European Journal of
Oral Sciences

Eur J Oral Sci 2020; 1–9
DOI: 10.1111/eos.12705
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European Journal of
Oral Sciences

Suboptimal light curing and direct exposure to water of two contemporary composites: degree of conversion, sorption, solubility, and Knoop hardness

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Wikant AW, Gedde UW, Hakeberg M, Örtengren UT. Suboptimal light curing and direct exposure to water of two contemporary composites: degree of conversion, sorption, solubility, and Knoop hardness.
Eur J Oral Sci 2020; 00: 1–9. © 2020 The Authors. Eur J Oral Sci published by John Wiley & Sons Ltd

The water sorption and solubility of two polymer resin-based dental composite materials were assessed in order to evaluate the effects of immediate post-cure water exposure on the water sensitivity of the composites. Each material was tested with two different light curing setups. The radiant exposure of the two curing setups differed by a factor of 5. After exposure to water and subsequent drying, the Knoop surface hardness was measured. The change in the degree of conversion in both water and air storage medium within the first 24 h after curing was monitored by Raman spectroscopy. No significant differences in the degree of conversion were detected 24 h after curing. Samples exposed to the lower irradiation dose showed higher solubility and a lower surface hardness than the samples exposed to the higher irradiation dose. Early exposure to water did not cause detectable differences in the ongoing polymerization process. Increase in radiant exposure reduced the fraction of unbound constituents and increased the crosslink density, thereby reducing the plasticity of the material.

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Key words: dental materials; hardness; light curing; polymers

Accepted for publication May 2020

During recent decades, polymer resin-based dental composite materials (hereafter referred to as dental resin-based composites) have been the main type of material used for the direct restoration of teeth. The favourable adhesion to the tooth structure of dental resin-based composites permits the use of less invasive preparation techniques than are necessary for amalgams. The resin-based composite materials are, however, technique sensitive and proper polymerization is crucial (1, 2), as water has been shown to cause unwanted effects in dental composites, such as polymer degradation and leakage of constituents (3–6).

In the present study, the term 'water sensitivity' is used to describe the unwanted effects of water exposure, such as induction of the loss of mechanical properties, as well as the degradation and dissolution of composite constituents. The water sensitivity of dental composites is clinically important as increased water sensitivity may reduce the longevity of the restoration and the biocompatibility of the material (3, 5, 7, 8). The incorporation of water facilitates the release of unreacted monomers and other constituents from the composite material into the oral cavity and increases erosion and degradation (9, 10).

Light-sensitive initiator systems (380–550 nm, e.g., camphorquinone) are currently being used to provide an efficient and controllable start of the polymerization process in dental composites (11, 12). The absorbed light splits the initiators, forming free radicals that activate addition polymerization and the formation of a three-dimensional polymer network. The efficiency of this process is often evaluated by measuring the degree of conversion (i.e., the extent of conversion of aliphatic double bonds in the vinyl groups) using, for example, Raman or infrared (IR) spectroscopy (3, 13–15). However, the polymerization of dental resin-based composites depends on both intrinsic factors (such as monomer formulation, the type and amount of photoinitiator, and material translucency) and extrinsic factors (e.g., radiant exposure, temperature, and the distance between the light source and the material). The process continues after completion of the light-curing procedure, in a phase lasting for several hours: this is often referred to as the post-irradiation phase (16, 17). From a clinical perspective, the light-curing procedure is heavily dependent on the operator, and it is therefore important to investigate the outcomes of erroneous and suboptimal light curing. Uncured material is easy to detect on inspection; however, after a few seconds of exposure to curing light the composite material will appear hard. Therefore, a ‘low-cure’ group of specimens were also studied to compare their sorption, solubility, and surface hardness with those of specimens cured according to, or better than, the instructions provided with the materials by the manufacturers (Table 1).

Unavoidable exposure to water in the oral cavity after a completed restoration process can influence the ongoing post-irradiation polymerization, as the free radicals driving the polymerization, as well as interchain hydrogen bonds, can be affected by the presence of water (18). A decrease in the degree of conversion has been shown to increase the elution of unbound constituents *in vitro*, but the potential effects of the immediate exposure of light-cured dental composite materials to water have hitherto been insufficiently studied (19, 20).

Gravimetric sorption and solubility tests are often used to assess the extent of water incorporation and solubility of dental composites and are part of the standardized test array for evaluating dental resin-based composites (4, 21). These tests require that the light-cured materials are stored under dry conditions for a substantial period of time before exposure to water, and that the exposure is limited to 7 d. However, further increase in sorption and solubility after 7 d has been reported (3, 21, 22). To mimic a more clinically relevant scenario, the present study includes samples immersed in 37°C water immediately after light-curing and stored under these conditions for different periods of time up to 180 d.

The current work is based on findings from an earlier study (3), in which water sorption and solubility were tested on experimental composite blends. The former study revealed that replacing the monomer bisphenol A-glycol dimethacrylate (Bis-GMA) with ethoxylated bisphenol A-glycol dimethacrylate (Bis-EMA) reduced the water sorption of the composite (3). In the current study, the materials chosen allow comparison of a commercial product containing Bis-GMA and triethylene glycol dimethacrylate (TEGDMA) with a product containing more hydrophobic monomers (such as Bis-EMA and urethane dimethacrylate, UDMA), according to the safety data sheets. By narrowing down the type of composites to only conventional, high-viscosity composites, the number of differing factors is kept to a minimum.

The aim of this study was to investigate the effects of light curing on the water sensitivity of two conventional high-viscosity dental composites when the materials are exposed to water in a manner relevant to their clinical use.

Material and Methods

Two light-curable contemporary dental resin-based composites were tested: Voco Grandio (VOCO, Cuxhaven, Germany) and Tetric EvoCeram (Ivoclar Vivadent, Schaan, Leichtenstein). Information acquired from safety data sheets and from information leaflets provided by the manufacturers on Voco Grandio (hereafter referred to as T1) and Tetric EvoCeram (hereafter referred to as T2) is listed in Table 1.

Sorption and solubility assessment

Distilled water (Grade 2 ISO 3696:1987) was used in all the tests (23). Six specimens were prepared for each group: groups were defined according to the type of resin composite (T1 or T2), the intensity of the curing light (High or Low) and the five durations of water immersion (24 h, and 7, 30, 90, and 180 d) (Fig. 1) Specimens were made in Teflon moulds (produced at the technical laboratory of the Royal Institute of Technology in Stockholm, Sweden) according to ISO 4049:2009 with the following modifications (24): (i) the specimen diameter was reduced from 15 to 10 mm to ensure complete coverage of the specimen with the light-curing lamp tip; (ii) there was no pre-immersion drying of the specimens, and the specimens were immersed in water within 5 min after light curing; (iii) the duration of water sorption and solubility was extended to 180 d; and (iv) to evaluate the effect of light curing, a group of specimens for each material was subjected to suboptimal light curing (designated the low-cure group). A digital calliper (model ND 287; Heidenhain, Traunreut, Germany) was used to determine the size of the specimens.

Light curing

To minimize the variation in irradiance, the curing light source (Bluephase G2; Ivoclar Vivadent) was used with a corded power supply, with the light curing tip being kept perpendicular to the specimen surface and in contact with the plastic sheet covering the specimen throughout the curing period. The output of the light curing unit was controlled and recorded before and after each treatment of every group of specimens with the use of a BlueLight MARC resin calibrator (BlueLight Analytics, Halifax, NS, Canada). The light curing setting used for the high-cure

Table 1

Details of the materials used in the study

Material/Contents	CAS	Amount
Grandio (Voco, Cuxhaven, Germany)		
Bisphenol A-glycol dimethacrylate (Bis-GMA)	1565-94-2	2.5–5 wt%
Triethylene glycol dimethacrylate (TEGDMA)	109-16-0	≤2.5 wt%
Total polymer matrix		28.6 vol.%
Inorganic filler		71.4 vol.%
Tetric EvoCeram (Ivoclar Vivadent, Schaan, Liechtenstein)		
Bisphenol A-glycol dimethacrylate (Bis-GMA)	1565-94-2	2.5 < 10 wt.%
Urethane dimethacrylate (UDMA)	72869-86-4	2.5 < 10 wt.%
Ethoxylated bisphenol A-glycol dimethacrylate (Bis-EMA mix, avg. Mn ≈ 540)	41637-38-1	2.5 < 10 wt.%
Total polymer matrix		46 ± 1 vol.%
Inorganic filler		54 ± 1 vol.%

Data regarding monomers used are available at: https://www.voco.dental/en/portaldata/1/resources/products/instructions-for-use/e1/grandio_ifu_e1.pdf, for Grandio and at: http://www.ivoclarvivadent.com/en/p/all/products/restorative-materials/composites/tetric-evoceram for Tetric EvoCeram. Complemented with information from the safety data sheets provided by the manufacturers.

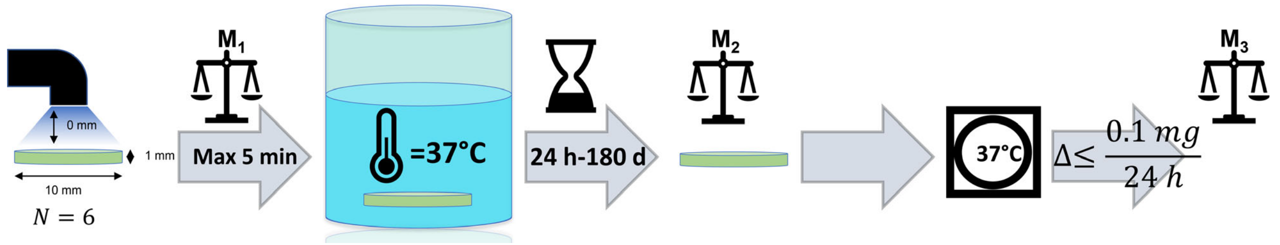

Fig. 1. Illustration of the procedure for sorption and solubility tests. Six specimens were made for each group and each was weighed (M_1). Within 5 min after completing the light-curing procedure, the specimens were immersed in water and stored in a heating cabinet at approximately 37°C for up to 180 d. At specific time points during this period (24 h, and 7, 30, 90, and 180 d), specimens were removed from the water, blotted dry, and weighed (M_2). The specimens were dried in a desiccator inside the heating cabinet, kept at the same, stable temperature. The mass was checked daily, until the change in mass over 24 h did not exceed 0.1 mg (M_3).

groups was the 'High' setting on the G2 curing unit, which gave an optical curing duration of 20.2 s, with a mean ± SD irradiance (Mean of the mean watt/area from each light curing control test, executed in triplicate before and after the treatment of each of the sample groups) of 1,317.7 ± 51.1 mW cm^{-2} and a mean ± SD radiant exposure (mean cumulative energy delivered to the specimen surface) of 26.6 ± 1.0 J cm^{-2}. The spectral peak measured was at 455.25 nm. The low-cure setting gave an optical curing duration of 5.18 s, with a mean ± SD irradiance of 716.3 ± 16 mW cm^{-2} and a mean ± SD radiant exposure of 3.7 ± 0.1 J cm^{-2}.

Before immersion in water, the mass of each specimen (n = 120) used for sorption and solubility testing (M_1) was obtained, and the thickness and the diameter were measured using a micrometer device to calculate their volume (V = 92.4 ± 3.9 mm^3) and surface area (A = 193.6 ± 1.9 mm^2) (both given as mean ± SD). Each specimen were immersed in a separate dram glass containing 3 ml of water within 5 min of completion of the light-curing procedure and were removed from the water after 24 h, and 7, 30, 90, and 180 d. After removal from the water, the specimens were blotted dry, and weighed again (M_2). The specimens were then transferred to marked dram glass vials (one specimen per vial), and placed in a desiccator at 37°C. The specimens were regularly weighed until a stable mass (no mass change exceeding 0.1 mg recorded within 24 h) was achieved (M_3).

The water sorption (W_{sp}), water solubility (W_{sol}), and mass gain normalized to the initial specimen volume (V) were obtained according to:

$$W_{\mathrm{sp}} = \frac{M_2 - M_3}{V}, \tag{1}$$

$$W_{\mathrm{Sol}} = \frac{M_1 - M_3}{V}, \text{ and} \tag{2}$$

$$\text{Mass increase} = \frac{M_2 - M_1}{V}. \tag{3}$$

The uptake of water and the other parameters are, however, expected to be proportional to the polymer content. The relative polymer matrix volume fraction provided by the manufacturer was used to calculate the estimated matrix-related water sorption ($\mathrm{W_{spMatrix}}$), and the estimated matrix-related water solubility ($\mathrm{W_{solMatrix}}$) with reference to the volume of the polymer phase:

$$W_{\mathrm{spMatrix}} = \frac{M_2 - M_3}{V * (1 - \text{filler particle volume fraction})}, \tag{4}$$

$$W_{\mathrm{SolMatrix}} = \frac{M_1 - M_3}{V * (1 - \text{filler particle volume fraction})}, \text{ and} \tag{5}$$

$$\text{Mass increase(matrix)} = \frac{M_2 - M_1}{V * (1 - \text{filler particle volume fraction})}. \tag{6}$$

Surface hardness assessments

Three specimens with the optimal surface (i.e. smooth surface without microscopic crack formations, air bubbles or irregularities) were chosen to test for Knoop surface hardness, as this setup provided sufficient statistical power. Ten indents were made randomly on each specimen, providing a total of 30 indents for each group. A 15 s dwell-time and 100 g load were chosen, based on the results of a pilot study. The Knoop hardness number (KNH) was calculated according to:

$$\mathrm{KHN} = \frac{\text{load (kgF)}}{\text{Impression area (mm}^2\text{)}} = \frac{P}{C_{\mathrm{p}} L^2}, \tag{7}$$

where L is the length of indentation along the long axis, C_{p} is a correction factor determined by the indenter shape (in this case: 0.43997), and P is the load in kgF.

Degree of conversion assessed by Raman spectroscopy

Specimens for degree of conversion estimation were made using the setup described for the sorption and solubility tests, except that the specimen size was changed to 5 mm in diameter, and the Raman spectroscopy was performed on the underside of the specimens to avoid oxygen-inhibition layer effects. Each composite was divided into low cure (5 s) and high cure (20 s) light curing groups, and each test condition was run in triplicate (three specimens, each tested three times). After the initial degree of conversion analysis, made within 5 min after completion of the irradiation, the specimens were stored individually in marked dram glasses, either dry or immersed in 3 ml of water. The dram glasses containing water included nine glass beads, each with a diameter of 5 mm, to prevent the specimen from lying flat, securing maximal water–specimen surface interaction. The storage temperature was 37°C. Degree of conversion analysis was performed on all specimens 3 and 24 h after the irradiation.

The degree of conversion was determined in a Fourier transform (FT) Raman spectroscope (Spectrum 2000R NIR-Raman; Perkin-Elmer, Waltham, MA, USA, https://www.perkinelmer.com/no/product/sp10-quant-algorithms-pk-1-user-license-l1101024) using the reflection mode to calculate the area ratio of the peaks representing the aliphatic (1,639 cm^{-1}) and aromatic (1,608 cm^{-1}) double bonds. The determination was performed with 60 scans at a resolution of 4 cm^{-1} in the spectral region 1,560–1,675 cm^{-1}, using a laser power of 1.2 W.

The calculations were performed using Perkin-Elmer SPECTRUM 10 software. The spectra were first modulated with the 'smooth' function, and the start and end points of each peak were visually determined. The area ratio was calculated on uncured specimens (A_{Uncured}), and on each of the cured specimens (A_{cured}) at each time interval (both for 5 s and 20 s light curing setups).

The degree of conversion (DC) was calculated according to:

$$\text{DC} = \left(1 - \left(\frac{A_{\text{Cured}}}{A_{\text{Uncured}}}\right)\right) * 100, \qquad (8)$$

where A_{cured} is the ratio of aliphatic to aromatic double-bond peak areas of the cured specimens, and A_{uncured} is the equivalent ratio for the material before polymerization.

Statistics

The following null hypotheses were formulated: (i) there is no statistically significant difference in sorption or solubility between the specimens subjected to suboptimal light curing and those light cured for 20 s; and (ii) there is no statistically significant difference in degree of conversion between the specimens immersed in water directly after irradiation and those stored in dry conditions. Based on the assumption that all specimens of each material originated from a homogeneous population, a general linear model (GLM) for repeated measures was used to evaluate the sorption and solubility data, and to test for differences between groups for the outcome measures. The model assumptions were analysed for equality of covariances and error variances using the Box and Levene's tests, respectively. The Pillai and Tamhane T2 (not assuming equal variances) test statistics were used to test for statistically significant differences within and between groups, respectively. The Box tests showed adequate results, but Levene's test indicated a slight violation in several models, particularly for the 24 h data. However, the models are robust considering the measures over time. A value of $P < 0.05$ was used in all tests. The statistical program IBM SPSS Statistics for Windows (Version 23.0, released 2015; IBM, Armonk, NY, USA) was used for the statistical analyses.

Results

Statistically significant differences were found in solubility and mass gain between the light-curing groups for both materials (Figs. 2A–C and 4A–C). However, no statistically significant difference in sorption was found between the low-cure and high-cure groups (Fig. 3A–C).

Mass gain

The results for the GLM analyses of mass increase are shown in Fig. 2. All groups showed a significant increase in mass after exposure to water, and the greatest increase in mass occurred within the first 7 d. The GLM analysis indicated significant differences between the high- and low-cure groups for material T1, with the increase in mass being greater in the high-cure group after water exposure than in the low-cure group. This was true for both the composite and the matrix-specific estimations. There was no significant difference in mass gain between low- and high-cure groups

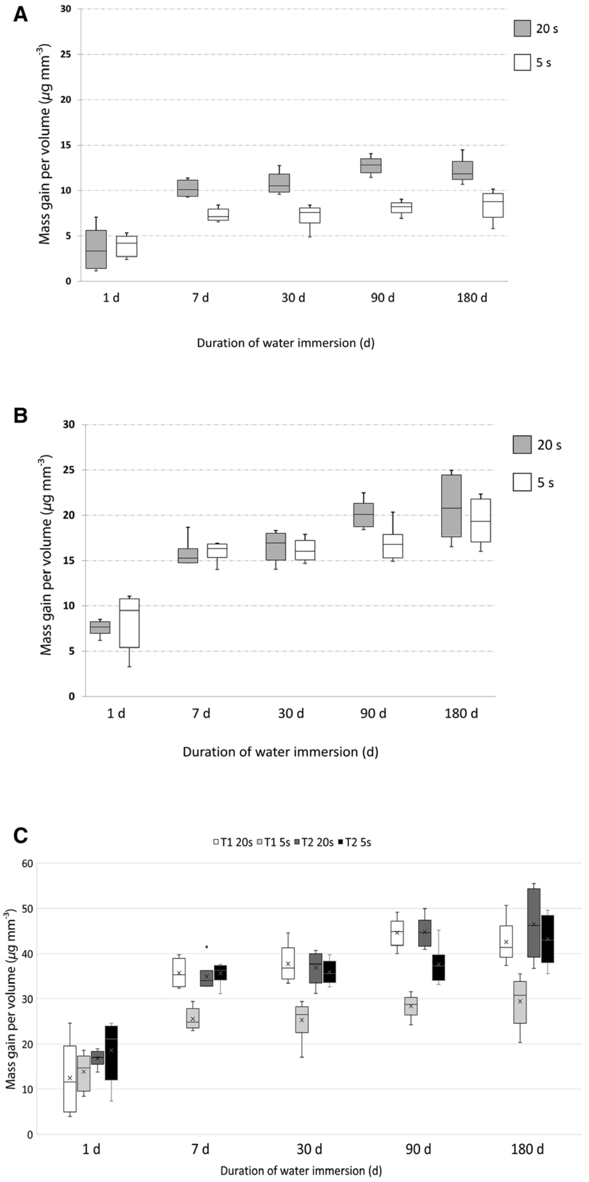

Fig. 2. Mass gain per days of water immersion. (A) Mass gain of Grandio (material T1). (B) Mass gain of Tetric Evo-Ceram (material T2). (C) Calculated matrix-related mass gain for all four groups. Boxes represent the first and third quartiles, and the horizontal line inside each box represents the median. Whiskers illustrate the maximum and minimum values, and outliers are represented as dots.

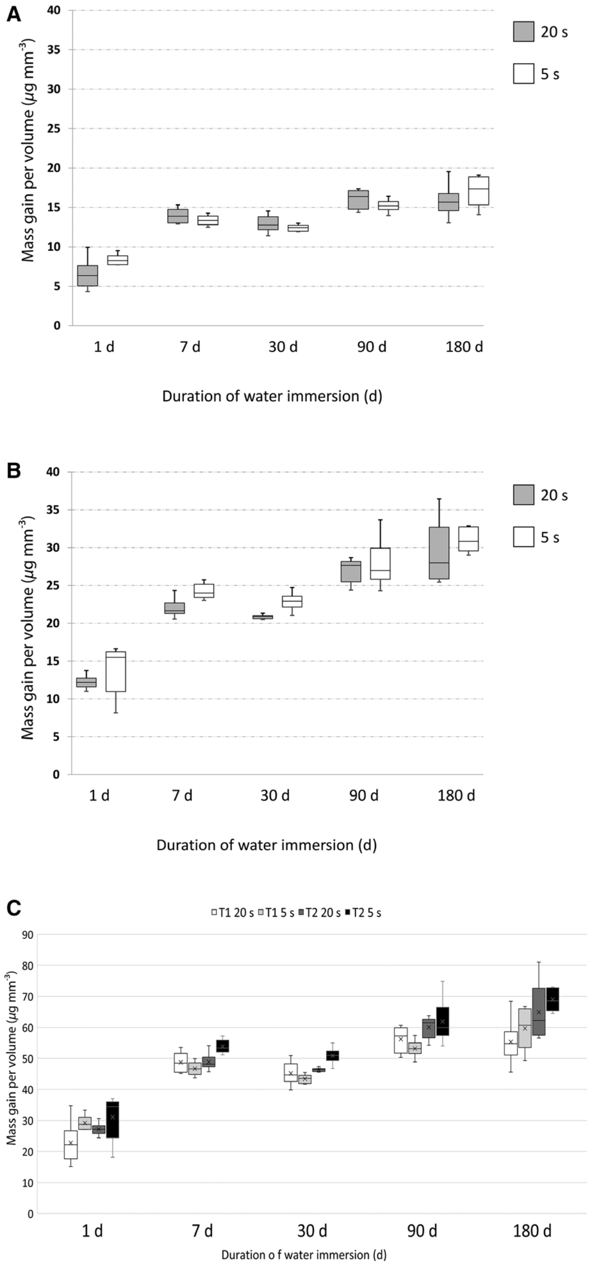

Fig. 3. Water sorption after different time periods (5 s or 20 s) of exposure to radiation. Data represent mass gain per days of water immersion. (A) Sorption of Grandio (material T1). (B) Sorption of Tetric EvoCeram (material T2). (C) Calculated matrix-related sorption for all four groups. Boxes represent the first and third quartiles, and the horizontal line inside each box represents the median. Whiskers illustrate the maximum and minimum values.

for material T2. In the matrix-specific volume estimations, the T1 low-cure group showed lower values than the other three groups, defined according to material and light curing setup over the water-exposure durations tested (Fig. 2A).

Water sorption

The GLM statistical analysis revealed a significant increase in water sorption with increasing exposure duration for all the materials, regardless of the curing setup. Most of the increase in water sorption values occurred during the first 7 d. Between 7 and 100 d, the water sorption values increased further, by approximately 10 μg mm^{-3}, which represents 20% of the average water sorption increase during the first 7 d. The uptake between 90 and 180 d was small, largely within statistical scatter. A significant difference was observed in the water sorption pattern between the two materials tested over the total duration of the water-exposure period; the water sorption of material T2 was almost twice that of material T1 (Fig. 3A,B).

Water solubility

The high-cure group of each material had a statistically significantly lower solubility than its low-cure counterpart (Fig. 4A,B). The GLM analyses revealed a significant increase in solubility over time, for both the composite materials and the matrix estimations (Fig. 4A–C). However, according to the GLM analysis, all four groups showed a distinct increase in solubility when compared in the matrix estimation (Fig. 4C).

Knoop hardness of the surface

For both materials, the low-cure group had a lower hardness than the high-cure group after exposure to water within the first 30 d. No change in surface hardness over time was observed for the high-cure groups (i.e., from 24 h to 180 d), but a significant decrease in surface hardness was observed in the low-cure group of material T1 among specimens exposed to water for longer than 24 h, which reached a constant level after 7 d. For material T2, the low-cure group showed a significant increase in surface hardness after 180 d compared with the value after 24 h, approaching the values for the high-cure group at 180 d (Fig. 5B).

Degree of conversion

Initial degree of conversion tests (before water immersion) showed higher values for the high-cure groups than for the low-cure groups. Regardless of duration of storage, the differences after 3 h in the degree of conversion between the groups were essentially erased (Fig. 6A,B), the only exception being the T2 low-cure water storage group for which a lower degree of conversion was found compared with the other T2 storage groups. The high-cure air storage group of T2 showed no further change in degree of conversion after 3 h, whereas the other groups of T2 showed a change in degree of conversion over a longer period (Fig. 6B). After 24 h of storage, the degree of conversion of the T2 groups was at the same level, despite differences in both curing method and storage medium. For T1 groups, the scatter in results within each group was larger, and there was an overlapping of the peaks. However, both the group mean and group median of the low-cure groups were lower than those of their high-cure counterparts.

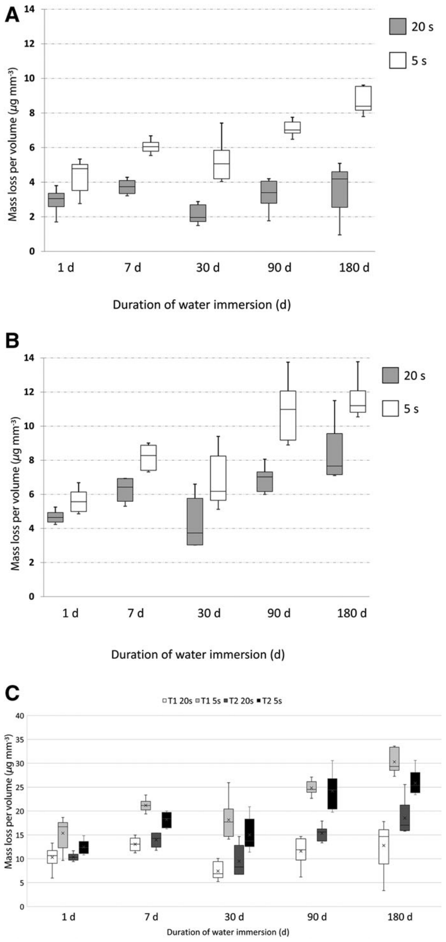

Fig. 4. Water solubility after different time periods (5 s or 20 s) of light curing. Data represent mass loss per unit of volume over days of water immersion. (A) Solubility of Grandio (material T1). (B) Solubility of Tetric EvoCeram (material T2). (C) Calculated matrix-related solubility for all four groups. Boxes represent the first and third quartiles, and the horizontal line inside each box represents the median. Whiskers illustrate the maximum and minimum values.

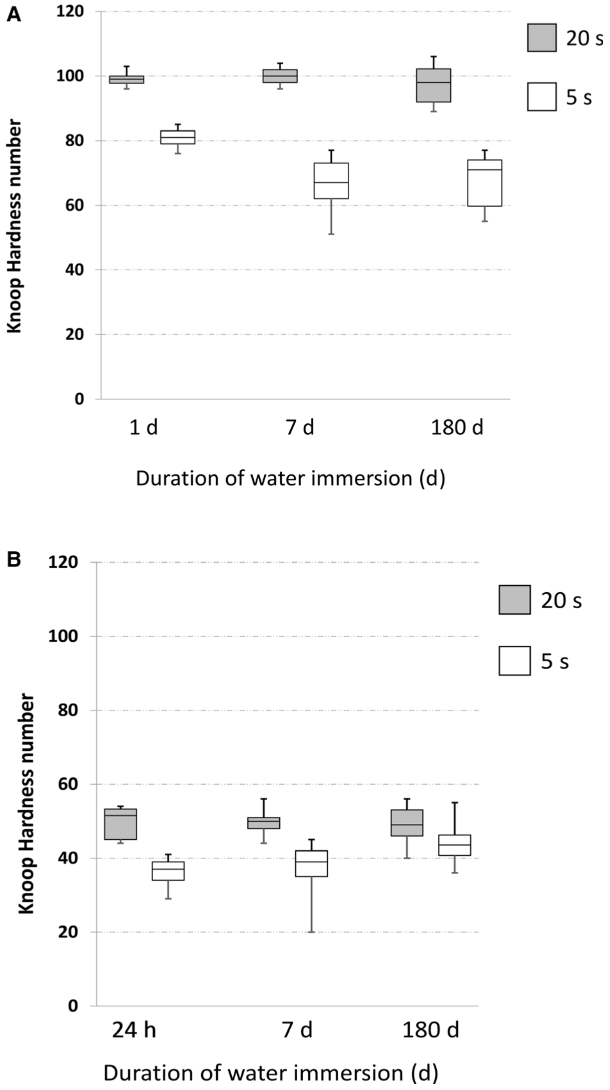

Fig. 5. Effect of 'low-cure' (5 s) and 'high-cure' (20 s) light curing, and duration of immersion in water, on Knoop surface hardness of Grandio (material T1) (A) and Tetric EvoCeram (material T2) (B). Boxes represent the first and third quartiles, and the horizontal line inside each box represents the median. Whiskers illustrate the maximum and minimum values.

Discussion

This study is based on experimental methods that deviate from the standard methods used to assess sorption and solubility. The clinical use of dental restorative materials involves immediate introduction of such materials into a moist environment, which lasts throughout the service life of the material, and the method used here therefore included exposure to water within 5 min after completion of irradiation. In order to allow for comparison of materials as well as to simulate a 'worst-case scenario', a group of specimens exposed to suboptimal light curing was included. To secure reproducibility and minimize the risk of human error, the lowest automatically controlled radiant exposure settings available on the light curing unit were used. It can be argued that the current low-cure settings are still too high to be referred to as a 'worst-case scenario', as even lower radiant exposures will lead to a 1-mm-thick material that will appear solid. The findings nevertheless suggest that the observed differences in the performance of the material appeared measurable and consistent, even with the current settings. The diameter of the specimens used for the sorption and solubility tests was reduced to avoid the need to light cure the specimens in overlapping sections. The Bluephase G2 curing unit was chosen because of its homogeneously distributed light and the inherent possibility to adjust both duration and energy output to relatively low values (11, 25, 26).

The radiant exposure (i.e., irradiance × time) affected both the solubility in water and the surface hardness of the materials tested, in disagreement with the first null hypothesis. Most of the water sorption and solubility changes occurred within the first 7 d after light curing, which is in accordance with the

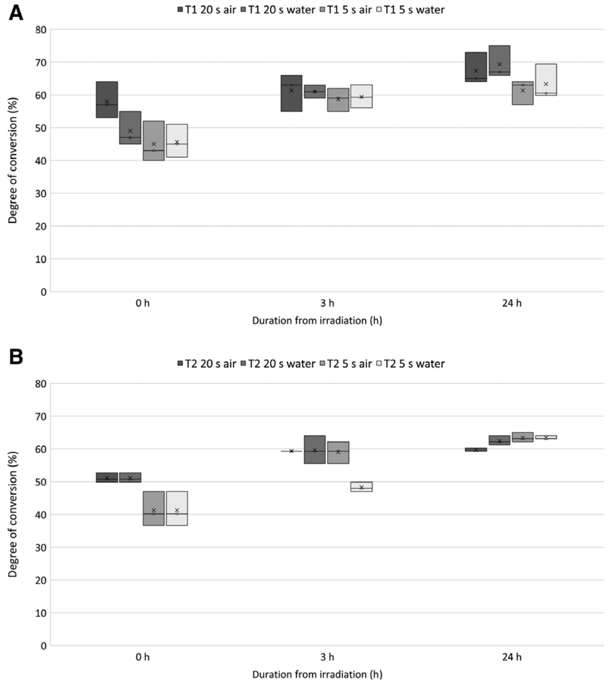

Fig. 6. Degree of conversion over time for storage both in water and in air, as well as for 'low-cure' (5 s) and 'high-cure' (20 s) groups. (A) Grandio (material T1). (B) Tetric Evo-Ceram (material T2). The horizontal line inside each box represents the median, and the mean is illustrated with a cross. The boxes illustrate maximum and minimum group values. Each test was performed in triplicate, and each test run contained the mean values of 60 consecutive Fourier transform (FT)-Raman scans.

results reported by others using setups with dry post-irradiation storage before exposure to water (3, 21, 27). According to the statistical model used, there was a significant difference in the water sorption pattern between the two materials. The water sorption of T2 was almost twice that of T1 (Fig. 3A,B). Most of this difference can be attributed to the higher filler content in T1; the final water sorption levels in the polymer matrix differed by only 20% between the two materials. The solubility in water decreased with increasing radiant exposure, which is in accordance with expectation: the amount of soluble fraction is higher in materials exposed to a low radiant exposure.

Under dry storage conditions, the increase in degree of conversion during the first 24 h post-irradiation has been assessed to represent 19%–26% of the final degree of conversion value after 24 h (16, 28). The current findings suggest that this process was unaffected by the exposure to water. The degree of conversion was constant by 24 h post-irradiation and was independent of the radiant exposure, which confirmed the second null hypothesis. The finding that the degree of conversion was essentially the same for the low-cure and high-cure groups of both materials at 24 h post-irradiation is at first sight confusing. It is believed, however, that the more significant leakage of low-molar-mass species (TEGDMA and UDMA, which lack aromatic double bonds) from the materials cured by the low radiant exposure increases the initially lower degree of conversion of these materials, so that after 24 h of water exposure this reached levels comparable with those of the materials exposed to the high radiant exposure. The monomers TEGDMA and UDMA have been found to elute within hours, and the degree of conversion assessed by Raman spectroscopy is thus expected to increase as a result of the migration of these monomers (5, 29–32). According to leakage studies, TEGDMA and UDMA have a tendency to migrate faster than Bis-GMA and Bis-EMA (32). For each material, the difference in solubility between the high-cure group and the low-cure group indicates the characteristic sensitivity to suboptimal light curing. Such differences may be caused by several factors, such as monomers used, filler content, or initiator systems. However, it seems impossible to determine the sensitivity to water solubility from the surface hardness based on the results of this study.

A low radiant exposure causes more limited structural changes of a polymer (i.e., a lower crosslink density and only a few trapped chain entanglements) than seen in a polymer subjected to a higher radiation dose. A polymer with a low crosslink density shows, according to the Flory–Rehner equation, a lower equilibrium water uptake and a more extensive migration of low-molar-mass species than a polymer with a higher crosslink density (33).

As the gravimetric test-setup used for sorption and solubility testing detects only changes in mass, the nature of the elutes cannot be identified, but some deduction may shed light on the nature of the migrating compounds. The highest total mass loss from any of the materials used in this study was 5.6 mg per gram of composite material, or 3.3 wt.% of the polymer matrix mass; this was found in the samples exposed to water for 180 d. These results are in accordance with data presented by Ferracane *et al.* (32) on the migration from filler-free homopolymers of the monomers listed in the safety data sheets of the two materials used (32). The same study concluded that the rate of elution was higher for TEGDMA and UDMA than for Bis-EMA and Bis-GMA (32).

Even though this was not evaluated in the present work, it is plausible that the inorganic filler particles contribute, to some extent, to the overall mass loss. Some types of inorganic filler particles undergo surface corrosion when exposed to water (34,35). If the surface of the filler particles is deteriorating, any covalent filler–matrix integration also weakens, ions diffuse out from the bulk material, and space may be created along the filler particles. The onset and extent of such corrosion and particle elution depend on the type of filler particles used, but this is not stated in the safety data sheet or in any of the information provided by the manufacturers of the current materials.

For both materials, the low-cure group had a lower hardness than the high-cure group after exposure to water within the first 30 d. No change in surface hardness over time (i.e., 24 h to 180 d) was observed for the high-cure groups, but a significant decrease in surface hardness was observed in the low-cure group of material T1 in specimens exposed to water for longer than 24 h, which reached a constant level after 7 d. For material T2, the low-cure group showed a significant increase in surface hardness after 180 d compared with the surface hardness after 24 h, approaching the values of the 180 d high-cure group (Fig. 5B).

A relationship between surface hardness and degree of conversion within the same material has been observed (36, 37), and the Knoop hardness was therefore determined on the top surface of three specimens of each group after the final drying stage for specimens exposed to water for 24 h, and 7 and 180 d. The Knoop hardness tests revealed permanent changes in surface hardness in the groups exposed to suboptimal light curing. Surface erosion of inorganic filler particles leads to degradation of the filler–matrix interaction and an increase in free volume (38). Changes in hydrogen bonds between the polymers also have considerable effects on the mechanical properties (39). Water weakens these interchain forces, reducing the mechanical force needed to cause both transient and permanent rearrangement of non-crosslinked polymer regions. The use of pre-polymerized filler particles (as in material T2) may promote enhanced filler–matrix integration, and such particles do not suffer from erosion in the same manner as inorganic filler particles. This could explain the increase in surface hardness found for material T2 exposed to water for 180 d, as the other filler particles may have been removed from the surface.

The use of pre-polymerized filler particles may explain several of the differences found between the two materials. The organic filler fraction in low-cure T2 has a similar structure to that of the polymer matrix in high-cure T2, thereby reducing the difference between the two light curing setups in this project. The similarities in matrix structure are reflected in the comparable results in mass gain after water exposure, as well as in the small changes in Knoop surface hardness in low-cure T2 (compared with low-cure T1). If the fraction of inorganic filler is reduced, the surface deterioration of these particles will not affect the surface of materials to the same extent.

Water sorption and solubility tests are standardized procedures applied when evaluating dental resin-based composites: they are used to facilitate the choice of materials and to ensure that the materials meet specified minimum requirements (24). In the case of dental resin-based composites, the standard specifies careful drying of the specimen (often for several days) after curing before exposure to water. This allows post-irradiation polymerization to continue under dry conditions. The Nordic Institute of Dental Materials (NIOM) reported a water sorption of material T1 of 10 μg mm^{-3}, and a solubility value of -0.9 μg mm^{-3} after 7 d of exposure to water. For material T2, the water sorption was reported to be 17 μg mm^{-3} and the solubility to be -2.3 μg mm^{-3}. Compared with the results of the present study, it is evident that the increased radiant exposure, in combination with dry post-irradiation storage, reduced the susceptibility of the material to water. Therefore, a standard should be used with caution when evaluating clinical performance, as the purpose of standards is not clinical performance testing.

At present there is no standardized setup (in terms of load and duration) available for the Knoop hardness testing of dental composites. This causes difficulties when comparisons are to be made between different studies. The load and dwell time used in the present study were based on the results of pilot studies.

This study indicates a correlation between suboptimal light curing and the magnitude of the elution of species from the dental composites tested. The surface hardness of dental composites produced by suboptimal light curing showed irreversible changes upon exposure to water. The current findings illustrate the importance of optimal light curing and suggest that best clinical practice involves more extensive light curing than the minimal recommendations presented by the manufacturer.

Acknowledgements – Voco and Silvia Jarchow are acknowledged for supplying the composite material, Grandio. We also thank Ivoclar Vivadent and Robert Forsberg for providing the dental composite Tetric EvoCeram, as well as for the loan of light curing units for pilot projects. Mathieu Mouhat and Dr Payam Pourmand, KTH Royal Institute of Technology are thanked for assisting in the weighing of samples and for providing instructions on the use of relevant laboratory equipment and instruments.

Conflicts of interest – No conflicts of interest.

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