysis of variance, SD: Standard deviation, min: Minimum, max: Maximum

the mean water solubility of the three-year expired group differed significantly between all three time points.

The representative SEM images of each group were shown in Figure 3. Although they had similar appearance at x1,500 magnification, three-year expired dental composite had more irregularities on its surface at x3,500 magnification. Some spaces were observed on all of the three specimens at different magnifications.

Discussion

Microhardness, degree of conversion, and water sorption/solubility are important properties of dental composites, and serve as important predictors for material performance. The null hypothesis that expiration date had no effect on conversion degree, microhardness and water sorption/solubility of dental composites was partially confirmed by the results (Tables 2, 3),

as there was only statistically significant difference in the water sorption of the groups after 28 d.

The resistance of the dental composite to different forces in the mouth was evaluated based on microhardness (11,12). The longevity, strength, and durability of the composite in load bearing areas are also dependent on hardness (13). The hardness of a dental composite is affected by material type, water absorption, aging, and reactions on the material surface (14). Due to its effect on other physical properties, hardness is an important property in characterizing and ranking dental restorative materials (15). A greater hardness can be achieved via extensive polymerization and cross-linking (16), and is affected by various material characteristics such as monomer system, dilution concentration, initiator concentration, and loaded particle type and amount (17). Previous research indicated that the minimum Vickers hardness of a dental composite was 50 (18), where all of the mean hardness Vickers measurements in

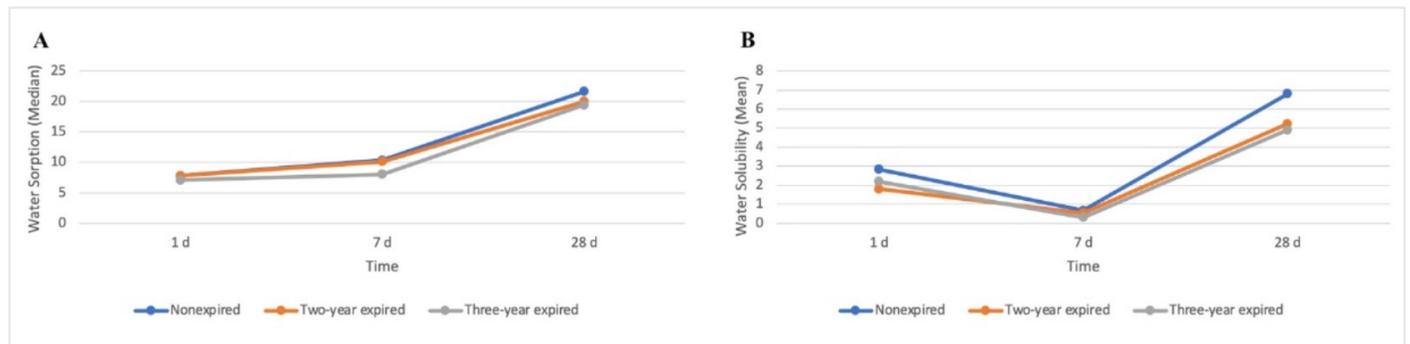


Figure 2. Line chart of the values of water sorption (A) and water solubility (B)

Table 3. Comparison of water sorption and solubility in terms of inter and intragroups

		Non-expired	Two-year expired	Three-year expired	p
Water sorption (µg/mm ³) after 1 d	Mean ± SD	7.79±2.25	7.46±2.54	7.88±1.60	0.927 ¹
	Median (min.-max.)	7.77 (3.88-12.37) ^A	7.77 (4.00-12.50) ^A	7.07 (6.00-11.00) ^A	
Water sorption (µg/mm ³) after 7 d	Mean ± SD	11.44±5.55	11.30±4.77	8.80±2.71	0.279 ¹
	Median (min.-max.)	10.31 (3.85-24.07) ^{AB}	10.09 (5.56-19.44) ^{AB}	8.00 (5.88-14.81) ^A	
Water sorption (µg/mm ³) after 28 d	Mean ± SD	21.98±1.53	19.75±1.76	20.01±2.25	0.017 ¹
	Median (min.-max.)	21.65 (20.19-25.24) ^{ab}	20.00 (16.67-22.00) ^{abB}	19.42 (18.18-25.49) ^{bb}	
p**		0.002²	<0.001²	0.001²	
Water solubility (µg/mm ³) after 1 d	Mean ± SD	2.83±2.65 ^A	1.80±0.71 ^A	2.18±1.06 ^A	0.442 ³
	Median (min.-max.)	2.83 (-0.97-8.25)	1.92 (0.95-2.78)	2.78 (0.00-3.00)	
Water solubility (µg/mm ³) after 7 d	Mean±sd	0.66±1.32 ^A	0.53±1.62 ^A	0.30±1.53 ^B	0.876 ³
	Median (min.-max.)	0.93 (-0.97-3.09)	0.00 (-1.98-3.00)	0.00 (-2.02-2.78)	
Water solubility (µg/mm ³) after 28 d	Mean±sd	6.81±1.43 ^B	5.23±1.54 ^B	4.90±1.85 ^C	0.050 ³
	Median (min.-max.)	6.54 (4.81 - 9.28)	4.81 (3.67-8.00)	4.85 (2.91-7.84)	
p**		<0.001 ⁴	<0.001 ⁴	<0.001 ⁴	

¹Kuskal Wallis test, ²Friedman test, ³Analysis of variance, ⁴Repeated analysis of variance, a-b: No significant difference for same lowercase among groups, A-C: No significant difference for same uppercase among duration

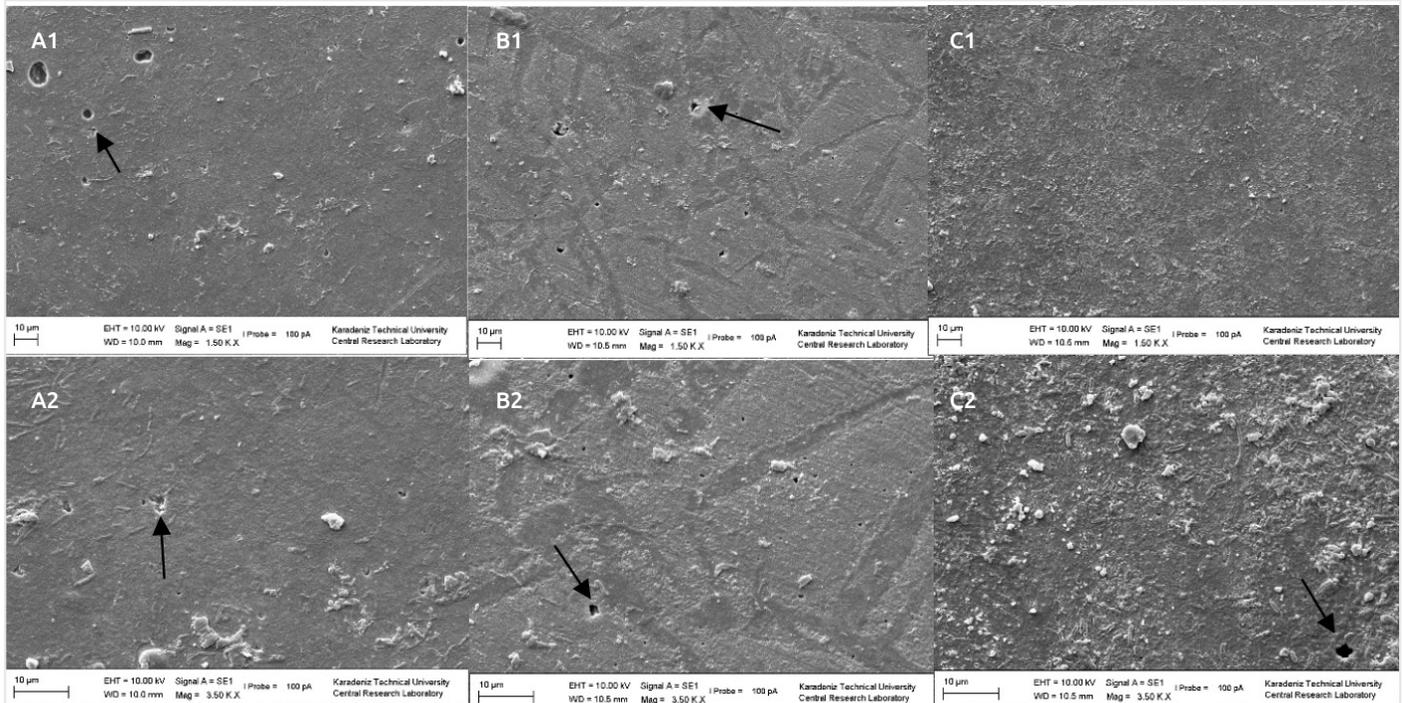


Figure 3. Sem images of non-expired (A1-A2), two-year expired (B1-B2) and three-year expired (C1-C2) dental composites at x1,500 and x3,500 magnifications, respectively. The black arrows show the spaces on dental composites at different magnifications

this study were substantially higher than 50. Further, there was no statistically significant difference between the hardness of the two expired groups and the nonexpired group. This was similar to the findings of a previous study, which reported that dental composites used 180 d after their expiration date did not have a significantly different hardness, with the exception one of one dental composite type (TPH Spectrum, Dentsply, USA) (6).

The degree of monomer to polymer conversion in a dental composite has an effect on its mechanical properties, color stability, and biocompatibility. The degree of conversion of a light-cured composite is dependent on the factors that affect light penetration, such as light scattering among particles, light absorbance by the photoinitiators, and pigment effects (19,20). More specifically, the parameters that affect the polymerization of dental composites include composition (e.g., photoinitiators, fillers, and organic matrix) (21), the light curing time and equipment (22), sample thickness (23), post-irradiation (24), and temperature of the material (25). All of these parameters were standardized in this study to isolate the effects of expiration date. The best indirect determinants of degree of conversion are Vickers and Knoop surface hardness measurements (26,27), while Fourier-transform infrared (FTIR) is considered a less sensitive technique (28). Polymerization might continue for 24 h after light curing (16), thus the bottom and top Vickers hardness measurements were only conducted 24 h after of light curing. A bottom/top hardness ratio of >0.8 is often accepted as the threshold value (29,30). All values in this study were above 0.8 due to optimal polymerization in under *in vitro* conditions. Further, it was impossible to conduct multiple hardness measurements at the same location on the composite specimens, which might affect the results. Overall, there was no statistically significant difference in the degree of conversion among the

groups. However, the three-year expired dental composite did exhibit the lowest degree of conversion. This may be attributed to the plasticization effect of the residual monomers (9), which can decrease the clinical success of the composite (19).

Water sorption and solubility of the two-year and three-year expired composites were compared with the nonexpired equivalent over immersion periods of 1, 7 and 28 d. All of the groups exhibited a continuous increase in water sorption over the 28 d period, where the water sorption was statistically higher after 28 d compared to 1 d. According to the ISO 4049 standard, the maximum allowed water gain is <40 µg/mm³ after 28 d (10). The water sorption of the nonexpired group was statistically higher than that of the expired groups after 28 d. This may be a desirable phenomenon, as the absorbed water can distend the matrix and minimize the shrinkage effect of polymerization (31). However, a larger coefficient of expansion than shrinkage value is not desirable, as this can lead to further stress on the restoration and tooth. These effects of water sorption should be further investigated based on microleakage or shrinkage studies with expired composites.

The water solubility of all of the samples was less than 7.5 µg/mm³, and there was no statistically significant differences between the groups at any time point. Thus, all three groups exhibited acceptable solubility behavior according to the ISO 4049 standard (10). The water solubility of a dental material can be correlated with its water sorption because water penetration into the material can lead to the leaching of unreacted components (32). However, this was not observed in the present study, where the three groups did not have the same ranking with respect to water sorption and the solubility level.

A previous study (33) on one-year expired dental composites reported similar findings to the present study regarding mechanical properties, including hardness and degree of conversion. A similar study also reported that there was no significant change in the modulus of elasticity and Vickers microhardness in one-year expired dental composites (2), while another study (34) on 15-month expired dental composites reported that the flexural performance did not change significantly. Further, a study (35) on the light curing of resins reported that the light curing properties remained constant for seven years after expiration, regardless of the storage conditions. The presence of preservatives, the temperature fluctuations, ambient conditions such as light, humidity and storage conditions may affect the characteristics of dental materials. As the materials are polymeric, their performances depend on the rate of degradation (36). The dental composites used in the present study were stored in the refrigerator and did not undergo significant changes in terms of microhardness, degree of conversion, or water solubility over time. This may be because of optimal ambient conditions and storage temperature.

The manufactures generally recommend the dental materials to be used up to 6 months after their expiration date. However, dentists use only small amounts of dental composites (6) and these materials may be used more than 6 months after their expiration date for some diagnostic purposes such as mock-up and temporary crowns (37). In this regard in this in vitro study two-year expired and three-year expired dental composites were compared with their non-expired equivalent.

Study Limitations

While these properties are important, other parameters such as radiopacity, optical properties, and surface roughness should be investigated further in expired dental composites. In addition, laboratory studies do not accurately represent clinical conditions, as they cannot fully reflect intraoral conditions such as saliva, masticatory forces, and the different irradiation distances of composite materials at various cavity depths. Thus, further investigation of other parameters and clinical studies are recommended.

Conclusion

Within the limitations of this study, it can be concluded that two- and three-year expired dental composites exhibit similar characteristics in terms of microhardness, degree of conversion, and water solubility to the nonexpired equivalent. As the degradation of dental composites is a complex process, it is advised that dentists adhere to expiration dates. Further investigation of more properties of expired composites is recommended to provide a better understanding of the effects of aging beyond the expiration date.

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Ethics

Ethics Committee Approval: There is no need for an ethics committee document.

Peer-review: Externally peer reviewed.

Authorship Contributions

Concept: K.D., Design: K.D., Data Collection or Processing: T.K., Analysis or Interpretation: T.K., Literature Search: T.K., Writing: K.D.

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