



UiT The Arctic University of Norway

Faculty of Health Sciences

Department of Clinical Dentistry

Dental composites - The effects of matrix composition, suboptimal light curing and water exposure

Aksel Waldemar Wikant

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Abbreviations and explanations

Abbreviation	Explanation
B/T	"Bottom-to-Top", refers to the ratio between measurements performed on both surfaces
Bis-EMA	Ethoxylated bisphenol A dimethacrylate
Bis-GMA	Bisphenol A-glycidyl dimethacrylate
BoPET	Biaxially-oriented polyethylene terephthalate, often referred to as <i>Mylar</i> , a registered trademark product of the of the DuPont - Teijin Corporation.
CQ	Camphorquinone
DC	Degree of conversion, the percentage of carbon-carbon double bonds that has been turned into single covalent bonds to form the polymeric resin.
DSC	Differential scanning calorimetry
EGDMA	Ethylene glycol dimethacrylate
FT-IR	Fourier-Transform Infrared spectroscopy
FT-Raman	Fourier-Transform Raman spectroscopy
GLM	General linear model, statistical test
GR	Grandio®, VOCO
HC	High-Cure, referring to the sample groups exposed to the highest radiant exposure in study II and III
HPMA	2-hydroxypropyl methacrylate
ISO	International Organization for Standardization
ISO/TC	International Organization for Standardization, technical committee
KNH	Knoop hardness number
LC	Low-cure, referring to the light-curing settings used for the sample groups exposed to suboptimal light-curing in study 2 and 3
LCU	Light-curing Unit
LED	Light Emitting Diode
PET	Polyethylene terephthalate
PTFE	Polytetrafluoroethylene
SEM	Scanning electron microscopy
TEC	Tetric EvoCeram®, Ivoclar
TEGDMA	Triethylene glycol dimethacrylate
T_f	Fictive temperature
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TMPTMA	Trimethylolpropane trimethacrylate
UDMA	Urethane dimethacrylate
UV-absorbers	molecules added to dental composites to absorb ultraviolet radiation, increasing the material resistance to degradation.

List of papers

The thesis is based on the following studies, and they are referred to with the corresponding roman numerals:

- I. The influence of bis-EMA vs bis GMA on the degree of conversion and water susceptibility of experimental composite materials**
Cornelio RB, Wikant AW, Mjøsund H, Kopperud HM, Haasum J, Gedde UW, Örtengren UT; *The influence of bis-EMA vs bis GMA on the degree of conversion and water susceptibility of experimental composite materials*, Acta Odontologica Scandinavica, 72:6, 440-447. 2014, DOI: 10.3109/00016357.2013.856467

- II. Suboptimal light curing and direct exposure to water of two contemporary composites: degree of conversion, sorption, solubility, and Knoop hardness**
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.*; European Journal of Oral Science 2020; 128: 345–353. 2020, DOI: 10.1111/eos.12705

- III. Suboptimal light curing and water exposure: an in vitro investigation in mechanical aspects.**
Wikant AW, Nilsson F, Capezza A, Hakeberg M, Gedde UW, Örtengren UT
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1 Abstract

Resin-based composite materials have dominated restorative dentistry in Scandinavian countries for over 20 years. Compared to dental amalgams, methacrylate-based light-curable composites provide superior aesthetics and additional treatment options that reduce the need to remove sound tooth tissue to acquire mechanical retention. However, the methacrylate-based composite materials are affected by water; the presence of water can cause a reduction in mechanical properties, elution of material content and induce degradation processes, decreasing the longevity of the dental restoration. Therefore, over the last decades, more hydrophobic monomers have been introduced in dental composites to counteract the adverse effects of water exposure.

Adequate light-curing is essential to ensure optimal mechanical properties (In this study: Knoop surface hardness, ultimate mechanical properties) of the composite. However, despite the required instructions on proper light-curing provided by the manufacturers, the use of light-curing units (LCU) with insufficient curing properties in dental offices has been documented worldwide. This thesis aimed to study the effects of suboptimal light-curing and monomer content on the water susceptibility of composites.

In Study I, experimental composite blends were used to evaluate the effect on the degree of conversion (DC: degree of carbon-carbon double covalent bonds converted to single covalent bonds, as revealed by Raman spectroscopy), water sorption and solubility when replacing the monomer bisphenol-A glycidyl methacrylate (bis-GMA) with the more hydrophobic analogue, ethoxylated bisphenol-A dimethacrylate (bis-EMA). Water sorption and solubility (the latter is defined as the transfer of constituents from the composite to the liquid phase) were measured gravimetrically at 24 h, 7 d and 30 d after light-curing. The DC was calculated 24 h post-cure. The water sorption and the trapped water content within the material after drying increased (negative solubility results) with increasing content of bis-GMA, indicating that the hydroxyl groups found in bis-GMA increased the water susceptibility within the span tested.

In studies II and III, changes in physical and mechanical properties caused by water exposure in combination with reduced light-curing were investigated. Contemporary dental composites with similarities in monomer content to the experimental materials utilized in Study I were tested. In Study II, water sorption, solubility and surface hardness were compared in samples exposed to either sub-optimal light-curing or a “high-cure” where the light curing parameters

were at or above the limits recommended by the manufacturers. The DC was determined through Raman spectroscopy 5 min, 3 h and 24 h after light-curing. The samples were stored in water for up to 180 d. The results showed that the samples exposed to suboptimal light-curing had increased water solubility and reduced surface hardness after 7 d of water immersion compared to the “high-cure” sample groups. Despite the differences in solubility, the DC differed insignificantly between the curing groups at 24 h post-cure, and water did not appear to affect the result.

In Study III, the mechanical effects of water exposure and suboptimal light-curing were investigated. Here, identical materials and curing parameters to those used in Study II were employed, with samples exposed to suboptimal light-curing compared to the high-curing sample group. In addition to sample groups stored in water, groups of samples in dry storage were added as controls. A bi-axial flexural test was performed on the samples 30 and 90 d after light-curing. The top surface and fracture surfaces created in the bi-axial flexure test were studied using scanning electron microscopy. Furthermore, differential scanning calorimetry and thermogravimetry were performed to determine the glass transition temperature and the water content within the samples after water storage respectively.

The results showed that suboptimal light-curing and water exposure decreased the physical and mechanical properties of the dental composite and increased the rate of degradation within the experiments' duration. The DC, as a measure of curing, may not provide sufficient information on the state of material curing, as differences in solubility and mechanical properties were observed despite similar values in the DC.

In conclusion, the current thesis adds knowledge, novel perspectives and strengthen the current understanding of the effects of light-curing as well as the importance of proper handling of dental resin-based composite materials.

2 Introduction

Despite significant improvements in oral health during the last decades, dental restorative treatment is still an essential procedure in dental health care. For example, in 2019, 3/4 of the 18-year-olds in Norway had received restorative dental treatment at least once in their life. Since the use of amalgam has decreased in the Scandinavian countries due to environmental legislation, the primary option for permanent direct restorations is dental resin-based composite materials. Today's resin-based composite materials (hereafter referred to as dental composites) are the first choice for dental restorative treatment, due to the adhesive retention of the filling, reducing the need for removal of sound tooth tissue to create mechanical retention. Also, the convenience of rapid curing by curing units emitting visible, blue light provides an effective one-setting treatment procedure. Combined with the tooth-mimicking aesthetics of dental composites, further indications of non-invasive additive treatments have also come about in the recent years. These materials are indicated for dental restorative and additive treatment in anterior and posterior teeth in patients of all ages.

But the use of light-cured dental composites is not the “quick and easy fix” as it might be presented. According to research on the clinical use, maintenance and control of light-curing units, there are several potential challenges for reaching sufficient light curing; the irradiance (i.e. radiant energy influx) provided by the curing units in the dental clinics is more than often insufficient, and the maintenance of such units is often neglected (1–6). Suboptimal light-curing has been shown to have adverse effects on the physical properties of dental composites in-vitro. Reduced surface hardness, increased potential for elution of material constituents, and reduced fracture resistance have been documented (7–11).

The oral environment represents several challenges to any dental restorative material and one of the most apparent is the constant exposure to moisture. Water diffuse into the bulk of dental composites and can cause deteriorating effects on the mechanical properties of the dental restoration (11–15). Exposure to water is known to facilitate elution and erosion, as well as chemical softening and degradation of dental composites (16–21). Beyond the aspects of reduced mechanical properties of the fillings, the elution of composite constituents may cause other effects such as increased biofilm growth, and changes in the protein expression of human cells (22,23).

Despite the well documented deteriorating effects of water on adequate cured dental composites from in-vitro studies, and the compelling evidence of insufficient light-curing happening in the dental clinics, the performance of such materials in-vivo seems to be high. Reports have claimed a 10- year survival rate of dental composites higher than 80 % (24,25), and the last decades of research suggests very few harmful effects for the patients related to the use of these materials (26). However, proper handling of these materials have been shown to be essential to produce a long-lasting dental restoration (27–29).

During the last decades, new constituents have been introduced to improve the performance of composites. Addition of new monomers, showing a more hydrophobic nature have been reported to reduce the degradative effects of water on the composites in vitro, which have been implicated to improve the performance in vivo.

The current legislation for market approval of medical devices states that “..*They* (i.e., medical devices, or in this case, dental composites) *shall be safe and effective and shall not compromise the clinical condition or the safety of patients, or the safety and health of users or, where applicable, other persons, provided that any risks which may be associated with their use constitute acceptable risks when weighed against the benefits to the patient and are compatible with a high level of protection of health and safety, taking into account the generally acknowledged state of the art.*” (30). However, this statement is only applicable when the device has been handled in accordance with the instructions provided by the manufacturer. To the author, the extensive use of dental composites worldwide and the reported occurrence of inadequate of maintenance and control of light-curing units in dental clinics seemed worthy of concern.

As mentioned, the effects of water exposure are well documented *in-vitro*, as are the detrimental effects of insufficient curing. However, the knowledge on the combinational physical effects of suboptimal light curing and prolonged exposure to water appears limited, despite the clear indications of its relevance in the available scientific literature.

2.1 Composition of dental composites

Composites are made of a polymer reinforced with covalently bonded filler particles. The matrix is formed by the polymerization of monomers, forming an amorphous, atactic and highly cross-linked network (31). For dental composites the monomers are commonly methacrylates, more specifically, dimethacrylates are the major type but mono-methacrylates and trimethacrylates are also used (Table 1). Other types of monomers are also available, but they are not further discussed in this thesis.

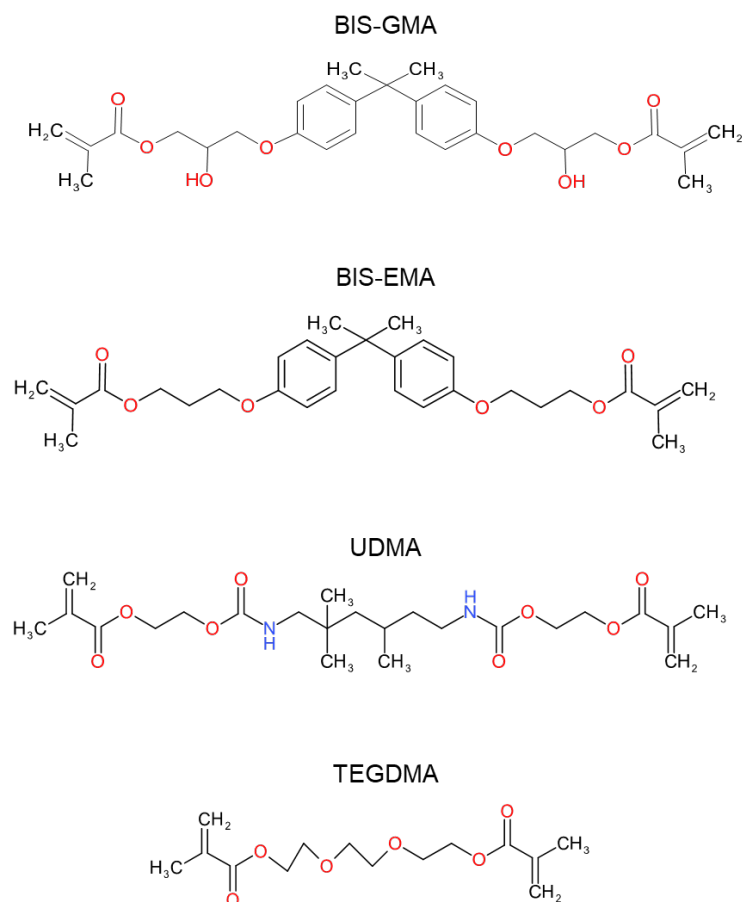


Figure 1: Commonly used monomers in dental composites

The dimethacrylate monomer has two reactive sites at the molecular ends, each being a carbon-carbon double bond ($C=C$) allowing polymerization via a free radical mechanism (32–34). The obtained crosslinked polymers of the different dental composites are copolymers, they are made up of two or more types of repeating units. Traditionally, the most commonly used monomers are the highly viscous di-methacrylates (e.g. bis-GMA) diluted with a less viscous monomer such as TEGDMA (13,35). In the further development of composites, other monomers (e.g. bis-EMA, TMPTMA and HPMA, etc.) have been included to make materials with higher DC, workable consistency and tailored mechanical and hydrophobic properties (11,35,36).

Abbreviation	Name	CAS number
Bis-EMA	Ethoxylated bis-phenol A di-methacrylate	41637-38-1
Bis-GMA	Bisphenol A-glycidyl methacrylate	1565-94-2
EGDMA	Ethylene glycol di-methacrylate	97-90-5
HPMA	2-Hydroxypropyl methacrylate	25703-79-1
TEGDMA	Tri-ethylene glycol di-methacrylate	109-16-0
TMPTMA	Trimethylolpropane tri-methacrylate	15625-89-5
UDMA	Urethane di-methacrylate	72869-86-4

Table 1: Examples of monomers used in dental composites

As dental composites are copolymers made of several methacrylate-based monomers, the polymerization process form near-statistical copolymers; the sequence distribution show some deviation from that obtained by statistical laws. The disordered chain structure prohibits crystallization and thus solid material structure is glassy. The type and fraction size of the monomers used in the composite impacts the structure of the forming polymer matrix, and its mechanical properties.

The type and concentration of intermolecular forces affects both the polymerization process and the formed polymer matrix (37,38). Polar intermolecular forces have been reported to affect physical properties such as impact strength, modulus of elasticity and flexural strength of the polymerized material (39–41).

Today, filler particles make up to approximately 30 – 70 % of the volume (50 – 85 % by mass) of dental composites depending on the desired viscosity, mechanical and physical properties of the material (42). The filler particles reduce the volumetric effects of the polymer matrix on the composite (42,43). The relatively high content of filler particles reduces the polymerization shrinkage and thermal expansion, and increase the tensile and compressive strength of the composite (42,43). The filler particles are also used to deliberately adjust the radiodensity of dental composites, making such materials readily detectable by X-ray, in order to allow detection of proximal secondary caries.

The filler particles used in dental composites vary in size and shape, from the irregular shaped particles with a size span from 1 – 50 μm to the equiaxed nano-fillers sized smaller than 100 nm (42,43), to filler particles with a high ratio of length to its cross-section (such as fibre or filament particles) are all available in dental composites with various indications of use. By

adjusting the type, load (and orientation) of filler particles, clinical properties such as surface smoothness, hardness and workability (viscosity) of the material can be adjusted (42,43).

The coupling between the polymer matrix and the filler particles is of utmost importance to the mechanical and physical properties of the composite (44,45). The coupling agent forms a covalent link between the surface of the inorganic filler particle and the polymer matrix and facilitates the transfer of mechanical stress between the phases (46,47). This integration of the filler particles anchors them to the polymer matrix, which counteract possible cavitation along the filler particle surfaces due to polymerization shrinkage. (46).

The most used coupling agents in dental composites are different organosilanes, such as γ -methacryloxypropyl trimethoxysilane. The silane coupling agents usually contain methacrylate group(s) on the end facing away from the filler particle that, through radical copolymerization, is covalently integrated into the polymer chain (48).

A final group of components in dental composites are additives (42). By adding initiator systems sensitive to visible light, the dental practitioner can start the polymerization process by using a curing light. The inhibitors prevent the initiation of polymerization during storage and application of the material, whereas other constituents such as pigments and UV-absorbers enhance the aesthetics and increase the durability of the finished dental restoration. The addition of pigments and “opaquer” substances optimize the level of translucency and the colour of the finished restoration (42).

2.2 Light curing

The curing of dental composites using electromagnetic radiation was introduced in the 1970s, and the technology has been incrementally refined over the last 50 years (49). Today, these curing units use visible light between 380 – 500 nm in wavelength (i.e., violet, blue and cyan). The currently most common curing device is based on the LED (light-emitting diode) technique. These units having a radiant exitance (i.e. power intensity) greater than $1000 \text{ mW}/(\text{cm})^2$ that, according to the manufacturers, can provide an optimal curing of a 2 mm material layer within seconds (50).

Still, from a clinical perspective, the light curing of composite materials is a highly sensitive procedure that require adequate amounts of energy to be delivered to the material (34,50). In

addition to the radiant exitance, the duration of the light-curing affects the degree of polymerization (51–53). The product of the incident radiant power received by the sample surface (i.e. irradiance) and the duration is often characterised as the *radiant exposure* (or *energy density*) and is given in $\text{mJ}/(\text{cm})^2$ (54). Dental composite materials need a sufficient amount of radiant exposure in order to achieve an optimum level of curing (42,51,55). Light curing of a 2 mm layer of dental composite has been estimated to require a radiant exposure of 12 000 to 16 000 $\text{mJ}/(\text{cm})^2$ depending on the mechanical properties used to define the state of cure (51,55). However, as there are several definitions used to describe adequate light-curing in in-vitro studies, no consensus is achieved yet (to the knowledge of the author). Therefore, physical properties of cured dental composites, such as surface hardness, resistance to mechanical stress and strain, and water sorption and solubility, have been used to describe the effects of light curing through in vitro studies.

Low radiant exitance (light intensity emitted from the curing unit light tip) is often caused by degradation of the curing unit, lack of maintenance of the curing unit, or erroneous placement or angulation of the light curing unit (4,56,57). With low influx of photons into the dental composite, the photons are not able to penetrate as far down into the material. This reduces the “depth of cure”, leaving a high degree of curing on the surface while deeper segments of the material are left with a lower degree of curing (22,58).

Short (less than 5 s) duration (and high intensity) of the light-curing have been shown to cause more heterogenic polymer matrix structures, as a high initial radical formation takes place, forming dense clusters of polymerized matrixes surrounded by uncured monomers. As the clusters grow in size, the concentration of radicals decreases due to radical-radical termination (two radicals form a covalent bond), giving rise to a less dense matrix structure (59).

The documentation needed in the approval process for sale of contemporary dental composites on the EU market is based on composite material samples that are cured to or beyond the recommendations of the manufacturer (60). However, optimal dental restorative treatment on living, breathing patients can be considerably more difficult to accomplish in a clinical setting, compared to the controlled settings in a laboratory environment, and light curing is one of several procedural steps (61,62). Low radiant emittance (i.e., light intensity) from light-curing units due to lack of adequate maintenance, or LCU tip damage/contamination has been documented in dental clinics world-wide, further increasing the probability for the occurrence of suboptimal curing of composite-based dental restorations (1,4,6,56,57,63).

2.2.1 Assessing the state of curing of dental composites

One commonly used method is to evaluate the “completeness” of curing through the ratio of the surface hardness at the top and bottom of a 2 mm sample. Surface hardness is the ability of the surface of the material to withstand wear or indentations, and there are several variants of tests, however the principle is the same; By subjecting the material surface to a predetermined force normal to the surface plane for a predetermined duration through an indenter, the plastic deformation can be evaluated and quantified (64–66).

The degree of carbon-carbon double bond converted to covalent single bonds (DC) during polymerization is commonly used to evaluate the “completeness” of the polymerization process (35,67,68). By comparing the amount of methacrylate carbon-carbon double bonds (C=C) in an unpolymerized material sample to the amount in a cured sample, it is possible to estimate the percentage of these double bonds converted to single carbon-carbon bonds during polymerization (69–72). Therefore, a DC of 50 % of the dimethacrylate-based polymers commonly used in dental composites does not imply that half of the monomers are unbound monomers, as each monomer have 2 such methacrylate groups. The DC values found in methacrylate-based dental composites are estimated to be between 50 and 70 % (32,35,42). For monomer mixtures, the type of monomers used has an impact on the DC-value (32,38,39,73).

Spectroscopic analysis is often used to assess the DC of dimethacrylate polymers. Raman spectroscopy utilizes the inelastic scattering of light; only a few photons (10^{-8}) undergo an energy transfer to normal mode vibration; the exact change in frequency is sensitively recorded by the spectrometer. Raman spectroscopy is used for the determination of the content of carbon-carbon double bonds and phenyl double bonds in a sample (70,71,74,75). By detection of the weak, inelastic scattering of electromagnetic radiation (e.g., Raman scattering) from the sample surface when lit with a monochromatic laser, the Stokes/anti-Stokes shift in photon energy can be mapped as a function of wavelength. The vibrational frequency of a molecule is specific to the type of chemical bonds within it and the specific configuration of the molecule (75). By mapping of Raman scattering from bonds in different molecular configurations on known samples, a library of such shifts has been produced. This allows for the identification of specific shifts in wavelengths related to the carbon-carbon double bonds in methacrylate groups as well as the double bonds in the phenyl ring structures (70,71). By comparing the change in ratio in the Raman scattering related to the carbon-carbon double bonds in the methacrylic group to that of the stable, unreactive phenyl double bonds, the change in available carbon-carbon double

bonds between an uncured sample and a cured sample can be determined. The converted fraction (to the total amount in the uncured sample) is described as the degree of converted carbon-carbon double bonds, or the DC-value (70,76).

2.3 Water susceptibility of dental composites

In this thesis, water susceptibility is used as a term for the effects caused by water exposure (i.e., reduction of mechanical properties, water uptake, elution of constituents, and degradative processes). Water is adsorbed and absorbed by the dental composite and promotes degradation and elution of material constituents. The negative effects of water exposure on the physical properties of composites have been documented (11,77–80). The dissolution of water molecules between the polymer molecules within the densely packed matrix can cause plasticization, as the water molecules occupy inter-polymer space and interrupt secondary forces between the polymers (81). Several changes to the material, such as volumetric changes (swelling), elution of unbound constituents, and alteration of mechanical properties has been described as effects caused by plasticization (36,59,82–85). The extent of these plasticizing effects has been shown to depend on the monomer used in the matrix, as the monomer structures determine the occurrence of secondary forces (i.e., hydrogen bonds and transient intermittent secondary forces) (36,59,82–85).

Degradation (breakage of covalent bonds and secondary forces) of dental composite materials have been reported (11,86–88). Many of the findings have been linked to erosion on the surface inorganic filler particles or degradation of the coupling agents between the polymer matrix and the filler particles (16,43,78,86). Degradation of the polymer matrix due to hydrolysis, oxidation of functional molecular groups and even chain scission have been described (11,89–91). These theories have often been derived through the detection of the molecular products of the aforementioned degradation mechanisms, such as formaldehyde, methacrylic acid and 3,3-[propane-2,2-diylbis(4,1-phenyleneoxy)]di(propane-1,2-diol) (11,90).

According to the literature, the reduction of intermolecular forces and influx of water facilitates elution of unbound species. Degradation products such as oligomers, monomers, and ions from filler particles from the surface and the bulk of the material have been detected (9,19,92–95). Despite the well documented potential shortcomings of the light-curing of dental composites in dental offices world-wide and the water susceptibility of these materials documented *in-vitro*, the effects of the two factors combined appears, to the author, to be less documented.

2.3.1 Assessment of the water susceptibility

The diffusion-driven incorporation of water in dental composites is usually categorized into two modes. Firstly, diffusion of water molecules between the polymer molecules within the densely packed matrix according to Henry's law (96). Secondly, micro voids in the polymer matrix are filled with water through diffusion (96,97). The first mechanism can cause changes in volume, alter mechanical properties, and facilitate elution of unbound constituents (11). The other provide an increased surface for water-composite interaction, thereby increasing the potential elution of material constituents.

2.3.1.1 Gravimetric water sorption and solubility testing

The term "water sorption" is used to describe the integration of water through both adsorption (water adhered on the surface of a material sample) and absorption (water incorporated into the bulk of the material). For dental composites, the water sorption is time and temperature dependent as the influx of water is diffusion-controlled (81,98,99). Gravimetric water solubility testing is the quantification of mass loss caused by elution from the material tested, in a given amount of water, at a specified temperature.

Gravimetric water sorption testing is done by exposing the material sample to water or humid conditions for a predetermined duration, after an initial determination of its mass (M_1). The increase in sample mass after ended water exposure is described as water sorption. To determine and quantify the solubility of the same sample, it is dried until stable mass is achieved ($M_2 - M_1$). The solubility of the sample is determined by subtracting the mass of the dried sample from the initial sample mass before water exposure ($M_1 - M_3$).

Water sorption and solubility are usually expressed as mass per unit surface area or volume. This allows for the comparison of results from tests performed on samples of different size. For quality control for market approval, gravimetric water sorption and solubility testing is performed in accordance with the ISO 4049 standard.

2.3.1.2 Biaxial flexure test

Water and light curing affect the mechanical properties of composites (10,11,29,51,78,100). Therefore, mechanical testing can be used to determine the changes caused by water, both quantitatively and as changes in quality. Flexure tests can be used to determine the maximal flexural stress and strain and thus fracture energy (a quantity closely related to fracture toughness) (42,101). The microstructure of the dental composites (e.g., the type and fraction of monomers, the size, morphology and volumetric fraction of filler particles, cracks/deformations

within the material) affects the mechanical properties of the material (102). The biaxial flexure test is performed on disc-shaped samples centred on a ring support, by a piston applying axial load on the centre of the sample. The piston moves with a fixed speed, and the force and the deflection of the sample is measured continuously until fracture.

2.3.1.3 Scanning electron microscopy (SEM)

The SEM analysis allows for high resolution imaging of a solid sample, with a resolution in the nanometre range. In dental material sciences, SEM is a technique frequently used for the analysis of qualitative microscopic changes (e.g. chemical and mechanical degradation) (82,86,103–106). The SEM imaging is used to investigate any differences in the integration of filler particles within the polymer matrix after prolonged water exposure (22,105,107).

2.3.1.4 Differential scanning calorimetry (DSC)

Dental composites are based on glassy polymers which undergo a glass transition, which by DSC is detected as a stepwise increase in the heat capacity, i.e., an endothermal step (Fig. 2). By monitoring and comparing the heat flux in a sample to a reference material, any endo/exothermic transitions (e.g. glass transition temperature, crystallization, melting) can be detected. (31). DSC has been utilized to assess the glass transition temperature (T_g), and its value is of utmost importance for the mechanical properties of the glassy polymer (33,88,108–110).

The glass transition temperature (T_g) is defined as the midpoint of the measured transition range (31). The T_g of amorphous polymers denotes the transition from liquid or rubber-state to glass. When a molten polymer made from the dimethacrylates relevant to this thesis is cooled below the T_g , it will undergo a transition into a glassy, amorphous state. Cooling the polymer past the T_g region results in an increase in the elastic modulus by a factor of 200 to 1000, and a sudden drop in the coefficient of thermal expansion (the slope in the specific volume-temperature) is observed (31). The T_g is strongly dependent on the monomer types, on the molecular architecture and on the presence of low molar mass species, such as water. The T_g value detected in any given experiment is dependent on the methodology chosen; for example, in differential scanning calorimetry, the rate of temperature-scanning affects the measured T_g . Therefore, the measured T_g in an experiment is usually described as the *kinetic glass transition temperature* (31).

According to Gedde et al, the fictive temperature (hereafter T_f) is the temperature at which a glass would be in equilibrium if brought to that temperature from its given state (31). The T_f further provides information about the thermal history for the specific sample, as it indicates the temperature where the material has been able to reach an equilibrium state in terms of specific volume (V) and enthalpy (H) (31). Unlike the kinetic glass transition temperature, T_f is unaffected by the parameters used in the analysis. The T_f is estimated through DSC analysis by determining the heat flow ($W g^{-1}$) above and below the transition temperature range and extrapolate where area A and B in Fig. 2 are the same.

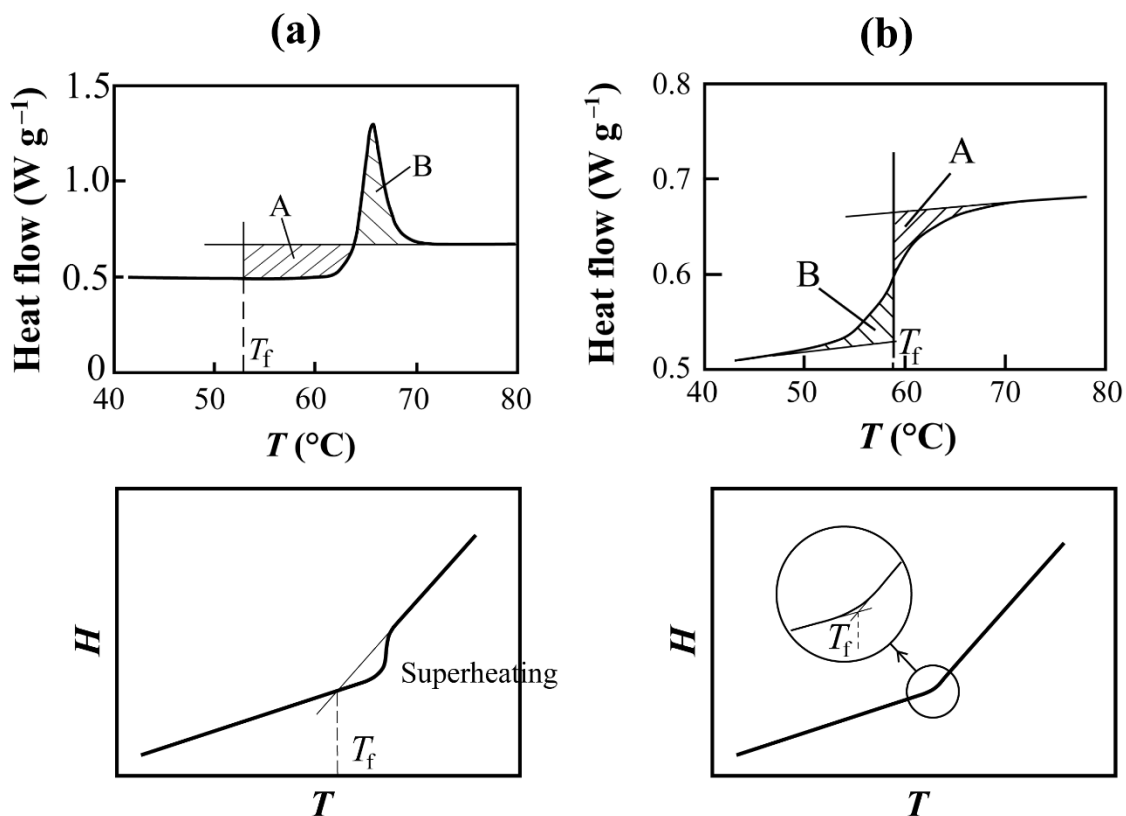


Figure 2: Assessment of the fictive temperature, with and without the occurrence of super heating. Illustration from Applied Polymer Science (2021) with permission from the authors (110).

Fig. 2 shows the assessment of the fictive temperature (T_f) of two polymers. The upper graphs are DSC thermograms, while the bottom graphs are the integration of the same data, where the enthalpy (H) is depicted as the Y-axis, and the temperature (T) on the x-axis. The T_f is the temperature where the enthalpy line above the transition temperature range (liquid) intersects with the one under (glass). Fig. 2 (a) show a slow glass transition with superheating (detected as a hysteresis peak, the area B in thermogram a), while (b) shows a transition without superheating.

Physical aging is the structural recovery of the specific volume to a state of equilibrium. When keeping a quenched amorphous polymer sample at a stable temperature below its T_g , the specific volume of the sample will decrease over time. This is called volume recovery, as the material is “recovering” to an equilibrium state. The practical aspect of physical aging can be observed in dental composites in several ways, such as material shrinkage, or formation and propagation of micro-cracks within the material bulk due to increased shrinkage stress. A material that has undergone physical aging, will show memory-effects when the temperature is changed, and this may be in the form of a hysteresis peak (the peak over area B in Fig. 2a) (31).

2.3.1.5 Thermogravimetric analysis (TGA)

Thermogravimetry involves a continuous measurement of mass of a sample during heating; the thermogram shows mass plotted as a function of temperature. As the temperature increases, evaporation of volatile compounds and decomposition of organic molecules occur, and the onset temperature of these processes can be detected. TGA can be used to detect and quantify the volatile compounds, and the organic and the inorganic content within the sample. Furthermore, TGA can reveal differences in polymer curing in 2 samples of the same composite, by detecting differences in the onset temperature for the material decomposition.

3 Hypothesis and aims

The negative effects of water exposure on dental composites are well described *in vitro* studies, and these effects have been documented over several decades. Studies have documented light-curing units of poor quality or the occurrence of improper maintenance of such equipment in dental clinics world-wide. Still, the documentation of the combinational effects of suboptimal light curing and prolonged exposure to water appears limited, despite the clear indications of its relevance in the available scientific literature. Here, the main goal was to gain knowledge of how the combination of water exposure and insufficient light curing can affect the physical properties and water susceptibility of dental composites made from conventional dimethacrylate monomers.

The working hypothesis of the thesis: light-curing regime of dental composite materials will affect water susceptibility (the extent of water sorption, solubility, degradative processes, and reduction of mechanical properties) of the cured material, and that the extent of these effects depends on the monomer composition of the material.

The general aim of this thesis: to investigate the water susceptibility of dental experimental and contemporary composites with similar monomer composition, and limited light curing on physical and mechanical properties and mass change over time.

The aim of Study I: assessment of the influence of the bis-EMA content on the DC and its effect on the water sorption and solubility.

The aim of Study II: to determine the water sorption and solubility of two contemporary dental composites, exposed to a radiant exposure below the manufacturers recommended levels, over 180 d. The following aspects were given extra attention, in an attempt to increase the clinical relevance:

- The total radiant exposure used for each sample
- The duration between light-curing and water exposure (no pre-immersion drying)
- Differences in inorganic filler content and monomer constituents.
- The duration of water exposure was set to 180 d

The aim of Study III: to investigate the effects of reduced radiant exposure according to the setup of Study II, water immersion and time on the mechanical properties of two contemporary

dental composites. In addition, Study III was aimed to qualitatively investigate changes in material structure by using microscope (SEM) and thermal analysis (TGA and DSC) and mechanical testing.

4 Materials and methods

4.1 Graphical depiction of the methodology of each study

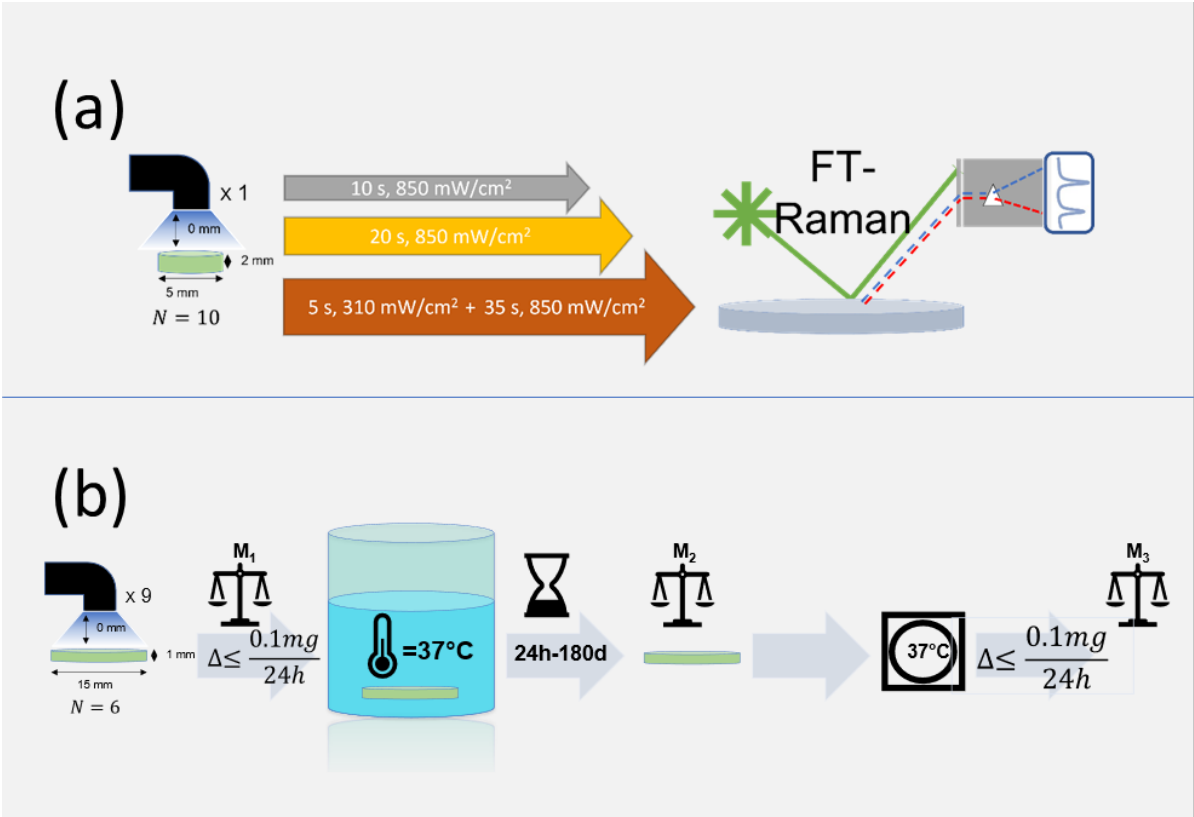


Figure 3: Graphical depiction of study I: a: DC performance by FT-Raman spectroscopy gravimetric and b; water sorption and solubility testing

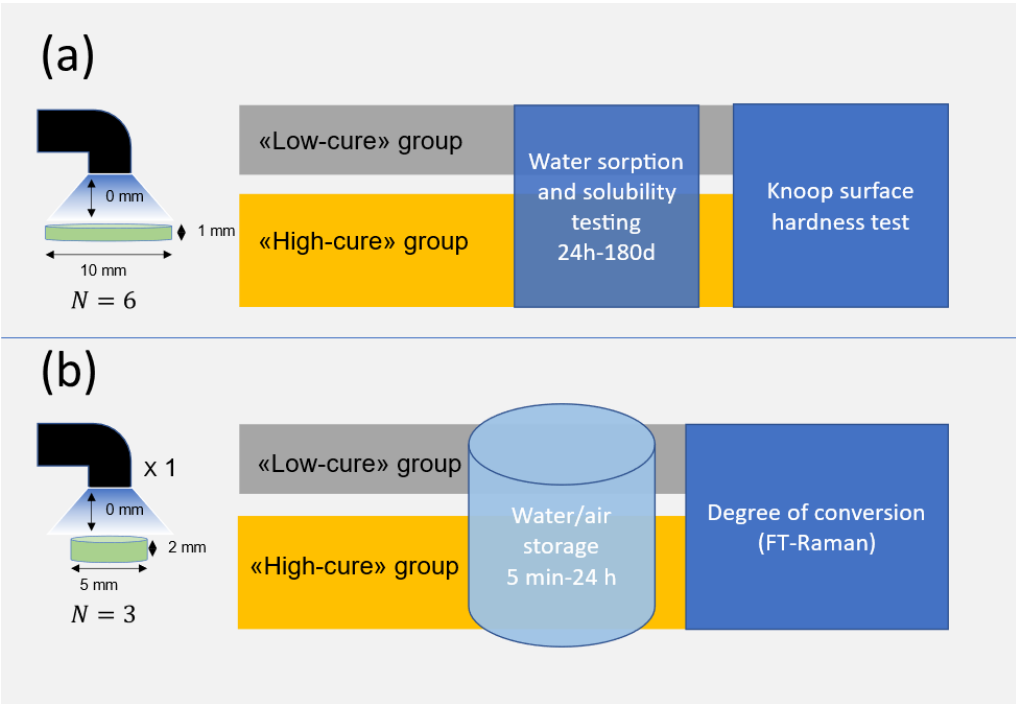


Figure 4: Graphical depiction of study II. (a): water sorption and solubility test followed by Knoop hardness test on the same samples. (b) depicts the DC estimations by Raman spectroscopy

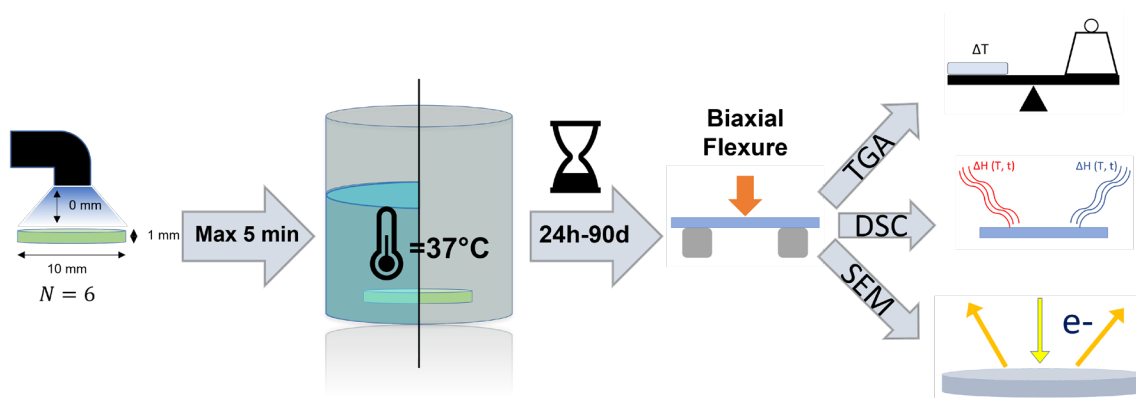


Figure 5: Graphical depiction of study III

4.2 Materials

For study I, experimental composite materials were used. The experimental blends were made to mimic actual dental composites used for direct restorative treatment in terms of handling (e.g., viscosity, filler content, ability to be light cured). Four different blends of composite were assessed, with the only difference between them were the content of bis-GMA and bis-EMA monomers.

Monomers	Composite 1	Composite 2	Composite 3	Control
Bis-EMA	60	45	30	0
Bis-GMA	0	15	30	60
UDMA	20	20	20	20
TEGDMA	20	20	20	20

Table 2: Monomer composition (in weight percentage of the total organic matrix) for the different mixtures tested in study I.

For all 4 composite mixtures, a combination of camphorquinone (0.1%) and dimethylaminoethylbenzoate (0.2 %) were used as initiators. Butylhydroxytoluene (0.05 %) were added as an inhibitor to prevent unwanted polymerization and for control of the speed of the reaction. The filler content was kept identical for all mixtures at 72.8 wt %, with 66.4% of dental glass (0.7 μm) and 6.4 % of fumed silica.

The composite mixtures were provided by a manufacturer (VOCO GmbH, Cuxhaven, Germany), based on instructions provided by the investigators. The mixtures were made within

the production line of the manufacturer, which ensured that the material consistency and manufacturing quality was satisfactory for all mixtures.

In study II and III, commercially available dental composites were used to investigate how contemporary products were affected by insufficient light curing in terms of water susceptibility. Two different products were chosen based on the results of study I and the monomer content listed in their SDS respectively. The dental composite was provided by each manufacturer respectively, ensuring that all the material provided for each study from each of the brands were made from the same batch.

		Grandio®, Voco Gmbh	Tetric EvoCeram®, Ivoclar Vivadent AG
Substance	CAS	Amount (GR)	Amount (TEC)
Bis-GMA	1565-94-2	2.5-5 wt. %	2.5 < 10 wt. %
TEGDMA	109-16-0	≤2.5 wt. %	
UDMA	72869-86-4		2.5 < 10 wt. %
Bis-EMA	41637-38-1		2.5 < 10 wt. %
Polymer matrix in total		28.6 vol.% (13 wt. %)	46 ±1 vol.% (24,5± 1 wt. %)
Inorganic filler		71 vol.% (87 wt. %)	54 ± 1 vol.% (75.5 ± 1 wt.%)

Table 3:: Composition of dental composites tested in study II and III.

4.3 Sample production

4.3.1 Samples for Degree of conversion tests

For estimations of DC, FT-Raman spectroscopy was utilized. To increase the accuracy and performance of this analysis, the sample thickness was set to 2 mm. According to the results from a pilot study and the DC analysis in study I, the increase in thickness of the samples from 1 mm to 2 mm did not cause significant difference in DC between the top and bottom of the sample. The sample production was identical to the one used for the water sorption and solubility test samples in all other aspects than the mould diameter (5 mm) and depth (2 mm).

4.3.1.1 Light curing of samples for degree of conversion estimation

In Study I, 3 different light curing setups were tested (table 4). The Celalux 2 LED LCU (VOCO GmbH, Cuxhaven, Germany) was utilized on all samples. Notably, the third curing set up had a “soft start” of 5 s with low irradiance followed by 35 s with 850 mW/(cm)².

Curing setup	Duration (s)	Irradiance (curing light intensity) in mW/(cm) ²	Radiant exposure at 0 mm at the LCU tip (J/(cm) ²)
1	10	850	8.5
2	20	850	17
3	5+35	310+850	31.3

Table 4: The light-curing setups used in Study I.

For study II, the light curing was performed to and beyond the recommendations listed in the “instructions of use” for the HC sample groups, while the LC sample groups received a radiant exposure lower than recommended lower limits. A corded LCU (Bluephase G2, Ivoclar/Vivadent, Schaan, Lichtenstein) was used with identical curing setups as for the sorption and solubility testing (table 5). The samples used for assessment of mechanical properties in study III were also made and light-cured in the same manner and using the same equipment as in study II.

4.3.2 Samples for water sorption and solubility testing

The production of samples was performed using polytetrafluoroethylene moulds. For study I, the sample mould was made from a square 1 mm thick polytetrafluoroethylene plate with a 15 mm circular hole. The plate was placed on top of a square steel plate with a polytetrafluoroethylene cover, identical in outer dimensions of the plate with the hole. The two plates were clamped together using metal paper clips. In study II and III, the sample mould was made of polytetrafluoroethylene, with circular wells ($\varnothing=10$ mm). The sample diameter was reduced to accommodate only 1 curing cycle. The sample thickness was kept identical at 1 mm for all studies.

The dental composite was added to the mould and thin film of transparent 0.50 μm thick polyethylene terephthalate sheet (PET) was placed on top of the composite. A microscope glass slide was used to press down the composite to distribute the material in the sample mould in an attempt to avoid gaps or air bubbles. The glass slide was then removed, and the tip of the light-curing unit (Celalux 2 in study I, Bluephase G2, Ivoclar/Vivadent, Schaan, Lichtenstein in study II and III) was placed perpendicular to the sample, in contact with the PET sheet.

After finished light-curing, the samples were removed from the mould and the edges trimmed for any excess material using a scalpel. The sample thickness and diameter were controlled with a digital calliper to be within 0.1 mm deviation from the wanted diameter or thickness, and the samples were transferred to a marked dram glass vial.

4.3.2.1 Light curing of samples for water sorption and solubility testing

In study I, the light-curing of the samples were performed in 9 overlapping sections. Each overlapping section was cured with a 20 s exposure duration and a power emitted from the LCU (radiant exitance) of $850 \text{ mW}/(\text{cm})^2$. As the LCU curing tip was placed in contact with the glass covering the sample during light curing, the influx of energy into the composite sample surface (radiant exposure = irradiance x duration) is estimated to be identical to the radiant exitance provided by the LCU. The samples were cured from the top side only, based on the results achieved in DC analysis performed in study I, where no difference in DC between the bottom of the samples and the top was recorded. The LCU was controlled before curing of each sample group with a radiometer (Bluephase Meter, Ivoclar/Vivadent, Schaan, Lichtenstein).

In study II and III, the samples were cured with 2 different curing setups, described in table 5. The light curing methodology was identical in study II and III, as well as the materials tested.

Due to the adaptations made to the sample mould a single light-cure was performed on the top side of each sample, in contrast to the 9 overlapping runs performed in study I. The LC light-curing setup resulted in a material consistency that was clinically indistinguishable from the HC group. The similarity in consistency between the composite curing groups after light curing was important in relevance to a clinical setting, as it was impossible for the operator to distinguish one sample group from another (HC vs LC groups) visually or through tactile inspection. As the LC settings was one of the pre-set settings on the LCU used, we could accurately and precisely reproduce these parameters.

Curing setup	Duration (s)	Irradiance (curing light intensity) in mW/(cm) ²	Radiant exposure at 0 mm from the LCU tip (J/(cm) ²)
“Low-cure” (LC)	5.2	716 ± 16	3.7 ± 0.1
“High-cure” (HC)	20.2	1317 ± 51	26.6 ± 1.0

Table 5: The light-curing setups used in Study II and III.

In study II, the LCU energy output was controlled before the curing of each group of samples using a BlueLight MARC resin calibrator (BlueLight Analytics, Halifax, NS, Canada). In Study III, the same LCU as utilized as in study II, and the irradiance was controlled for consistency using a Bluephase Meter dental radiometer (Ivoclar/Vivadent, Schaan, Lichtenstein) between groups.

4.4 Assessment of the water susceptibility

4.4.1 Water sorption and solubility testing

In study I, the water sorption and solubility were assessed according to protocol described in ISO 4049:2009, with the exceptions of light curing only one side of the samples (according to the findings from the DC estimations) and storage time used. Six samples of each composite mixture were made for each water exposure duration (24 h, 7 d and 30 d), to a total of 72 samples. The samples were first dried in individually marked, open glass vials in a desiccator, at 37 ± 1 °C in total darkness. The samples were weighed each day, until a constant mass within a 24 h period was detected.

When stable mass within 24 h was achieved (*mass 1*), the samples were immersed in 10 ml double distilled water in capped dram glass vials. The samples were stored in darkness at 37 ± 1 °C for 24 h, 7 d and 30 d. At the end of the storage duration, the samples were removed from the water, blotted dry, and waived in the air for 1 min before mass determination (*mass 2*). Then, the samples were dried in a desiccator kept at 37 ± 1 °C until stable mass within 24 h was achieved (*mass 3*).

The water sorption and solubility were calculated in micrograms per cubic millimetres from the following equations:

$$\text{Water sorption} = \frac{(\text{mass 2} - \text{mass 3})}{V}$$

$$\text{Solubility} = \frac{(\text{mass 1} - \text{mass 3})}{V}$$

Where *mass 1* is the sample mass prior to water immersion, *mass 2* the sample mass after water storage, *mass 3* is the sample mass after drying, and *V* is the sample volume.

For study II, a more clinically relevant approach was attempted, by excluding the pre-immersion drying stage, and reducing the light curing to a more clinically relevant level (only a single light-cure cycle for each sample). A group of samples exposed to suboptimal light-curing was included, to investigate the impact of insufficient light curing on water susceptibility (table 5). Therefore, mass 1 of the samples were determined within 5 mins of finished light-curing, followed by water immersion. Determination of mass 2 and mass 3 was identical to the

procedure described for study I. The duration of the water exposure was extended, by including sample groups exposed to water for 90 d and 180 d.

As the dental composites tested differed in terms of filler particle content, an estimation of water sorption and solubility per polymer matrix volume was added, in addition to the calculations performed in study I. The motivation for the calculations were to attempt a comparison of the sorption and solubility despite the differences in inorganic filler content. For these calculations the assumption was that the water sorption and solubility mainly took place in the organic matrix fraction.

$$\text{Matrix – related Water sorption} = \frac{\text{mass 2} - \text{mass 3}}{V * (1 - \text{inorganic filler particle volume fraction})}$$

$$\text{Matrix – related solubility} = \frac{\text{mass 1} - \text{mass 3}}{V * (1 - \text{inorganic filler particle volume fraction})}$$

4.4.2 Degree of conversion (DC)

The DC calculations in study I and II were determined using Raman spectroscopy, performed in collaboration with the department of Fibre and Polymer Technology (KTH Royal Institute of Technology, Stockholm, Sweden). The reflection mode of FT-Raman spectroscopy (Spectrum 2000R NIR-Raman, PerkinElmer, Waltham, Massachusetts, USA) was used to calculate the difference in area of the peaks representing the aliphatic (1639 (cm)⁻¹) and the aromatic (1608 (cm)⁻¹) double bonds between an uncured sample and the cured sample. The analysis was performed using 32 scans in study I at a 4 (cm)⁻¹ resolution in the spectral region 2000–1000 (cm)⁻¹. In study II, the number of scans were increased to 64, to improve the signal detection in the analysis. The laser power was set to 1 W, and the peaks of the aliphatic double bonds were determined before and after curing each composite blend. The calculations were performed using software Spectrum 10 (PerkinElmer, Waltham, Massachusetts, USA).

In study I, 30 samples of each material were made for the DC testing (10 for each light-curing setup). The samples were tested on both the top and bottom surface. As no statistically significant difference was found between the top and bottom of the samples in study I, only the top surfaces were tested in study II. Based on the results from the first study, 3 samples from each group and duration were tested 3 times each in study III.

In study I, the samples were left in darkness at 23 ± 1 °C for 24 h prior to the Raman spectroscopy analysis to allow for post-irradiation-curing. The rationale was that the DC evaluations would be performed on a material state relevant to the water sorption and solubility testing setup.

In the second study, the motivation for the Raman analysis was to investigate the development of the DC within the first 24 h after light curing, and if the post-irradiation curing was affected by the presence of water during that time. Therefore, samples stored in water were compared to samples stored dry. Analyses was performed within 5 min after ended light curing, followed by new tests at 3 and 24 h after light curing.

4.4.3 Knoop surface hardness

After the sorption and solubility testing (immersed in water, then dried) in study II, Knoop surface hardness tests were performed (ZHV μ -A, Indentec Hardness Testing Machines, Stourbridge, UK) on the surface of the samples. The test was performed based on the assumption that any lingering reduction in hardness after the samples have dried could be explained by permanent changes within the material itself.

Based on results from a pilot test, 15 s dwell time with 100 g load was used. Three samples from each group were tested, with 10 indents per sample. The Knoop hardness was calculated using the following formula:

$$KHN = \frac{\text{load (kgF)}}{\text{Impression area (mm}^2\text{)}} = \frac{P}{C_p L^2}$$

where L is the length of indentation along the long axis, C_p is a correction factor determined by the indenter shape (0.43997), and P is the load in kgF.

In an attempt the to avoid bias (e.g., air bubbles, cracks) on the test area, all test surfaces were individually inspected and performed by the same operator for all tests. Because the surface hardness of the samples reached a plateau after 7 d of water exposure the 30- and 90-days sample groups were not included in the result.

4.4.4 Bi-axial flexure test

The test setup was chosen to accommodate flexural testing on disc-shaped samples based on the sample design from Study II. This way the material samples of study II and III were kept identical in terms of size, shape and material product chosen. Also, initial testing showed similar patterns of sample fracture when tested, providing well defined fracture surfaces and minimal surface damage.

The sample was carefully placed on a brass ring (diameter = 8 mm) directly after storage (dry or wet, 37 ± 1 °C) and loaded at the middle with a piston (diameter = 0,7 mm) at speed of 10 (mm)/min using a Lloyd LRX (Fareham, England). The loading rate was determined after a pilot test, in an attempt, to avoid viscoelastic deformation. The maximal tangential stress at sample fracture, Q_{max} , was measured in MPa, and the deflection of the central piston at fracture. All the pieces of the fractured samples were then stored to protect the fracture edges until further fracture surface analyses was performed.

4.4.5 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

The samples from the bi-axial flexure test with the most extreme values were chosen for further analysis in TGA and DSC. The rationale was that any mechanical deterioration or changes would be most prominent in these samples. The TGA provided information on the decomposition behaviour, the percentage of inorganic filler content, and remaining water content in the dental composite samples after water storage for up to 90 d. DSC was utilized to determine the glass transition temperature (T_g , here calculated as the fictive temperature) of the light-cured samples after water storage.

The TGA was performed using a TGA/SDTA 851 module (Mettler-Toledo, Switzerland) on 45 mg sample pieces in a nitrogen atmosphere. The samples were heated from 30 to 900 °C at 10 °C/min. For the DSC analysis (DSC 820 module, Mettler-Toledo, Switzerland), 16 mg sample pieces were first cooled then heated in a nitrogen atmosphere, from room temp to -80 °C, and back up to 500 °C.

4.4.6 Scanning electron microscopy (SEM)

SEM imaging was used for assessing both the sample surface and the fracture surfaces of the samples that had been stored in water and subjected to biaxial flexural testing. Earlier studies have described possible degradative pathways for dental composites, both for the organic matrix and surface of inorganic filler particles, and even for the integration (i.e. binding) of filler and matrix (11,12,15,16,87). In Study III, any differences in filler integration were of particular interest.

The morphology of the sample top and fracture surfaces were investigated in a table-top SEM, TM 1000 (Hitachi, Japan) before one sample from each group were finally chosen for high-resolution imaging using an FE-SEM S-4800 (Hitachi, Japan), based on the results of the biaxial fracture test. Before high-resolution SEM imaging, the samples were coated using an Agar 208RH High-Resolution Sputter Coater for 15 s using a Pt/Pd target, leaving a 2 nm conductive coating layer.

4.5 Statistics

All statistical tests were performed using IBM SPSS statistics software. The level of significance was set at $p < 0.05$ for all tests.

In study I, One-way ANOVA and Tukey's Post-Hoc tests were employed detect and quantify any differences between the composite mixture groups with the data from the DC analyses. Also, a paired T-test was performed to compare the DC at the top and bottom of the samples. The correlation between DC and the sorption and solubility values was analysed by Pearson correlation test.

For study II the statistical tests were performed to test the validity of the following null hypotheses:

1. 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.
2. There is no statistically significant difference in DC between the specimens immersed in water directly after irradiation and those stored in dry conditions.

The assumption that all specimens of each dental composite originated from a homogeneous population at the start of the experiment were foundation for the statistical analyses in study

II. Therefore, a general linear model (GLM) for repeated measures was used to evaluate the sorption and solubility data, and to test for differences between groups. The model assumptions were analysed for equality of covariances and error variances using the Box and Levene's tests. The Pillai and Tamhane T2 test statistics were used to test for statistically significant differences within and between groups, as equal variances were not assumed.

In the third study, the null hypothesis was that suboptimal light-curing protocol would not cause changes in Q_{max} or the T_g . A GLM for repeated measures was used to evaluate the development of the mechanical test parameters between the exposure groups considering both the exposure medium (water or air) and light-curing setup. Within- and between-group effects were evaluated for the two materials tested, and interaction terms for the covariate's exposure medium and light-curing dose. Shapiro-Wilkinson's test of normality was performed on all sample groups to evaluate the distribution of the results. In addition, the homogeneity of variance was assessed with Levene statistics.

5 Results

5.1 The influence of bis-EMA vs bis GMA on the degree of conversion and water susceptibility (Study I)

Water sorption increased significantly with increasing bis-GMA content when the materials had been exposed to water for 7 d or longer. The solubility was negative for all groups, both after 7 d and 30 d of water exposure, and the negative values were more pronounced as the bis-GMA content increased. A correlation was found between the content of bis-EMA and the reduced values for sorption and solubility, for all storage times used, when the materials were cured for 20 s.

The DC of the bottom of the composite samples from the monomer blends with high bis-EMA content was significantly higher than the control when irradiated for 20 s or longer (Table 6, curing setup 2 and 3). No statistically significant difference was found between the DC results on the top and bottom of the samples.

COMPOSITES	SETUP 1	SETUP 2	SETUP 3
COMPOSITE 1	71.5 (0.7)Aa	69.0 (6.1)Da	72.5 (3.9)Fa
COMPOSITE 2	64.4 (2.8)Bb	66.2 (3.7)Db,c	68.3 (3.2)Fc
COMPOSITE 3	56.7 (3.9)Cd	60.4 (3.8)Ed	60.8 (3.8)Gd
CONTROL	61.7 (4.4)Be	58.9 (2.5)Ee	60.6 (3.9)Ge

Table 6: The DC measured on the bottom of the composite samples for the different light-curing setups tested in study I.

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

No significant differences in DC were detected between the LC- and HC-groups after 24 h post-cure, despite the difference in radiant exposure and water immersion. Furthermore, no significant differences in water sorption were detected between the LC- and HC-groups. However, reduced radiant exposure led to a significant change in water solubility; the LC-groups showed a higher solubility than did the HC-groups. The estimations of matrix-related sorption and solubility showed similar trends between the two materials despite differences in monomer composition, with the LC-groups showing higher solubility values than the HC-groups.

The surface hardness of the LC samples stored in water for 7 d or more decreased significantly between 24 h and 7 d of water exposure (and then dried). The Knoop hardness was not significantly altered in the HC group even after 180 d of water exposure (please see the main findings of studies summarized on p. 38-40).

5.3 Suboptimal light curing and water exposure: an in vitro investigation in mechanical aspects (study III)

The bi-axial flexure strength test showed that the maximal stress needed to fracture the two composite materials decreased with increasing storage time for the HC groups, regardless of the storage media (i.e., water, air) used. The HC groups could withstand higher stresses than did the "low-cure" samples, both after 30- and 90-days of storage. The differences were significant. Regardless of the level of radiant exposure, water immersion reduced the fracture stress.

Regarding the DSC analysis, the TEC samples immersed in water displayed two separate glass transitions, with a shift in T_g of the main transition from 37 to 52 °C (Fig. 6, black line marked 3). The high temperature transition was most likely associated with the pre-polymerized composite-based filler particles included in the material.

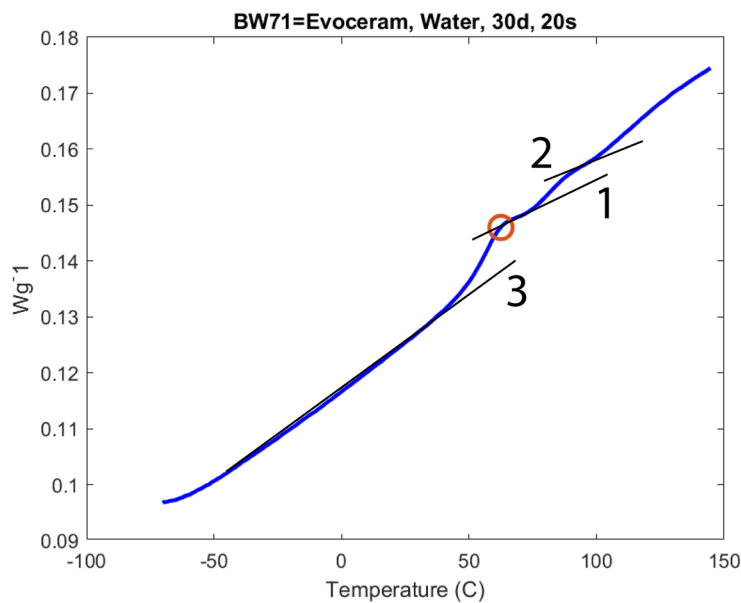


Figure 6: an example of a sample with 2 glass transitions, here marked as black lines numbered 1 and 3. The black line marked 2 indicate the end of the second transition. The red circle marks the hysteresis peak for the first transition.

The peaks of hysteresis were smaller, indicating that these samples had not been in a "glassy" state while immersed in the water. Despite receiving the high radiant exposure during light-curing (HC group), the materials tested did not reach a "glassy" state. As the polymerization temperature was initially lower than the storage temperature (23 vs 37 °C), the polymerization rate halted as the polymerization temperature reached the storage temperature. However, as the

samples dried during storage (between bi-axial flexure testing and the DSC, see graphical depiction of study III, Fig. 5, p 22), the T_g increased as the plasticizing moisture was removed.

The SEM images of the "low-cure" top surface of the samples exposed to water for 90 d showed erosive degradation for both materials tested. Regarding the GR material (containing bis-GMA and TEGDMA monomers), the erosion seemed to be confined to the polymer matrix.

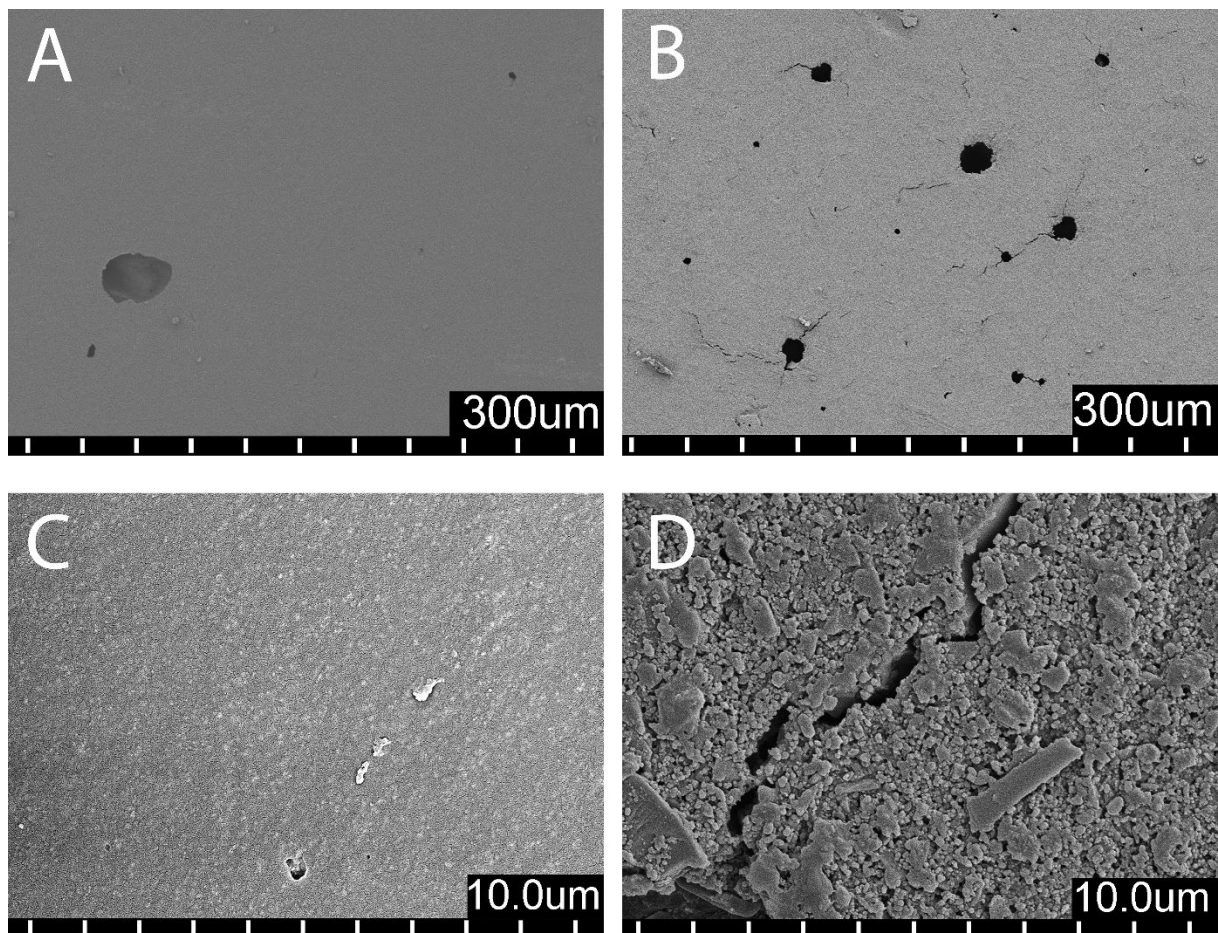


Figure 7: SEM images of the sample surface of the contemporary composite GR after 90 d of storage. Image A and C are from a sample light-cured for 20 s with $1304 \text{ mW}/(\text{cm})^2$ (HC group). Image B and D are the surface of a LC sample, exposed to 5 s of $716 \text{ mW}/(\text{cm})^2$ (pictures from study III).

For the TEC samples (including UDMA, bis-EMA and bis-GMA), the erosive degradation appeared less extensive. The erosion appeared localized to and around the filler particle boundaries.

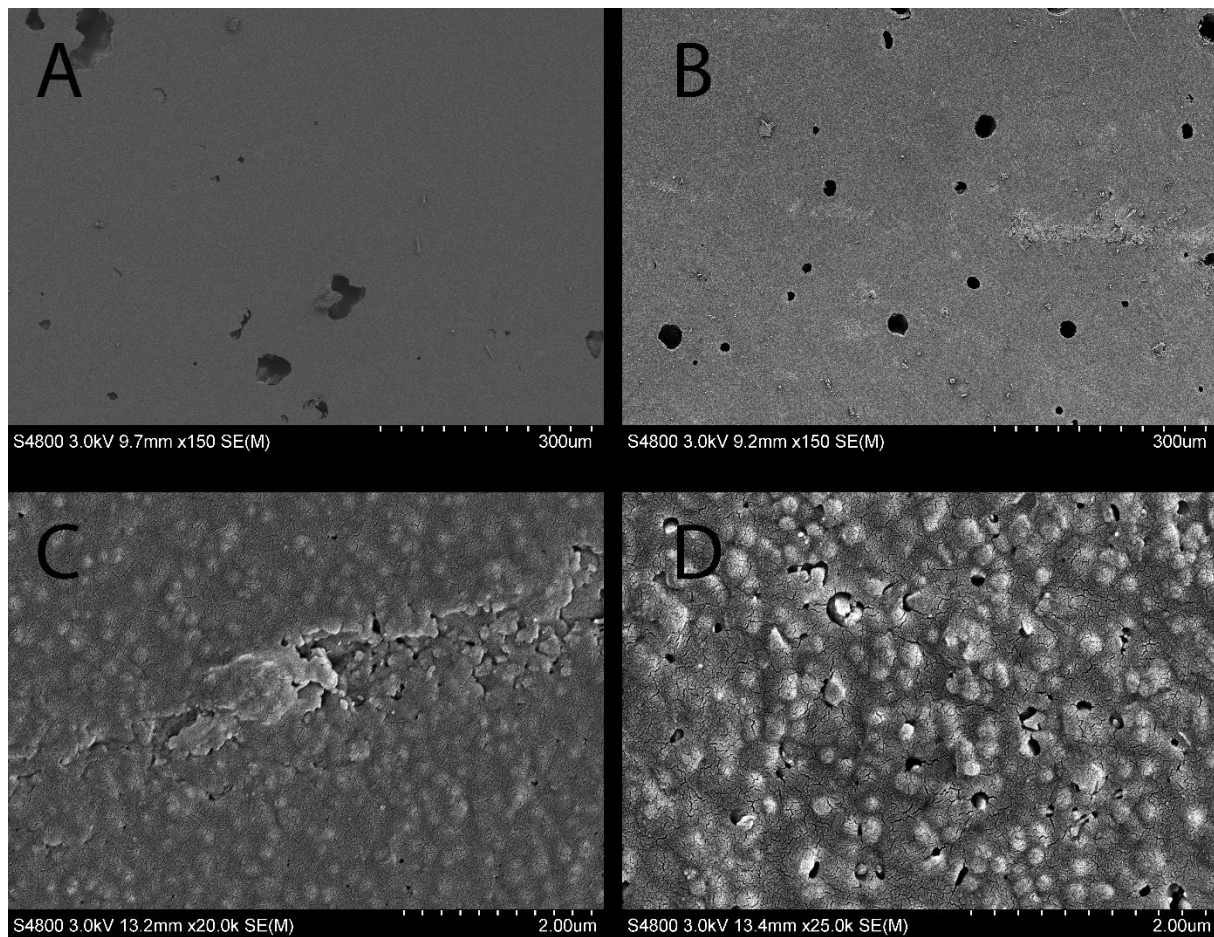


Figure 8: SEM images of the sample surface of the contemporary composite TEC after 90 d of storage. Image A and C are from a sample light-cured for 20 s with $1304 \text{ mW}/(\text{cm})^2$ (HC group). Image B and D are the surface of a LC sample, exposed to 5 s of $716 \text{ mW}/(\text{cm})^2$ (pictures from study III).

Study I: The influence of bis-EMA vs bis-GMA on the degree of conversion and water susceptibility of experimental composite materials

Method	Rationale	Main results
Water Sorption and Solubility Test	To identify and quantify the differences in water uptake and material solubility caused by changing and replacing the fraction of Bis-GMA with Bis-EMA. This would highlight the effects of the hydroxyl group found in Bis-GMA only.	Replacing the Bis-GMA fraction with the more hydrophobic Bis-EMA decreased the water sorption. Negative solubility values were reported after 7 days of water immersion, with higher negative values with increasing Bis-GMA fraction.
Degree of Conversion by Raman Spectroscopy	Test the changes in DC of experimental resin-based composite materials caused by the content of monomers with hydrophilic molecular groups, over a range of curing duration and light curing intensity.	When cured for more than 20s, the DC increased with increasing Bis-EMA fraction. The DC of mixtures with higher content of bis-EMA is affected by the presence of bis-GMA at lower energy density delivered from the curing device, suggesting that the restrictions caused by the presence of hydrogen bonds is dependent of the irradiation time used.

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

Method	Rationale	Main results
Water Sorption and Solubility	Evaluate the effects of sub-optimal light curing and immediate post-cure water exposure on the water sensitivity of the composites.	No difference in water sorption between the light curing setups was detected, however solubility in the low-cure groups were significantly higher than for the high-cure groups.
Fourier-Transform Raman Spectroscopy	Evaluate the effects of sub-optimal light curing and immediate post-cure water exposure on the DC development within the first 24 h after light curing.	Water exposure did not seem to have any effect on the DC development within the first 24 h after light curing. Both light curing setups reached similar DC values within 24 h post-cure despite a 5-fold difference in radiant exposure.
Knoop Surface Hardness Test	Evaluate any irreversible effects on the mechanical properties of the resin-based composite materials caused by water exposure.	For the low-cure groups, a significant reduction in surface hardness was detected in samples exposed to water for more than 7 d. The TEC samples seemed to regain surface hardness over time.

Study III: Suboptimal light curing and water exposure: an in vitro investigation in mechanical aspects

Method	Rationale	Main results
Piston-on-ring Flexure Test	Evaluate the effects of sub-optimal light curing and immediate post-cure water exposure on the water sensitivity of the composites.	The bi-axial flexure test showed that the maximal stress needed to fracture the two composite materials reduced with time for the "high-cure" groups, regardless of the storage media. The test also showed that the "high-cure" groups could withstand higher stress than the "low-cure" groups, both at 30 and 90 days after light-curing. The water exposure further reduced the stress needed to fracture the samples, regardless of the curing setup.
Differential Scanning Calorimetry	Evaluate the effects of sub-optimal light curing and immediate post-cure water exposure on the glass transition temperature (T_g).	Despite receiving more than the recommended (by the manufacturer) radiant exposure during light-curing, the materials had not reached a "glassy" state. The TEC samples immersed in water showed two distinct phase transitions, with a shift in the T_g of the main transition from 37 to 52 °C. The second transition is most likely caused by the polymer matrix in the pre-polymerized composite-based filler particles.
Thermogravimetric Analysis	Quantify any amount of inorganic filler particles and water within the samples, and investigate any changes in the onset of polymer degradation temperature to determine differences in matrix structure.	No water was detected. No difference in degradation temperatures was detected.
Scanning Electron Microscopy	Evaluate the top and fracture surfaces of the samples to look for qualitative changes caused by differences in light-curing and water exposure.	The SEM images of the top surface of the LC sample exposed to water for 90 days showed erosive degradation in both materials tested. For GR the erosion seemed to be related to the polymer matrix. For the TEC samples the erosive degradation appeared less extensive compared to the GR samples. The erosion was mainly on and around the filler particles.

6 Discussion

It has been shown that the presence of water have negative effects (i.e., swelling, degradation, elution, reduction of mechanical properties) on dental composite materials, and these effects have been detected in materials cured as recommended by the manufacturers (11,19,88,111). Improper maintenance and control of LCUs lead to low irradiance reaching the composite materials during curing, and this appears to be a widely occurring and well documented phenomenon (1,3,56,57). In an attempt to improve the understanding of the combinational effects of water exposure and less than recommended light curing, the focus in this thesis was on the effect of low radiant exposure and early onset water immersion.

6.1 Main findings

The working hypothesis of this thesis was that the light-curing of dental composites affects the water susceptibility of the cured material, and that the extent of such effects depend on the monomer composition. The main findings described in the included studies performed support this hypothesis.

The main finding of Study I was that the hydrophilicity and structure of the monomers tested affected the water sorption and solubility of the composite material. The hydroxyl groups of the bis-GMA monomer increased the water sorption. Monomer blends with a higher bis-EMA content than Bis-GMA showed reduction in the DC at low radiant exposures. By replacing the bis-GMA monomer with bis-EMA, the water sorption and solubility decreased. These conclusions are in accordance with findings reported (17,112–114).

The formation of hydrogen bonds between the polymer chains and the absorbed water molecules prevented evaporation of the absorbed water, causing negative solubility values after 7 d and 30 d of water exposure (the mass after drying is higher than the mass before water exposure). The water-induced mass gain increased with increasing bis-GMA content, indicating that the hydroxyl groups within the polymer matrix provided additional retentive force onto the water molecules. Negative solubility values has previously been reported (99,115–118).

The main finding of Study I supports the working hypothesis: replacing bis-GMA with the more hydrophobic bis-EMA monomer reduced the water sorption of the composite blends tested within a 30-day period.

In Study II, the reduced radiant exposure caused an increase in solubility over 180 d for both materials tested. This was in accordance with the working hypothesis. No significant difference in DC were found at 24 h post-cure, despite a 5-fold difference in radiant exposure between the two curing setups. Fonseca et al. found a positive correlation between DC and water sorption, however the correlation between DC and solubility were found not to be statistically significant (112). In the present study, no difference was detected between the HC and LC curing groups regarding sorption. The Knoop hardness results of the present study showed that the surface of the LC sample groups had a reduced surface hardness compared to the HC groups, even after drying. The reduction in Knoop hardness indicated irreversible degradative processes, as the changes persisted even after sample drying.

In Study III, both dental composites tested showed a reduction in maximal stress at fracture after 90 days compared to the 30 days samples for the HC groups. The HC groups could withstand higher stress than the "low-cure" groups, at both time intervals tested. Additionally, the samples immersed in water could not withstand the same level of stress before fracture as their counterparts stored in air. These findings are in accordance with the findings by Ferracane et al using 3 point bending test setup. They reported a reduction in fracture toughness within the first 6 months of water immersion for dental composites, however after 2 years post-cure, the flexural strength was only lowered in the samples exposed to "poor cure" (18).

Furthermore, the SEM analysis revealed erosive degradation on the surface of the LC samples exposed to water for 90 d for both the materials tested, with the more pronounced erosive features on the dental composite GR containing bis-GMA and TEGDMA. The erosive patterns observed differed between the materials, indicating different "paths" for the erosive degradation. For the TEC material, complete organic filler particles with smooth surfaces were observed, as well as gap formation between the inorganic filler particles and the polymer matrix. For GR, the erosion seemed to be more related to the polymer matrix, with crack formation and exposed filler surfaces.

The main findings in Study III were in accordance with the working hypothesis; reduction of the radiant exposure made the material more susceptible to water degradation. The results suggested that the composite based on bis-GMA and TEGDMA exposed to suboptimal light curing underwent more extensive erosive degradation than did the composite based on a more hydrophobic monomer blend (UDMA and bis-EMA also in the composite, reducing the bis-GMA content).

Interestingly, the T_g for the samples stored in air were the same as the storage temperature (37 ± 1 °C). A hysteresis peak indicated physical ageing of the materials. This was evident for both materials and also for both the HC and the LC groups. For both the TEC and GR samples stored in water, the distinct hysteresis peaks were not evident, suggesting that the samples had not undergone physical ageing to the same extent.

For the TEC material stored in water, the DSC analysis produced 2 phase transitions, and the major transition had a T_g of 52 °C (Fig. 6). The increase in T_g indicated further post-irradiation polymerization enabled by the increased mobility of the polymer segments due to the plasticizing effects of water (31,119). The second phase transition is most likely due to the content of pre-polymerized filler particles; however, another explanation could be the formation of a heterogenic polymer structure with microgel clusters. The microgel clusters would be surrounded in a less dense polymer structure during polymerization, that can also be detected as two or more glass transition temperature phase changes within the same material (36,120). The T_g of dental composites have been explored and the problem of using materials with a T_g that correspond to physiological oral temperatures have been documented (109,121–123). The T_g determined in the present study were within the temperature range found in the oral cavity, and such overlap in temperature can affect the performance of the material (109,121–123).

The scientific documentation of hydrolytic and hygroscopic degradation of dental composites (the polymer matrix, the filler particles and the integration of the two phases) have been summarized (11). The softening and degradation of the surface of dental composite samples stored in water for more than 60 d have also been documented (106,124,125). However, studies report increased surface hardness after 30 d of water exposure, suggesting that the initial influx of water causes increased polymer segmental mobility, thereby facilitating further polymerization (126,127). The latter supports the results achieved in Study III, as the change in T_g suggests configurational changes especially in the TEC samples after prolonged water immersion.

6.2 Methodological considerations and limitations

6.2.1 Materials

In Study I, the experimental composite materials tested were produced by a manufacturer after specifications made by the authors and based on previous studies (114,128,129). As the manufacturing of the material was performed by others than the research group, the quality control of ingredients and the manufacturing were to some extent outside of the research team's control. However, the mandatory internal quality control of the industrial production line bestowed upon any manufacturer by the Medical Devices Directive (MDD 93/42 EEC) and now Medical Device Regulation (MDR 745/2017) was considered as an assurance when choosing this route for material production. The use of a production line of a well-regulated and highly recognized manufacturer (of similar products) made it possible to produce batches of materials with the precision and accuracy in terms of constituents, content, and handling matching that of any commercially available dental composite. The experimental composites only varied in the monomer content of bis-GMA and bis-EMA, in an attempt to determine differences in water sorption, solubility and DC related to differences in monomer content.

The same contemporary dental composites were used in both Study II and III. The materials were chosen based on the monomer content listed in the SDS, as their monomer mixtures corresponded to the hypothesis of the project and the results achieved in the first study. Still, as these materials were commercial materials made by manufacturers, the exact content in terms of monomers, fillers and additives could not be verified. However, according to their SDS respectively, GR contained bis-GMA and TEGDMA. and TEC had UDMA and bis-EMA in addition to a lower bis-GMA content listed.

6.2.2 Sorption and solubility testing:

Gravimetric water sorption and solubility testing were performed in Study I and II. In Study I, the test parameters described in the ISO-standard was used, except for the extension of test parameters by adding 2 water immersion duration sample groups (24 h and 30 d in addition to 7 d described in the standard) and light curing from the top only. Despite that the composite blends used being experimental, the sorption and solubility results at 7 d were comparable with the results from contemporary commercial products and within the ranges of approval stated in the standard (60,118). Furthermore, the results indicated that most of the water sorption and solubility occurred within the first 7 d of water exposure, in accordance with previous findings (11,13).

Gravimetric method for sorption and solubility are flawed to some extent due to the fact that the two phenomena do not occur consecutively or separately. As water is incorporated into the composite material, the elution of unbound constituents also occurs. Since the wet composite sample is being weighted directly after water exposure, the mass measured only reflects the net mass increase (initial sample mass + absorbed/adsorbed water - eluted mass). Also, despite drying the wet samples to a stable mass (within a 24-hour period), any residual water unable to escape the material will reduce precision of the sorption and solubility parameters. It was unclear whether the prolonged water exposures used in study II and III would increase the inaccuracy of the measurements due to potentially increased elution and water absorption over time. Therefore, in study III, the TGA was utilized in an attempt to detect and quantify any residual moisture within the dental composite samples exposed to water for 90 d. The analysis detected no residual water within the samples tested.

The sorption and solubility test methodology described in ISO 4049:2009 does not claim any clinical relevance, and the standard is meant for assessment of quality by conformity between batches of the same material. Light-curing in accordance with the manufacturers recommendations are not always easy to achieve or even possible to verify in a clinical setting (50,56,57,130,131). Therefore, some of the procedural steps described in the ISO-standard (i.e., light-curing in multiple, overlapping sections, extensive pre-immersion drying, sample thickness of only 1 mm) is not applicable or even relevant for research attempting to claim clinical relevance. The methodology described in the standard does not account for differences in filler content, nor differences in the curing recommendations. As the water sorption and solubility mainly occur within the organic polymer matrix of the dental composites, differences in inorganic filler content would affect these measurements (132). Comparison of different dental composite product lines are also difficult at best due to such differences. Therefore, the methodology described must only be used with its limitations in mind (133,134). For example, the standard state that the light curing settings to be used on each (overlapping) section when light curing the samples are identical to the parameters recommended by the manufacturer to be used once on a material layer twice as thick in a clinical setting.

In Study II, several alterations to the methodology of the ISO 4049 standard were made in an attempt to accommodate more clinically relevant test parameters. The sample diameter size was reduced to remove the need for light curing in multiple overlapping sections. The sample mould used had a diameter corresponding to the light curing tip of the light curing device used (diameter = 10 mm), to accommodate the use of a single, continuous light pulse (only on one

side of the sample). Enhanced reproducibility was achieved by using curing modes programmed into the LCU software, electronically controlling the duration (and intensity) of the LCU unit.

No pre-immersion drying was performed. Instead, the samples were immersed within a 5 min after finalized light-curing, for more accurate simulation of the clinical use of the composite products tested. In addition, the duration of water exposure was extended to 180 d in Study II (and 90 d in Study III, the latter based on the results obtained in Study II).

To investigate the effects of sub-optimal light curing, groups of 5 s light curing exposures with lowered irradiance was added for comparison to the HC group. At present, no simple method seems available to evaluate the outcome of the light curing procedure in a clinical setting other than tactile inspection. The lowest electronically controlled light curing setting on the LCU was used (i.e., 5 s and $716 \pm 10 \text{ mW}/(\text{cm})^2$). This produced a material consistency that was indistinguishable from the HC samples for the operator, but with less than 14 % of the total radiant exposure of the HC group.

As the filler particle content and type (i.e., organic and/or inorganic) in the materials tested in Study II differed, calculations on the matrix-related water sorption and solubility were indicated. The sorption and solubility when only the polymer matrix volume was considered as available volume was calculated. These calculations were based on the data provided by the manufacturers, which must be used with caution. However, the TGA tests performed in study III did confirm the inorganic filler content, as we were performing the analyses for the third study. The matrix-related sorption and solubility calculations provided valuable insights about the effects of the material state caused by reduced curing, and the effect magnitude of the differences in tested monomer blends versus differences in light curing. According to the results obtained, the GR material was more sensitive to reduced radiant exposure, compared to the TEC material, as the matrix-related solubility between the LC and the HC groups of GR diverged.

For all the experiments performed, water with analytical grade purity was used. Impurities in the water could, in theory, cause unexpected reactions such as the formation of salts or changes in pH, which could in term affect the results of the analyses performed. It was decided to use distilled water for all studies in an attempt to reduce the probability of such unexpected reactions.

According to Soderholm et al. (1996), the use of distilled water may cause much lower elution from inorganic filler particles (16). These authors argued that this finding reduces the clinical relevance of in vitro studies using distilled water. However, the SEM imaging performed in study III revealed cavities surrounding filler particles on the surfaces of samples made from both of the composite materials tested. The cavities may indicate that the filler particles did erode over time, or at least that their integration with the polymer matrix failed after prolonged water exposure.

It can be hypothesized that the high purity of the water can cause osmotic pressure build-up in voids and cracks within the dental composite over time, as even a small amount of composite constituent elution would cause a concentration gradient between the surrounding water and pockets of water containing elutes. The presence of micro-voids along filler particles caused by failure in the filler-matrix integration and/or polymerization shrinkage could in theory increase crack propagation due to such osmotic pressure. The SEM imaging of the fracture surfaces in study III revealed a high occurrence of protruding filler particles and imprints caused by filler particles that had been “plucked” at fracture propagation in all sample groups tested. To the author, the occurrence of such imprints and protruding particles seemed to occur more frequently and extensively in the “low-cure” groups, however no objective evaluation was performed due to time constraints.

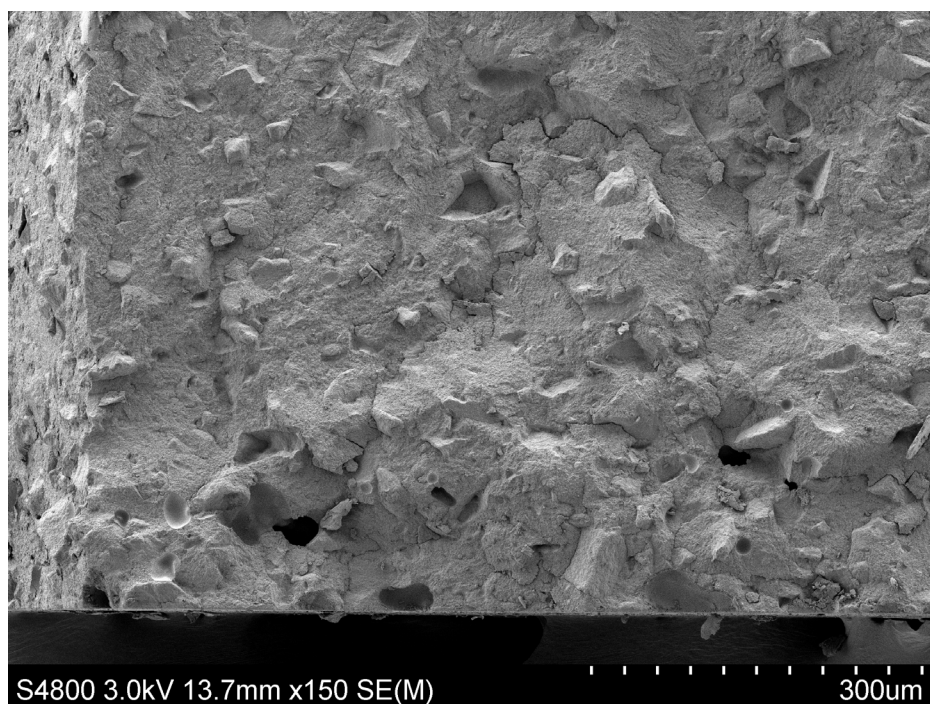


Figure 9: fracture surface of a GR sample exposed to water for 90 d. Examples of cavities and stripped filler particle surfaces can be seen on the fracture surface.

6.2.3 Surface hardness analysis

The test parameters used in Knoop surface hardness testing of dental composites (i.e., load, duration or dwell time, and type of test) described in the scientific literature vary (64,72,135). The lack of proper guidelines describing the test parameters for surface hardness testing of dental composites makes it difficult to compare results from one study to another. Differences in the fraction and type of monomers and filler particles in the contemporary dental composites further complicates comparison (124,136).

The differences between Vickers and Knoop hardness tests were evaluated in a pilot study. The form of the indenter makes Knoop surface hardness analysis more suitable for testing on thin, brittle samples and also for viscoelastic materials, by having a small indenter size and a shape that allow elastic and plastic deformation to occur more easily along one axis, making fracture propagation less likely (42). According to the literature, Vickers tend to have lower values than Knoop in tests performed on softer materials (137,138). This was also the findings in our pilot tests, showing larger, reproducible differences between samples that had been exposed to different light curing setups. In the same setup, different loads were tested, and the clearest difference between the “low-cure” and “high cure” group was produced with a load of 100 g with a dwell time of 15 s. Samples from the 30 d and 90 d immersion groups were excluded as no difference between the 7 d, 30 d and 90 d of immersion were detected in the pilot study.

The Knoop surface hardness test in study II was consistent over the entire sample surface for all samples tested, even after prolonged water exposure. Some initial deviating results were found to be inconsistencies in the sample surface when manual control of the indentation was performed (Fig. 11 right, showing an initially obscured sub-surface cavity, increasing the indentation size). The surface hardness test also revealed apparent structural changes on the surface when inspected with a microscope. The surfaces of the samples stored in water for more than 90 d appeared rougher (Fig. 11). The changes in surface structure were more prominent in the LC groups, and for the GR samples sub surface cavities were detected during surface hardness testing. These findings were not reported in study II, but they were one of the main motivations for study III.

6.2.4 Raman spectroscopy

For the DC tests in Study I and II, Raman spectroscopy was chosen after a pilot study. IR-spectroscopy was found to be unsuitable due to a vibrational state of water overlapping the wavenumbers where absorbance caused by carbon-carbon double bonds and aromatic double bonds were expected to be detected. Raman spectroscopy allowed for proper assessment of wet samples, as this overlap did not occur. The test protocol for DC is also well described and documented (139,140). The use of Fourier-Transform (FT) Raman spectroscopy allowed for less laser energy to be transferred to the samples (by reduction of the time of laser exposure on the sample). This was done to reduce the chance of unwanted additional polymerization due to heat and strong light exposure. It should be noted that the equipment used was considered old, and that the actual wattage output of the laser was estimated by the operators who were familiar with the equipment to be lower than the level reported by the system. The number of replicates (i.e., 3) could have been increased to make more accurate estimation, however the consistency in the data from study I suggested that the use of fewer samples would yield similar trends. The number of scans per sample were set to 64 to improve the output data.

6.2.5 Piston on ring flexural strength test

According to the results presented in Study II, the suboptimal light curing did increase the solubility and reduced the surface hardness of the dental composites tested. It could therefore affect other mechanical properties (11,79). In Study III, further investigation of the effects on mechanical properties caused by water exposure and suboptimal light curing was undertaken. Using biaxial flexural test the material is exposed to both tensile and compressive stress, as the sample is being subjected to increasing perpendicular forces in the centre of the disk until fracture (141,142). This gave opportunity for both quantifying any changes because of differences in light curing and/or water immersion duration. A piston-on-ring biaxial flexure test was used, as the design enabled testing of the same disc-shaped sample form as utilized in Study II, with the identical light curing setup (141,142). The results provided by the piston-on-ring flexural tests in Study III was therefore considered more relevant to the results previously achieved (in terms of size, shape and treatment of the samples tested). A 10 (mm)/min piston travel speed was chosen, in an attempt to reduce any viscoelastic deformation within the material during the load.

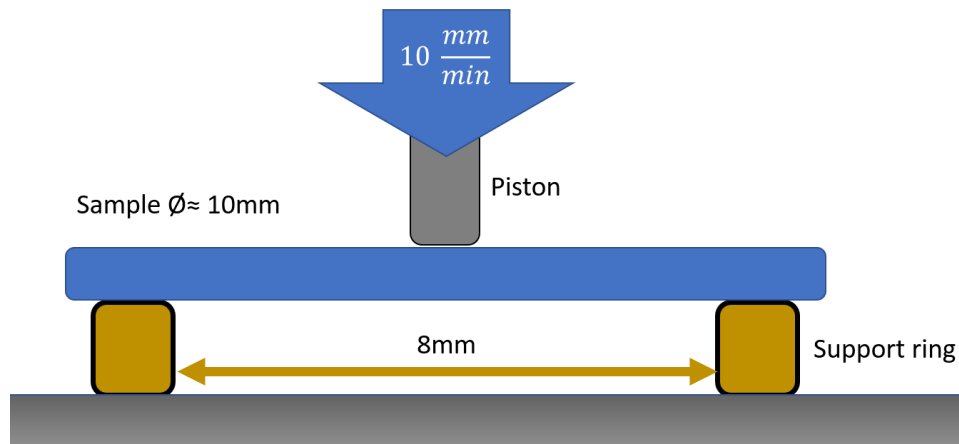


Figure 10: Illustration of the biaxial tensile flexure test.

The piston-on-ring test seemed to produce adequate precision as shown by the results in Study III. Most of the samples fractured into 3 or 4 pieces suggesting homogenic energy distribution within the samples tested.

6.2.6 TGA and DSC

The glass transition temperature determined with DSC or other forms of thermal or mechanical analysis is defined as the *kinetic glass transition*. It is affected by the methodology used for the given experiment (31). Therefore, direct comparison of values between studies are of less value. The fictive temperature utilized for glass transition temperature evaluation in study III is unaffected by the test parameters, however.

The comparison of the TGA results from each group could in theory provide indications of differences in crosslink density within the composites tested. Composites of identical composition may show different thermal stability as a result of differences in crosslink density. No such differences were detected.

6.2.7 Scanning Electron Microscopy

The SEM analysis revealed qualitative differences between the sample groups and provided information on the degradative processes observed. The high-resolution images obtained with a FE-SEM S-4800 (Hitachi, Japan) were essential for detecting changes in the surface morphology and the fracture surfaces. The initial SEM-imaging produced with a lower resolution did not provide enough detail to observe differences between the LC and the HC

samples, however it was acceptable as an initial evaluation of the samples for selecting the samples for high-resolution SEM imaging.

It may be argued that further chemical analysis of the surfaces such as energy dispersive X-ray spectroscopy or Raman/IR-spectroscopy could have provided further knowledge to the state of the fracture surfaces and the exposed filler particles. Indirectly analysis of the eluates found in the water used for sample storage could also have added further knowledge on the degradation processes observed. However, such analyses were not performed due to time- and economical constraints.

6.3 General discussion

Water molecules diffuse into the material bulk, causing both reversible (i.e., swelling, increased segmental movement) and irreversible changes (leakage, degradation, changes in DC) to the material. Changes within the material explained by interaction with the organic and inorganic material constituents, and alteration of the intermolecular forces between these constituents have been proposed (11,19,127). In Study II, the samples used for the sorption and solubility testing were investigated using light microscope as a part of the Knoop hardness test. Changes in the surface structure after prolonged water immersion and consequent drying were evident; roughening of the surface and crack formation was observed on the samples stored in water for more than 90 d (Fig. 11). These observed changes suggested a deterioration of the mechanical properties of the material surface within a timespan of less than a year.

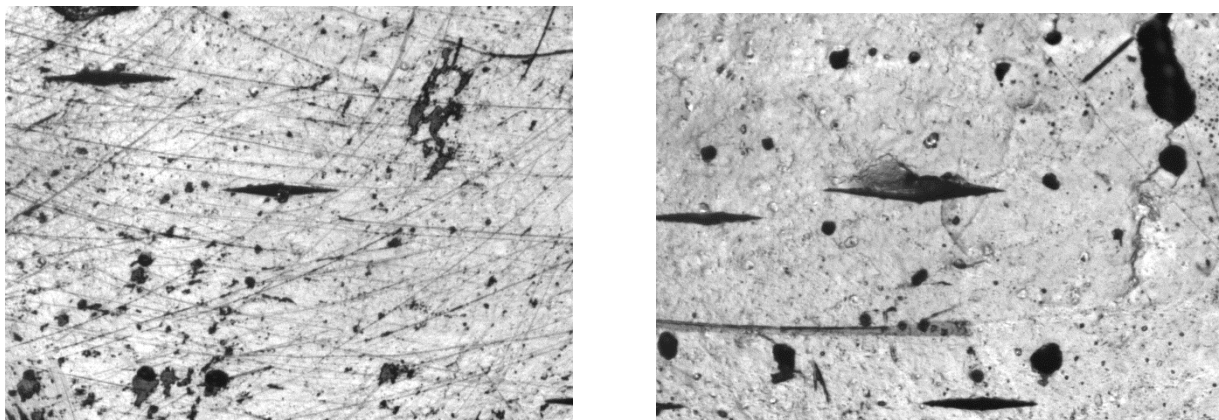


Figure 11: the top surface of a HC GR sample after 7 d (left) and 90 d (right) of water exposure (100X magnification). The indents from a Knoop surface hardness indenter can be seen on the surface. A cavity has been revealed as the indenter has broken through the top layer, making the indent much deeper than the surrounding marks. The images are from study II.

The SEM images in Study III showed erosive degradation on the top surfaces and qualitative alterations on the fracture surfaces of both materials tested, when exposed to less than recommended light-curing and stored in water for 90 d. The GR samples stored in water for 90 d showed erosive degradation that seemingly had removed the outer layer of polymer matrix, exposing inorganic filler particles and globular structures (most likely smaller globular inorganic filler particles) on a perforated and cracked composite surface. The TEC sample surfaces also showed signs of erosion, with gap formation along and surrounding protruding filler particles. From the SEM images it was unclear whether the gap formation was caused by

erosion of the filler particles or the surrounding polymer matrix. However, also empty cavities were observed suggesting that the filler particles were fully dislodged or eluted. Images from the fracture surfaces of the samples exposed to reduced radiant exposure light-curing and stored in water differed distinctly from the samples stored in air. The low-cured sample fracture surfaces were rougher, with partially exposed filler particles protruding further from the surface than in the samples stored in air.

Erosion of elements from the material implicates degradation of its structure. The hydrolytic degradation of dental composites have been investigated and have been shown to be linked to both the polymer matrix and the inorganic filler particles (11,16,17,19).

The SEM findings of Study III indicate that the polymer matrix, the filler particles, and the integration between these two phases may all be prone to degradation when the dental composites tested are exposed to less than recommended polymerization. The fact that the sample surfaces of the HC-groups showed less signs of degradation demonstrate the importance of following the light-curing recommendations made by the manufacturers.

Surface hardness depends on several mechanical properties such as compressive strength, ductility and the proportional limit (42). Apart from the influence of water, the surface hardness has also been linked to the DC. Still, the use of surface hardness measurements to estimate DC has proven to be difficult due to variations in inorganic filler loading and type in composite materials (18,136). In study II, the surface hardness of the LC samples of both materials tested were irreversibly reduced after 7 days of water exposure. The DC results did not deviate significantly after 24 h post-cure between the LC and the HC groups, suggesting that the changes in surface hardness must also be interpreted with the perspectives of time and storage conditions in mind.

The reduced hydrophilicity of bis-EMA (compared to bis-GMA) has been documented in neat resins. The difference has been ascribed to the higher flexibility, lower viscosity and lack of hydrogen bond forming groups compared to bis-GMA (112,114,143). Despite the hydrophilic properties of the hydroxyl groups found in bis-GMA, the ability to form hydrogen bonds do increase the initial material strength, and may provide positive effects on the polymerization reactivity and the impact strength of the material (41,144). However, these positive effects seem to be negated by the exposure to an effective solute (144). This trend was also observed in Study III, where the reduction in flexural stress needed to fracture the material samples was

significantly reduced for the GR samples after 90 d of water exposure, compared to the identical samples stored in air. The TEC material samples did not show the same reduction probably due to less bis-GMA content.

DC as a measure of the state of cure of dental composites is time dependent, as the polymerization process can continue for several hours post-irradiation (97,127,145). As shown in Study II, differences in DC detected minutes after irradiation can be undetectable after 24 h post-irradiation. A reduction in radiant exposure through shortened light curing duration and reduced irradiance should, in theory, yield a decrease of free radicals within the dental composite (42). Therefore, in Study II, the expected result of reduced radiant exposure for the “low-cure” group was a decrease in the DC, in accordance with results reported (52,58). Both materials showed lower DC values for the LC groups compared to the HC groups when DC was calculated directly after curing. However, the Raman spectroscopy performed showed insignificant differences in DC between the LC and the HC sample groups 24 h after light-curing. Thus, when reporting DC values, the time lap between curing and the DC measurement should be reported. In Study II, differences in solubility and irreversible reduction in Knoop surface hardness were apparent, despite similar DC values. These findings thus suggest that a measurement of the DC only is not sufficient when evaluating the curing state of a composite, as important differences in the polymer structure, not revealed by the DC measurements, can be present.

In addition, early water immersion of the samples did not affect the DC values significantly, compared to the samples stored in air. Increase in DC have been reported to yield lower solubility, (146,147). A similar tendency was found for only for GR.

In studies II and III, the differences in the mechanical properties and the water susceptibility of the HC- and LC- groups suggested that structural differences of the polymers formed was dominated by the radiant exposure. It has been hypothesized that a high formation rate of free radicals due to high radiant influx (high LCU intensity) may lead to shorter polymer chains with lower average molecular weight (36,83,148). A high concentration of free radicals increases the probability for crosslink formation and the rate of radical-radical termination in the early phase of the polymerization. This may cause areas of dense, highly crosslinked polymer matrix suspended in a less dense one. Theoretically, this may cause a heterogenic polymer matrix structures, with zones of high DC, high polymerization stress and high

concentrations of crosslinks surrounded by areas of polymer chains with higher molecular weight between crosslinks (82,148). The T_g of dental composites has been reported to be dependent on the polymerization temperature (149). In its uncured, liquid state, the T_g of the monomer blend is very low, typically lower than 0 °C. The increase in molar mass and intermolecular forces during polymerization increase the viscosity, and eventually cause a complete trapping of unreacted radicals in the vitrified polymer matrix (31,150). This will occur at a temperature close to the polymerization temperature.

Despite the exothermic polymerization of dimethacrylates and the high intensity LCUs used, the dental composites did not undergo a prolonged, extensive increase in temperature as a result of curing (130,151,152). High filler content within the material seems to reduce temperature changes, as the inert filler volume can “absorb” much of the thermal energy.

As the prolonged post-irradiation curing is taking place over several hours post-cure, the polymerization temperature is essentially equivalent to the highest temperature the material has had (over a certain period of time, i.e., minutes) within the first weeks post-cure (153–155). The DSC results from Study III underline the importance of the temperature after the initial light-curing phase, as the T_g of the materials tested correlates to the storage temperature, independently of light-curing parameters. The effect of storage temperature on the post-irradiance curing has been explored by others, and a majority reported significant effects (127,154,156–159).

One possible explanation for the detected increase in solubility in the LC composite samples in Study II may be lower crosslink formation during the post-irradiation phase. Glassy amorphous polymers with excessive volume and enthalpy show physical ageing (densification) over time, a process which is at its most rapid as the material temperature is close to the T_g (31,160). Physical ageing has been documented in dental composites with high filler content, and the presence of free radicals within the polymer matrix are have been documented even days after light-curing (154,161,162). As the densification of the polymer matrix brings the polymer chains closer, further cross-linking can occur due to the trapped free radicals (127,153,154,157,158). The results presented in Study II and III may indicate that a reduction in radiant exposure can cause an increase in mean molecular weight of the polymer chain segments between crosslinks (increased network parameter), allowing further restructuring of the matrix during polymerization reducing the glass transition temperature, and the potential for physical ageing (148).

Interestingly, the radicals formed during the polymerization seemed relatively unaffected by the immediate presence of water within the first 24 h, as the DC results from Study II developed in a similar manner as for the dry samples at all the 3 time points tested. As reported in other studies, radicals and reactive methacrylate groups will endure for several days/weeks post-irradiation (161,162). Leprince et al. reported that the concentration of trapped free radicals decreased rapidly within the first 24 h post-cure as post-irradiation polymerization, and that this initial process did not depend on the storage medium (150). However, after the initial 24 h, the storage medium did affect the rate of free radical decay, and that the samples stored in water underwent a more rapid decay compared to the samples stored in oxygen or air. An increase in temperature increased the rate of the free radical decay even further (150). Leprince et al. concluded that the increased free radical decay in water is due to further polymerization, through the plasticizing effect of water (150). The reduction in intermolecular forces further enable polymer segment movement and movement unbound monomers and free radicals. As the water diffusion is time-dependent, the effects of water exposure would depend on the material thickness, temperature, and rate of diffusion.

As long as the free radicals have not decayed, any increase in temperature above the current T_g or a reduction in the material viscosity will allow further polymerization, and thereby an upwards shift in T_g (31). In Study III, the lack of hysteresis peaks and the increase in T_g on the DSC results from some of the water samples support this theory. The presence of water increased the T_g through the forementioned plasticizing effects. As these samples had been stored in a dry container filled with protective cotton after the bi-axial flexure test to preserve the fracture surfaces, some extent of drying had taken place before the DSC analysis. The reduced amount of plasticizing water led to an increase in T_g of several degrees.

When considering the DC results from Study I and the knowledge gained from the results displayed in study III about T_g , the DC results do show the same trend. Increasing the radiant exposure from $8.5 \text{ J}/(\text{cm})^2$ to $31,3 \text{ J}/(\text{cm})^2$ did not cause any statistically significant increase in DC for any of the groups but one on the bottom of the samples. The only statistically significant difference between the light-curing setups could be seen between the 10 s and the 40 s light-curing for material group 2 (15 % bis-GMA and 45 % bis-EMA), with an increase in radiant exposure of more than 3.5 times, and the increase appears to be small. It may be that this finding is a type 1 error, or it could be a result of the prolonged light-curing setup, increasing the temperature during polymerization allowing for a slight increase in T_g .

6.3.1 Clinical aspects

In-vitro studies may not accurately reflect the complex interactions that occur in living systems, and the results of in-vitro studies may not be directly applicable to human patients. However, the results presented in this work exemplifies the importance of proper light-curing to ensure optimal mechanical properties and reduce the water susceptibility of dental composites used in direct restorative treatment. The results from Study II and III showed that the composites tested had increased resistance to mechanical forces, water solubility and degradation when light cured to and beyond the levels recommended by the manufacturer. Within the limitations of this thesis, these findings do indicate that the same circumstances would apply when using these composite materials in dental treatment on living patients.

In vivo, the transition temperature will be affected by the temperature in the oral cavity, allowing the material to reach a state of volumetric equilibrium in accordance with the oral temperature, and physical aging will only occur if the material experience an increased temperature over a sufficient duration within the first weeks (97). From study I and II, the gain in water sorption was most prominent within the first 24 h after water immersion, suggesting that the plasticizing effects increased most significantly within this period. Considering the reported patterns of free radical decay within the first 24 h, the early onset of water exposure would be the most effective in terms of synergic effects on the post-irradiation polymerization (150).

Increased post-irradiation polymerization may cause increased mechanical strength and reduced water susceptibility, and therefore, the early onset of water exposure of 37 °C would seem to be advantageous for the resultant material quality, at least in short term. Furthermore, the polymer matrix would be more able to undergo relaxation through polymer rearrangement, reducing internal localized stress concentrations within the matrix. From a clinical perspective, reduced internal stress within the polymer matrix would be considered favourable, as shrinkage may cause microleakage, microfractures, and reduced adhesion to the tooth structure (163). Water exposure can cause degradation in dental composites over time, as shown by this thesis and previous studies (11,17,87,88,164). According to the findings presented in this thesis, sufficient light-curing can mitigate and postpone this degradation.

7 Future perspectives

Despite the development of new ingredients of the resin-based composite restorative materials, the most effective factor for improving the clinical performance of dental restorative materials is education and information to the clinicians on the importance of proper handling of the dental material systems they use. Several studies on the actual use and maintenance of dental light curing units in the dental clinics around the world give clear indications that human error and ignorance is one of the mayor hurdles in the work of improving the clinical performance of dental composites (1,3,6,165). With increasing diversity in the contents of the materials indicated for direct restorative dental treatment comes greater need for competence and knowledge among the dental practitioners.

The change from dental records on paper to electronic patient journal systems produce new and unprecedented opportunities for increasing the clinical relevance of in-vitro dental material research in general. Within a few years, all dental practices (both public and private) in Norway will be required by law to participate in a national dental health data base within the “*Kommunalt pasient og brukerregister*”, that among other things can provide surveillance of the clinical longevity of dental restorations. On the in-vitro side, projects such as the “Biomatdb” and EUDAMED presents the development of international databases for storing and presenting relevant information on the chemical-physical, biological, and toxicological properties of biomaterials and the production and usage of such products. For the first time, it will be possible to evaluate the clinical performance of dental materials from millions of patient treatments.

By combining the data from in vitro testing of material properties (such as water sorption and solubility and mechanical properties) and the clinical survival data of the dental composite restorations, the relevance of the in-vitro test results can be evaluated from a perspective of clinical performance and longevity. The importance of testing of physical and mechanical properties would gain further relevance if clinical data could provide knowledge on relevant limits for the approval of new dental composites (166,167).

New production technology allows the manufacturers produce new filler particle shapes and materials, monomers, and initiator systems that has improved both mechanical and esthetical properties of the contemporary products over the last decades (107,168–170). The “classic” mechanical challenge with water susceptibility seems to be highly relevant still today (169,171,172).

As new ingredients for dental composites are introduced the importance of relevant and accurate measures material quality and consistency of material properties remain. However, with the increased filler fraction caused by nanometre scaled particle size and the addition of new constituents in dental composites, relevant inter-material comparison of test results gets more complicated. These differences highlight the need for re-evaluation of the standards used for market approval and product comparison, to ensure that the standards better reflect the increasing diversity in the materials being evaluated. This relates to the approval process for new dental material products to be released on the EU/EES market. In the approval process it is the manufacturers task to provide data to the governing body showing that the material in question perform as good or better than any limit level set in the relevant standards available. However, if these standards refer to fixed limit values, rather than some relative measure related to the properties of the material tested, the quality of the materials tested may not be found to be suboptimal despite low quality.

The importance or relevant testing methodology in the approval processes for dental materials cannot be overstated. According to the former chair of ISO/TC106 , *'Dental standards play a vital role in society by contributing to the quality and safety levels of products used in dental treatments and by the general public.* “ (173). From the authors perspective, there is a clear need for additional standard methodology that take into account the complexity and possible shortcomings that may occur in clinical use of these materials. For standards used for market approval, it would be highly relevant to add some form of “sub-optimal scenario” methodology, to compare such materials when receiving less-than-recommended light-curing and early/immediate water exposure after light curing. According to the ISO4049:2009, “...*The estimation of solubility is considered to be a manifestation of material quality.* To hold any merit, the quality of a material must be described in relation to the purpose of use.

As dentistry in many parts of the world are kept out of the general health care system, it has become more of a service for those that can afford it. A smile is more than just a statement of health; it is, among other things, also a statement of financial status. The focus on aesthetics among the patients is highly relevant for the dental practitioners, as their livelihood is directly linked to the patient’s inclination to pay for their services. This has made the manufacturers focus on ad-words such as *aesthetics*, *efficiency*, and *ease of use* rather than *longevity of service* in their sales-pitch of new dental composite products. By giving the patients and the dental practitioners access to relevant, objective information on the clinical performance of these products, one may hope for a shift in the focus towards the overall cost for the patient and the

longevity of the restorative materials. If so, the interest among the dental practitioners will also shift towards material properties (such as sensitivity to water) and the importance of proper light-curing and handling of dental composites.

8 Conclusions:

Within the limitations of the presented thesis, the following conclusions were drawn:

- The monomer content of the composite did affect the water sorption and solubility over time, and the effects became more apparent as the duration of the water immersion increased.
- When light curing of 20s (of 850 mW/(cm)²) or longer was applied, the substitution of bis-GMA with bis-EMA produced an increase in DC values in experimental composites.
- The radiant exposure did affect the water susceptibility of the contemporary dental composites tested. The intra-material comparison of samples subjected to either “high” or “low” radiant exposure showed reduced solubility and higher stress before fracture in the former groups.
- Degradation of the dental composites were observed after 90 d of water immersion, and the samples that received a “low” radiant exposure showed more extensive surface degradation, compared to those that received a “high” radiant exposure.
- The “low-cured” sample group showed reduced stress at fracture, irrespectively of composite material tested.
- The results presented strengthen the theory of structural differences being the major cause for increased solubility. The nature of these structural differences was not clear, however. The Raman spectroscopy and the thermogravimetric analysis performed did not reveal clear differences in the polymer matrix structure of the materials tested.
- The glass transition temperature appeared to be determined by the temperature of the composite material during polymerization and storage, however the plasticizing effect of water can modulate the glass transition temperature through increased post-irradiation polymerization.

The results achieved in this thesis could not disprove the main hypothesis formulated.

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Study I-III

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

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.

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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.

Aksel W. Wikant¹ ,
Ulf W. Gedde² ,
Magnus Hakeberg³ ,
Ulf T. Örtengren^{1,4} 

¹Department of Clinical Dentistry, Faculty of Health Sciences, Tromsø University, Tromsø, Norway; ²School of Engineering Sciences in Chemistry, Biotechnology and Health, Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden; ³Department of Behavioural and Community Dentistry, Institute of Odontology/Sahlgrenska Academy, University of Gothenburg, Gothenburg, Sweden; ⁴Department of Cariology, Institute of Odontology/Sahlgrenska Academy, University of Gothenburg, Gothenburg, Sweden

Aksel W. Wikant, Department of Clinical Dentistry, Faculty of Health Sciences, UiT The Arctic University of Norway, 9037 Tromsø, Norway

E-mail: Aksel.wikant@uit.no

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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, Liechtenstein). 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.

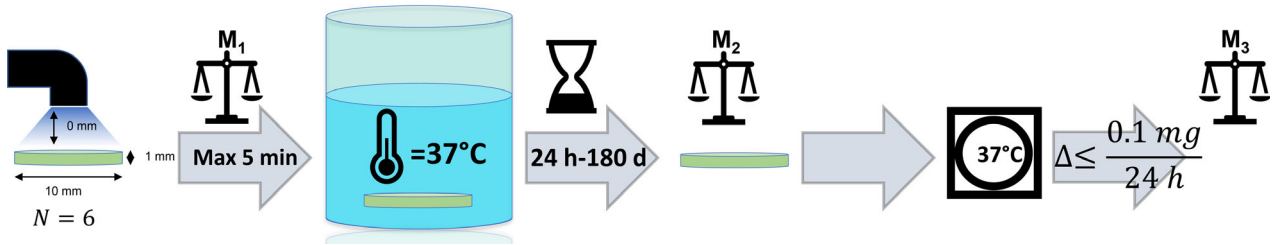


Fig. 1. Illustration of the procedure for sorption and solubility tests. Six specimens were made for each group and each was weighed (M_1). Within 5 min after completing the light-curing procedure, the specimens were immersed in water and stored in a heating cabinet at approximately 37°C for up to 180 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 \pm 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 $1,317.7 \pm 51.1 \text{ mW cm}^{-2}$ and a mean \pm SD radiant exposure (mean cumulative energy delivered to the specimen surface) of $26.6 \pm 1.0 \text{ J cm}^{-2}$. 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 \pm SD irradiance of $716.3 \pm 16 \text{ mW cm}^{-2}$ and a mean \pm SD radiant exposure of $3.7 \pm 0.1 \text{ J cm}^{-2}$.

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 ($V = 92.4 \pm 3.9 \text{ mm}^3$) and surface area ($A = 193.6 \pm 1.9 \text{ mm}^2$) (both given as mean \pm 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:

$$W_{\text{sp}} = \frac{M_2 - M_3}{V}, \quad (1)$$

$$W_{\text{sol}} = \frac{M_1 - M_3}{V}, \text{ and} \quad (2)$$

$$\text{Mass increase} = \frac{M_2 - M_1}{V}. \quad (3)$$

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 (W_{spMatrix}), and the estimated matrix-related water solubility ($W_{\text{solMatrix}}$) with reference to the volume of the polymer phase:

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

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

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

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:

$$\text{KHN} = \frac{\text{load (kgF)}}{\text{Impression area (mm}^2\text{)}} = \frac{P}{C_p L^2}, \quad (7)$$

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-11101024>) 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:

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

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

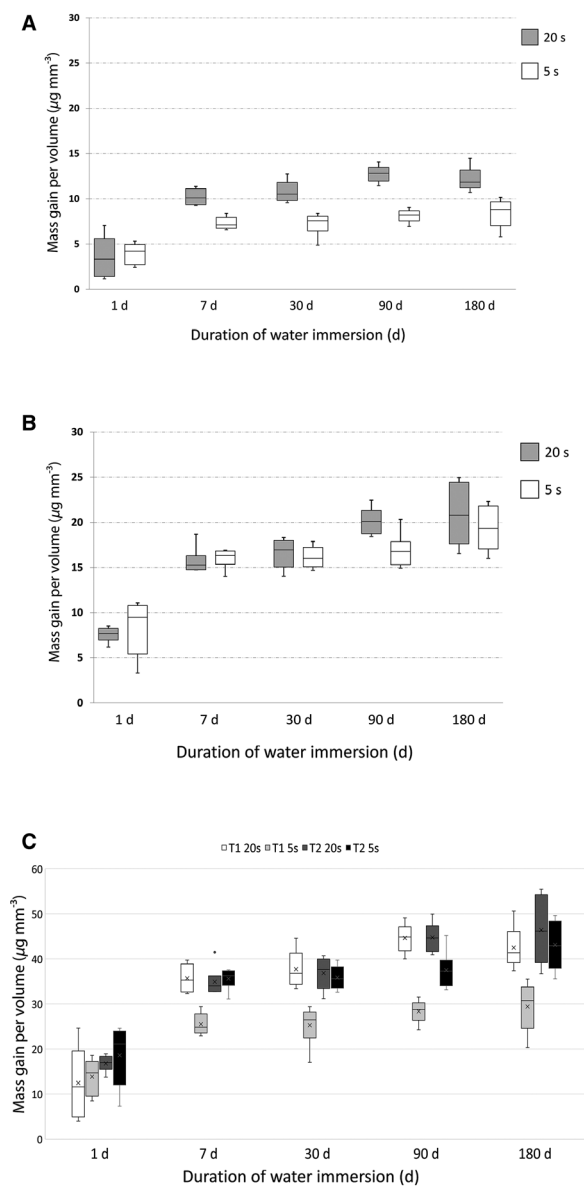


Fig. 2. Mass gain per days of water immersion. (A) Mass gain of Grandio (material T1). (B) Mass gain of Tetric EvoCeram (material T2). (C) Calculated matrix-related mass gain for all four groups. Boxes represent the first and third quartiles, and the horizontal line inside each box represents the median.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

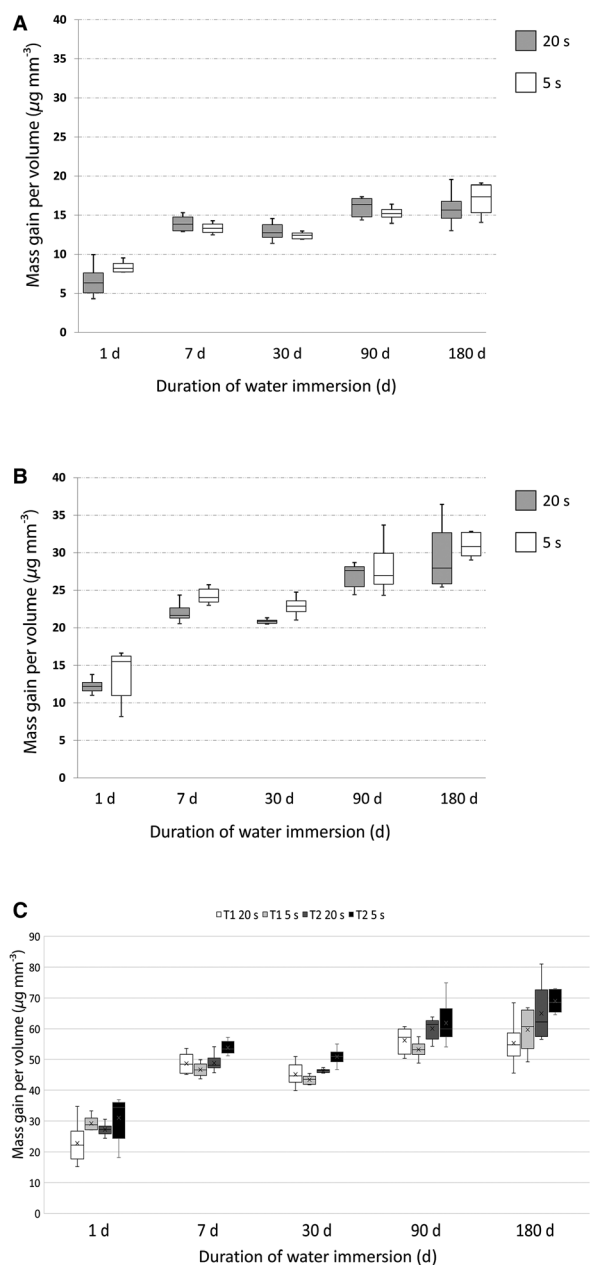


Fig. 3. Water sorption after different time periods (5 s or 20 s) of exposure to radiation. Data represent mass gain per days of water immersion. (A) Sorption of Grandio (material T1). (B) Sorption of Tetric EvoCeram (material T2). (C) Calculated matrix-related sorption for all four groups. Boxes represent 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 $10 \mu\text{g mm}^{-3}$, 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.

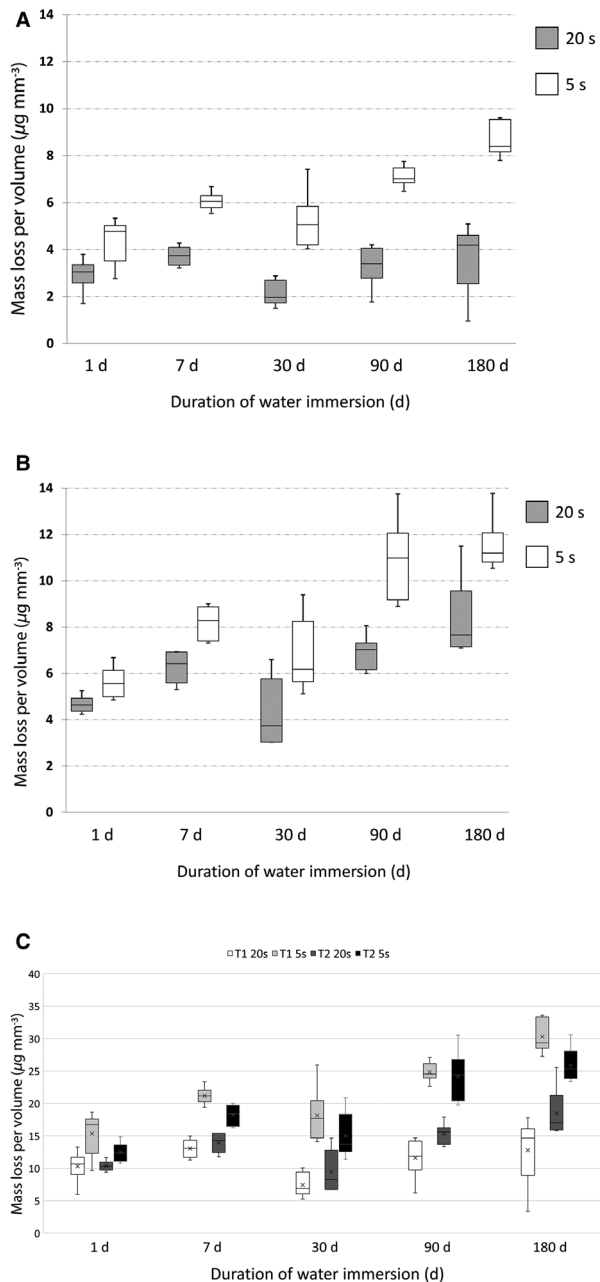


Fig. 4. Water solubility after different time periods (5 s or 20 s) of light curing. Data represent mass loss per unit of volume over days of water immersion. (A) Solubility of Grandio (material T1). (B) Solubility of Tetric EvoCeram (material T2). (C) Calculated matrix-related solubility for all four 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.

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

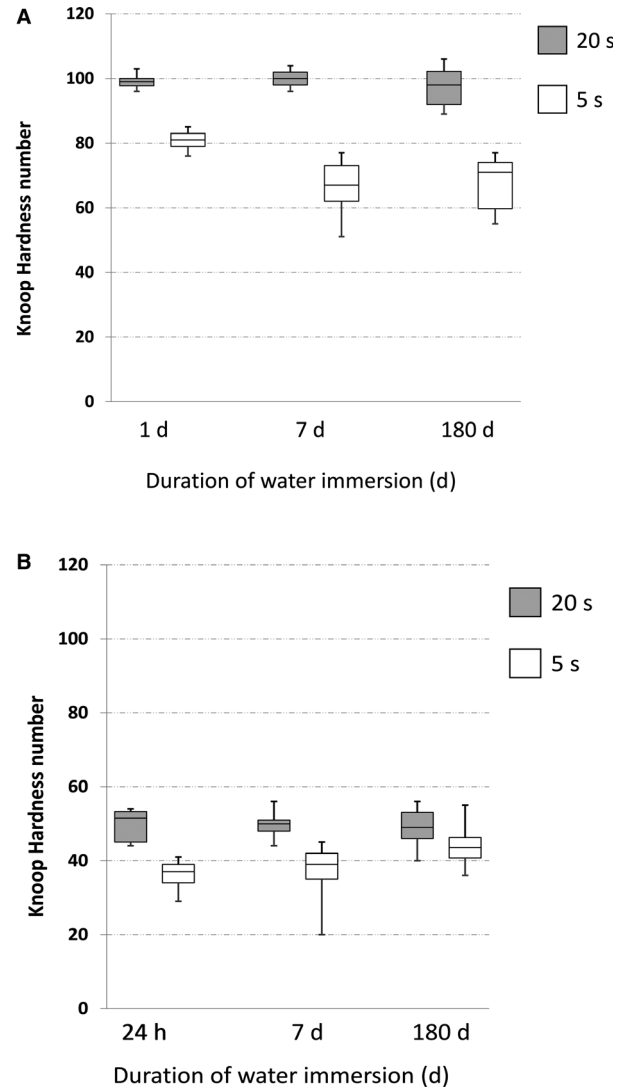


Fig. 5. Effect of ‘low-cure’ (5 s) and ‘high-cure’ (20 s) light curing, and duration of immersion in water, on Knoop surface hardness of Grandio (material T1) (A) and Tetric EvoCeram (material T2) (B). Boxes represent the first and third quartiles, and the horizontal line inside each box represents the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

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

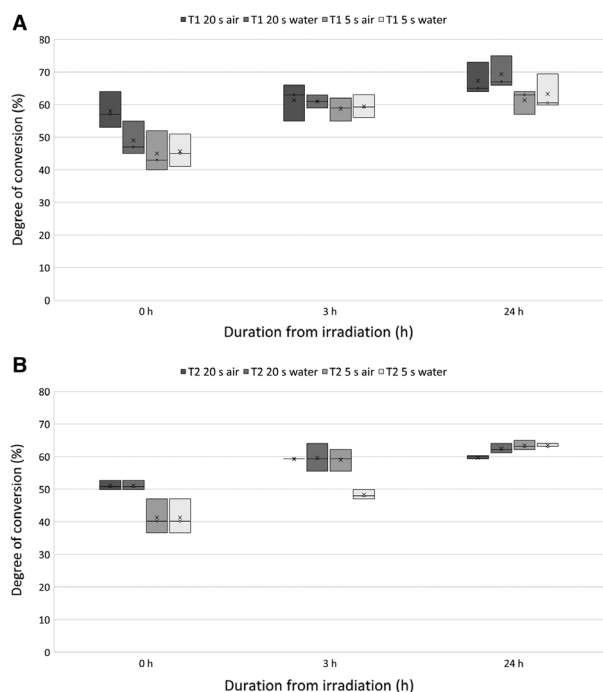


Fig. 6. Degree of conversion over time for storage both in water and in air, as well as for 'low-cure' (5 s) and 'high-cure' (20 s) groups. (A) Grandio (material T1). (B) Tetric Evo-Ceram (material T2). The horizontal line inside each box represents the median, and the mean is illustrated with a cross. 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.

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 \times 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 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 $10 \mu\text{g mm}^{-3}$, and a solubility value of $-0.9 \mu\text{g mm}^{-3}$ after 7 d of exposure to water. For material T2, the water sorption was reported to be $17 \mu\text{g mm}^{-3}$ and the solubility to be $-2.3 \mu\text{g mm}^{-3}$. 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.

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Suboptimal light curing and water exposure: an in vitro investigation in mechanical aspects.

Wikant AW, Nilsson F, Capezza A, Hakeberg M, Gedde UW, Örtengren UT

Aksel W. Wikant^a
Fritjof Nilsson^b
Antonio J. Capezza^b
Ulf W. Gedde^b
Magnus Hakeberg^c
Ulf T. Örtengren^{a,d}

^aDepartment of Clinical Dentistry, Faculty of Health Sciences, Tromsø University, Tromsø, Norway
Aksel W. Wikant: aksel.wikant@uit.no

^bSchool of Engineering Sciences in Chemistry, Biotechnology and Health, Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden
Fritjof Nilsson: fritjofn@kth.se
Antonio Capezza: ajcv@kth.se
Ulf W. Gedde: gedde@kth.se

^cDepartment of Behavioural and Community Dentistry, Institute of Odontology/Sahlgrenska Academy, University of Gothenburg, Gothenburg, Sweden
Magnus Hakeberg: magnus.hakeberg@odontologi.gu.se

^dDepartment of Cariology, Institute of Odontology/Sahlgrenska Academy, University of Gothenburg, Gothenburg, Sweden
Ulf T. Örtengren: ulf.ortengren@odontologi.gu.se

Corresponding author, present address:
Aksel W. Wikant, Department of Clinical Dentistry,
Faculty of Health Sciences,
UiT The Arctic University of Norway,
9037 Tromsø, Norway
E-mail: Aksel.wikant@uit.no

Abstract:

Dental resin-based composites used as direct restorative treatment show increased water susceptibility depending on the monomer blend and radiant exposure. The current project aimed to investigate the mechanical properties of two contemporary dental resin-based composites with two different monomer mixtures and suboptimal light-curing after 30 and 90 days of water storage. Forty-eight samples of each material were made. Twenty-four samples were made using 5 s of 715 mW/cm² irradiance ("low-cure" group) and compared to samples that were light-cured for 20 s with 1317 mW/cm² ("high-cure" group). The samples were stored either in water or air for 30- and 90-days post-cure. After storage, the samples were tested using piston-on-ring biaxial flexure and analysed with differential scanning calorimetry, thermogravimetric analysis, and scanning electron microscopy. Both materials tested showed a reduction in maximal stress at fracture after 90 days compared to the 30 days samples. Furthermore, the "low-cure" sample groups exposed to water for 90 days underwent surface erosion for both materials. For all samples stored in air, the glass transition temperature (fictive temperature) was equal to the storage temperature (37±2 °C), and a hysteresis peak indicated physical ageing. For one of the materials tested, the "low-cure" samples stored in water showed smaller hysteresis peaks and a double glass transition, indicating a difference in curing between the organic filler particles used in the material and the polymer matrix.

Keywords:

Composite, Monomers, Light-curing, Water, Bi-axial flexure

1. Introduction:

Dental resin-based composite materials (hereafter referred to as composite) used in direct restorative treatment degrade when exposed to water. The deterioration of the mechanical properties such as surface hardness, fracture toughness, and solubility over time have been well documented. Still, the extent of such effects appears small within the first year. These effects have been ascribed to swelling and hydrolytic degradation of covalent bonds within the polymer matrix and bonds between the inorganic filler particles and the polymer matrix.

The intent of restricting the water absorption has led to the use of monomers such as urethane dimethacrylate (UDMA) and ethoxylated bisphenol A dimethacrylate (bis-EMA). These monomers hold hydrophobic properties when compared to conventional monomers such as bis-glycidyl-dimethacrylate (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) and have been shown to reduce the water solubility and increase the degree of conversion in copolymer blends (Cornelio et al., 2014).

Highly crosslinked and properly cured dental composites have shown low water solubility and elution (Cornelio et al., 2014; Cuevas-Suárez et al., 2018; Wikant et al., 2020). Despite the information provided in the instructions of use by the manufacturers, research indicates a widespread occurrence of sub-optimal light curing of RCMs in the dental clinics (Barghi et al., 2007; Hao et al., 2015; Jadhav et al., 2009; Miyazaki et al., 1998). The reduction was most often caused by poor maintenance and instrument degradation.

The consequences of insufficient light curing of dental composites depend on the material's radiant exposure (irradiance*time). Too low radiant exposure would leave the material in an uncured state easily detected clinically. Still, a material that has received a radiant exposure far lower than the recommended limits provided by the manufacturer may appear hard on clinical inspection (Price, 2014). Sub-optimal light-curing reduces the material's mechanical properties and increases solubility (Catelan et al., 2015; Halvorson et al., 2002; Kopperud et al., 2013; Wikant et al., 2020).

An earlier study on experimental composites revealed that replacing the bis-GMA monomer with bis-EMA reduced the water sorption and solubility of the materials tested (Cornelio et al., 2014). The water solubility of 2 contemporary dental RCMs increased when exposed to less-than-recommended radiant exposure during light-curing (Wikant et al., 2020). Moreover, the Knoop surface hardness of samples was lower for the groups exposed to the lower radiant exposure, and the reduction depended on the duration of water exposure (Wikant et al., 2020).

As dental RCMs are multi-phased materials (i.e., organic polymer matrix and fillers), the effect of water exposure may be linked to either phase, the link between them, or both. It has been found that neat resins undergo water sorption, swelling, and elution of constituents, and the same trends have been reported in dental RCMs (Ferracane, 2006; Huang et al., 2002; McCabe and Rusby, 2004; Van Landuyt et al., 2011). The coupling agent providing covalent bonding between the organic polymer matrix phase and the inorganic filler particles have also been suggested as a plausible origin of failure; however, the results presented seems to be contradicting (Ferracane et al., 1998; Ferracane and Marker, 1992; Söderholm et al., 1984).

The (ultimate) flexural strength is the maximum flexural stress a sample can withstand before fracture (Q_{max}). The flexural strength of dental RCMs is often measured using a 3-point or 4-point bending setup of a rectangular bar-shaped material sample (Floyd and Dickens, 2006; Fróes-Salgado et al., 2010; Ortengren et al., 2000; Palin et al., 2003). However, biaxial flexure test setups seem to produce less variability in the data (Palin et al., 2003). Differences in light-curing (i.e., light-curing in overlapping

sections) of the sample have been mentioned as a contributing factor to the increased variability when using 3 or 4-point bending. The biaxial flexure test setup allows for the testing of disc-shaped samples with a diameter corresponding to the diameter of the light-curing tip (Palin et al., 2003). Using this sample and curing protocol, the same sample size could be used for sorption, solubility, and bi-axial flexural tests.

Results from a recent project in our research group showed that samples receiving a radiant exposure less than 4 J/cm^2 (5 s with 715 mW/cm^2) showed increased solubility and a reduction in Knoop surface hardness compared to identical samples exposed to a radiant exposure of $26,6 \text{ J/cm}^2$ (20 s, 1317 mW/cm^2) (Wikant et al., 2020). It was concluded that the differences were primarily based on differences in matrix composition and radiant exposure.

The present study investigated the maximum flexural stress before fracture (Q_{\max}) on dental composite materials with different monomer compositions and the effects of water storage (vs. air) and radiant exposure. Thermal analysis (TGA and DSC) was used to assess the thermal behaviour of the composites and determine their glass transition (fictive) temperature and degradation temperature. The fracture surfaces of the dental composite samples created in the flexural tests were further assessed using scanning electron microscopy (SEM) to visualize the microstructure. The null hypothesis was that not even a suboptimal light-curing protocol would cause changes in Q_{\max} or fictive temperature.

2. Materials and methods:

Two contemporary, commercially available dental composite materials for direct restorative treatments (Voco Grandio® and EvoCeram®) were tested and compared. Mechanical biaxial flexure tests (Qmax), thermal analysis (TGA and DSC), and Scanning Electron Microscopy (SEM) was used to assess the differences between the two composite materials and the effects of different treatments.

2.1. Sample preparation

The two composite materials (VOCO, Cuxhaven, Germany, hereafter GR) and Tetric EvoCeram® (Ivoclar/Vivadent, Schaan, Lichtenstein, hereafter TEC) were provided directly by the manufacturers. All the delivered material had the same batch number for each composite and was delivered in 3 g or 4 g syringes.

Table 1 and 2: Data for Voco Grandio® as listed in the MSDS and for Tetric EvoCeram® according to product information [ref] complemented by information from the Safety Data Sheet provided by the manufacturer. (<http://www.ivoclarvivadent.com/en/p/all/products/restorative-materials/composites/tetric-evoceram>).

Grandio®, Voco Gmbh

Substance	CAS	Amount
Bis-GMA	1565-94-2	2.5 – 5 wt. %
TEGDMA	109-16-0	≤ 2.5 wt. %
Polymer matrix in total		28.6 vol. %
Inorganic filler		71 vol. % (87 % by mass)

Table 2: Data of monomers found for Tetric EvoCeram® according to product information

(<http://www.ivoclarvivadent.com/en/p/all/products/restorative-materials/composites/tetric-evoceram>),

complemented by information from the Safety Data Sheet provided by the manufacturer.

Tetric EvoCeram®, Ivoclar Vivadent AG

Substance	CAS	Amount
Bis-GMA	1565-94-2	2.5 < 10 wt. %
UDMA	72869-86-4	2.5 < 10 wt. %
Bis-EMA (mix, avg. Mn ≈540)	41637-38-1	2.5 < 10 wt. %
Polymer matrix in total		46 ± 1 vol. %
Inorganic filler		54 ± 1 vol. % (75.5 ± 1 wt. %)

For each of the two composites tested, 24 cylindrical samples (1 mm thick, $\varnothing = 10$ mm) were prepared for both light-curing setups described by Wikant et al., 2020. The samples were made in a

white (poly)tetrafluoroethene mould, and the material was covered with a strip of mylar sheet during polymerisation. After polymerisation, the samples were removed from the mould, inspected visually for defects, and any excess material was trimmed off with a scalpel. The samples were then stored in separate, marked dram glasses. For the groups to be exposed to water, 5 ml of distilled water (Grade 2 ISO 3696:1987) were added within 5 min post-cure.

- High-cure light-curing setup (hereafter referred to as HC) with 20.2 s illumination, the mean irradiance of 1318 mW/(cm)² and mean radiant exposure of 26.6 J/cm².
- Low-cure light-curing setup (hereafter referred to as LC) with 5.2 s illumination, a mean irradiance of 716 mW/(cm)² and a mean radiant exposure of 3.7 J/cm².

The light-curing unit used for all samples was Bluephase G2 (Ivoclar/Vivadent, Schaan, Lichtenstein), and the RCM was at room temperature (≈23 °C) before light-curing. All samples were stored individually in capped dram glasses. 48 samples were made for each material, a total of 96 samples for both materials combined. The samples for each material were then split into four groups of 6 samples each. All sample containers were re-capped and stored in a heating cabinet at 37±1 °C for 30 and 90 days. The duration of water exposure was based on findings from earlier projects where the mass of samples exposed to water reached a more stable level after 30 days (Wikant et al., 2020). Dickens et al. found that material samples containing bis-GMA absorb moisture from the air over time (Dickens et al., 2003). Therefore, the capped dram glasses were stored in a desiccator during the storage period.

2.2. Mechanical biaxial flexure test

The biaxial test setup was chosen because it enables flexural testing on cylindrical samples, a prerequisite for the selected light-curing setup. Bi-axial flexural testing of dental composites has been found to produce more reliable results due to the more consistent light-curing of samples compared to 3-point bending designs (Palin et al., 2003).

After the predetermined storage duration of 30 d and 90 d, Piston-on-ball biaxial flexural tests were performed on all samples using a Lloyd LRX (Lloyd Instruments, Fareham, England) with the piston speed set to 10 mm/min. The wet samples were blotted dry and waved in the air for 30 s before being inserted into the test setup. Before fracture testing, the sample dimensions were controlled using digital Venier calliper (Cocraft, Claes Olsson). The force at fracture (N) and deflection (mm) were measured, and maximum radial and tangential stresses at the centre of the samples (in MPa) were calculated using the formula (Shetty et al., 1980):

$$Q_{max} = \frac{3P(1+\nu)}{4\pi t^2} \left[1 + 2 \ln \frac{a}{b} + \frac{(1-\nu)}{(1+\nu)} \left\{ 1 - \frac{b^2}{2a^2} \right\} \frac{a^2}{R^2} \right] \quad (\text{Eq. 1})$$

where P is load, t is the thickness of the sample, a is the radius of the support ring, b the piston radius (uniform loading at the centre), R the disc radius, and ν is the Poisson's ratio. After the biaxial flexural test, the sample pieces were collected and stored in individual marked containers filled with cotton wool to prevent any motions during transportation and storage.

2.3. Thermal analysis

The thermal properties of the different material compositions were assessed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

The thermal transitions of the different samples were assessed using a DSC 820 module (Mettler-Toledo, Switzerland). The DSC method consisted of a cooling ramp from 25 to -80 °C, followed by a heating ramp from -80 to 500 °C at a rate of 10 °C/min. A nitrogen flow of 50 mL/min was used. The samples were clean-cut, and 16.0 ± 0.5 mg of each sample was placed in a sealed aluminium pan.

The thermal stability of the dental material was estimated using a TGA/SDTA 851 module (Mettler-Toledo, Switzerland). The TGA method consisted of a heating ramp from 30 to 900 °C at a heating rate of 10 °C/min. A nitrogen flow of 50 mL/min was used. Samples weighing 45 ± 1 mg were placed in alumina crucibles for the TGA experiment.

2.4. Fractography by Scanning electron microscopy (SEM)

The morphology of the sample top surface and fracture surfaces were investigated in a tabletop SEM, TM 1000 (Hitachi, Japan), using an acceleration voltage of 10 kV and 6 mm working distance. The samples were placed on conductive carbon tape, and a minimum of two surfaces was investigated. The high-resolution images of 1 sample from each group were obtained in an FE-SEM S-4800 (Hitachi, Japan), using 3 kV and 8 mm working distance. The samples were coated in an Agar 208RH High-Resolution Sputter Coater for 15 s using a Pt/Pd target, leaving a ca. 2 nm thick coating layer.

2.5. Statistics

Statistical tests were performed for the biaxial flexural test results (Q_{max} values) to determine statistically significant differences between the groups. Shapiro-Wilkinson's test of normality was performed on all sample groups to evaluate the distribution of the results. In addition, the homogeneity of variance was assessed with Levene statistics. General linear models (GLM) for repeated measurements over time were performed to evaluate the development of the mechanical test parameters between the exposure groups considering both the exposure medium (water or air) and light-curing setup. Within- and between-group effects were evaluated for GR and TEC, and interaction terms for the covariates exposure medium and light-curing dose.

3. Results:

3.1. Bi-axial flexure test (Q_{max})

The homogeneity of variance and the Shapiro-Wilkinson's normal distribution test for the Q_{max} values displayed P-values higher than 0.05. Within the limits of the test due to low sample size, the data meet the assumption of homogeneity of variance and normal distribution. As seen in Figure 1, the estimated marginal mean Q_{max} values were consistently lower for samples stored in water than for corresponding samples stored in air, an effect that was particularly pronounced for the GR material.

For GR, the general linear model (GML) analysis revealed a significant change over time irrespective of light-curing time and media storage (Wilks' lambda, $p=0.001$). Also, a statistically significant difference for between-subjects effects was detected for storage medium ($p<0.001$) and light-curing setup ($p=0.015$).

For TEC, the GLM analysis indicated an overall change over time (Wilks' lambda, $p=0.025$) but no statistically significant values for the interaction terms of light-curing setup or media storage. The analysis showed significant differences concerning light-curing setup and media storage between groups.

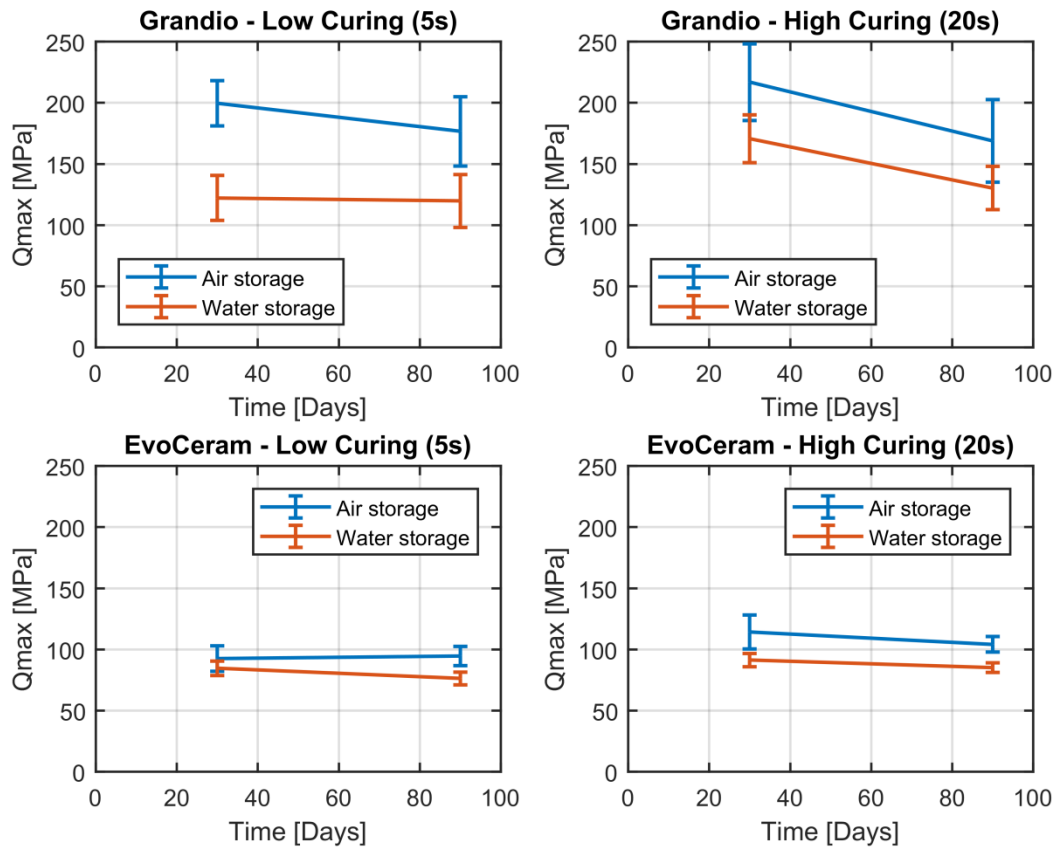
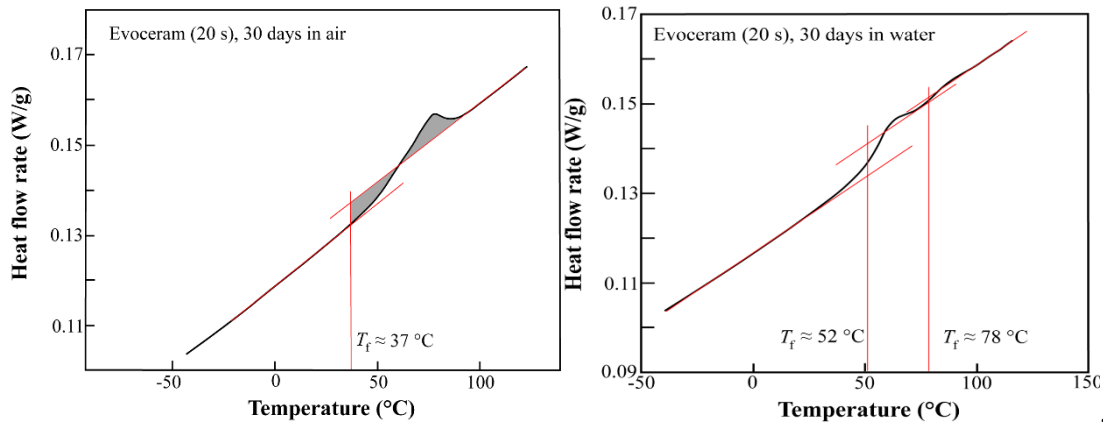


Figure 1. Marginal mean Q_{max} values (in MPa) as a function of storage time in either air or water at 37 °C for GR and TEC composites with 5 s or 20 s curing time. The error bars show one standard deviation.

3.2. DSC:

Calculations of the fictive temperature revealed that all the samples stored in air had approximately the same fictive temperature, 37 ± 2 °C, independent of material type, curing setup, and storage duration. For the GR samples, the samples exposed to water also showed a fictive temperature of 37 ± 2 °C, however for the TEC samples that were exposed to water, two transitions were observed. The fictive temperature associated with the transitions were 52 °C (major transition) and 78 °C. It is believed that water is plasticising the polymer converting it to a transitional rubbery material during water exposure and thus impeding physical ageing during the storage in water.

Figures 2a and b show DSC-thermograms focusing on the glass transition region. The cured samples aged in air displayed a unimodal glass transition with a marked hysteresis peak indicating significant superheating. All the samples aged 30 and 90 days in air showed essentially the same behaviour. The fictive temperature, which marks the intersection of the glassy and liquid lines, was practically the same for all these samples, 37 ± 2 °C. This indicates that all samples aged in air underwent physical ageing and that they reached an equilibrium state at the particular temperature; the fictive temperatures recorded were indeed equal to the ageing temperature used in the study (Gedde and Hedenqvist, 2019). A distinct hysteresis peak is also characteristic of physically aged samples (Gedde and Hedenqvist, 2019). The polymer content of the TEC samples is higher than that of the GR samples, and thus the intensity of the glass transition process is higher in the former set of samples. However, the air-aged GR samples showed a similar behaviour as the corresponding TEC samples.



Figures 2a (left) and 2b (right) show the DSC curves and the calculations of the fictive temperature. The area between the black line and the upper oblique red line at the hysteresis peak is replicated on the lower side of their intersection. The vertical red line marks the lower limit of the lower volume, making both the grey areas equal in size. The intersect of the vertical red line and the x-axis determine the estimation of the fictive temperature.

Fig. 2 b showed the typical behaviour of the TEC samples after ageing in water with much smaller hysteresis peaks and a double glass transition; the main glass transition (expressed in terms of a fictive temperature) appeared slightly above 50 °C, and a much smaller step in the heat capacity (i.e., weak glass transition) at close to 80 °C was also noted. In contrast to the samples stored in air, the samples had not been physically aged. It is suggested that the uptake of water plasticised the samples (i.e., lowered the glass transition temperature) close to the storage temperature (37 °C), leaving the samples in a thermodynamically liquid state outside the temperature window for physical ageing (Gedde and Hedenqvist, 2019). The GR samples showed a depression in the hysteresis peak (not a clear visible peak) after ageing in water, and a double nature of the glass transition was not confirmed. It is known that organic pre-polymerized filler particles are used in the TEC samples, which tentatively can be the reason for the double glass transition of the samples aged in water.

3.3. TGA:

At high temperatures (500-800 °C), the remaining mass of the TEC material samples was much less than for the GR material samples (around 86 vs. 73 wt. %), indicating a larger fraction of inorganic filler particles in the GR material samples. The major mass drop occurred between 300 and 500 °C with a centre at 400 °C for both composites. However, the initiation of the drop started earlier for the TEC material (ca 280 °C instead of 380 °C), which may be an effect of the presence of a pre-polymerised filler phase. The impact of storage time, curing time, and atmosphere were limited, shown by the overlapping curves (Fig 3).

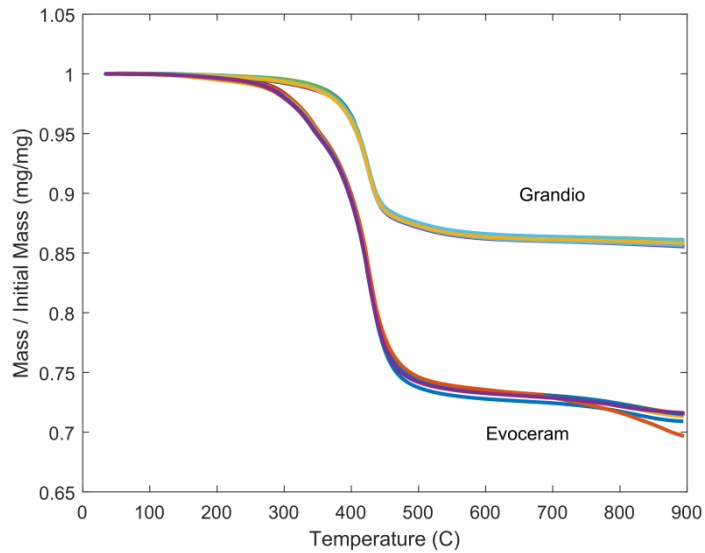


Figure 3: TGA analysis displays the mass loss as a function of sample temperature. The figure shows the difference in inorganic filler particle fraction between the tested materials. All 16 material combinations are displayed in this graph, but most curves overlap almost completely. Essentially, no differences between different storage media, storage times, or curing times could be detected.

3.4. SEM:

SEM fractography and top surface inspection showed distinct differences between TEC and GR (Figs. 5-9); TEC contained pre-polymerized composite particles of irregular shapes sized $300 \pm 100 \mu\text{m}$ with very small inorganic filler particles ($< 5 \mu\text{m}$). GR consisted of a bimodal distribution of globular structures smaller than $5 \mu\text{m}$, and irregular shaped larger particles (between $40 \mu\text{m}$ and $250 \mu\text{m}$) of inorganic filler particles.

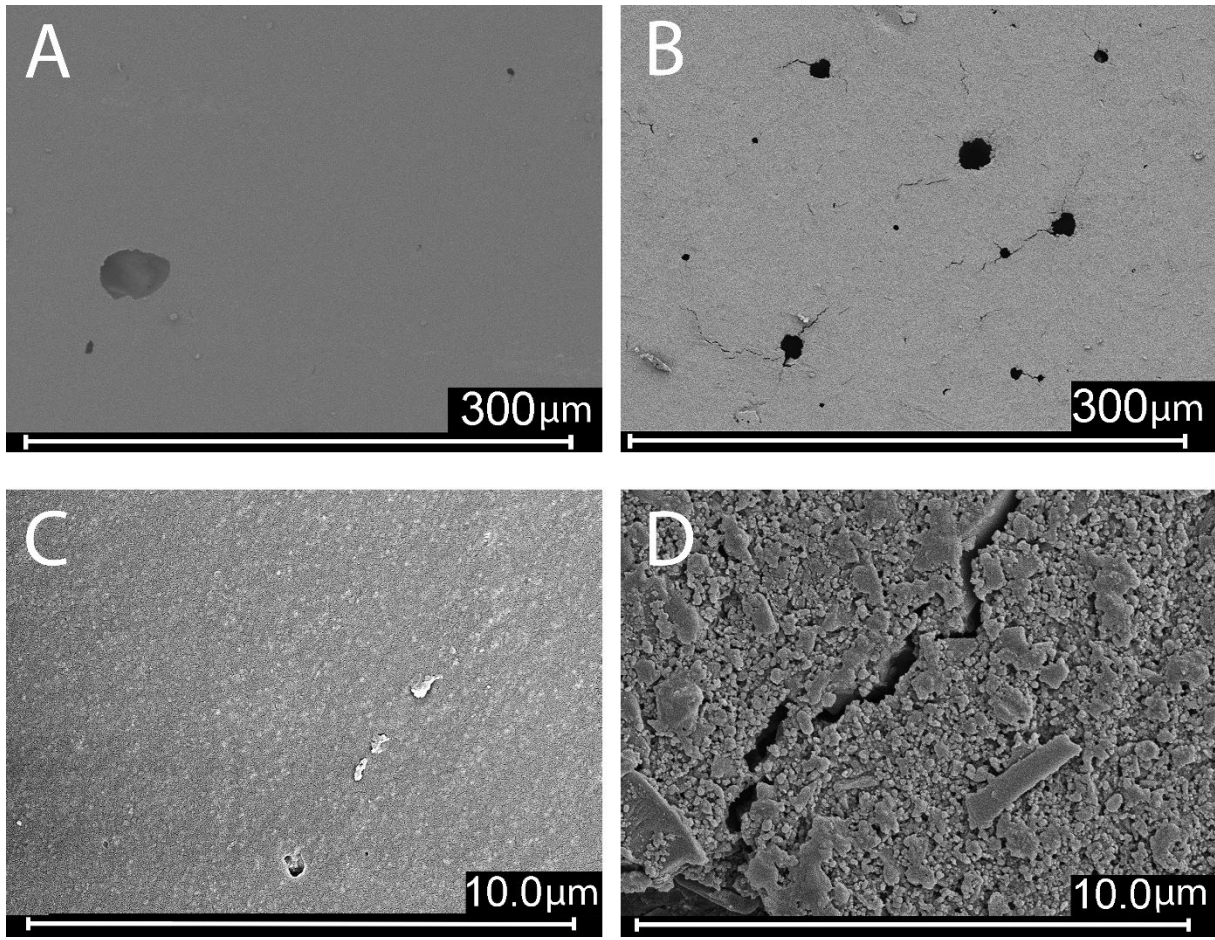


Figure 4: GR sample surface: Differences in light-curing caused changes in the sample surface after 90 d of water exposure. A and C is the HC, while B and D are the LC groups. The sample surface in the LC group underwent erosive degradation (B and D), which was not observed in the HC group (A and C).

“Brittle” features (i.e., erosion and fractures of the polymer matrix) were observed on the surface of the GR LC water group (fig. 4B and 4D). Globular structures ($\varnothing \approx 20\text{-}150\text{ nm}$) were visible, and the polymer matrix in between the globular structures was eroded. Also, fracture lines from and between the surface defects/ porosities could be distinguished, sometimes even clearly continuing below the surface layer (fig. 4D). The visible parts were 50-100 μm in length. No obvious indications of erosion were observed on the LC sample stored in air or the HC sample group exposed to water (fig. 4A and 4C).

Erosion was observed on the outer surface of the low-cure TEC material samples stored in water for 90 d; however, the erosive degradation appeared to be less extensive than for the GR material. When comparing the HC and the LC sample (Figs. 5C and 5D), the filler particles on the LC sample surface are more distinct as they protrude further out from the surface. The effect is caused by erosive degradation of the polymer matrix surface.

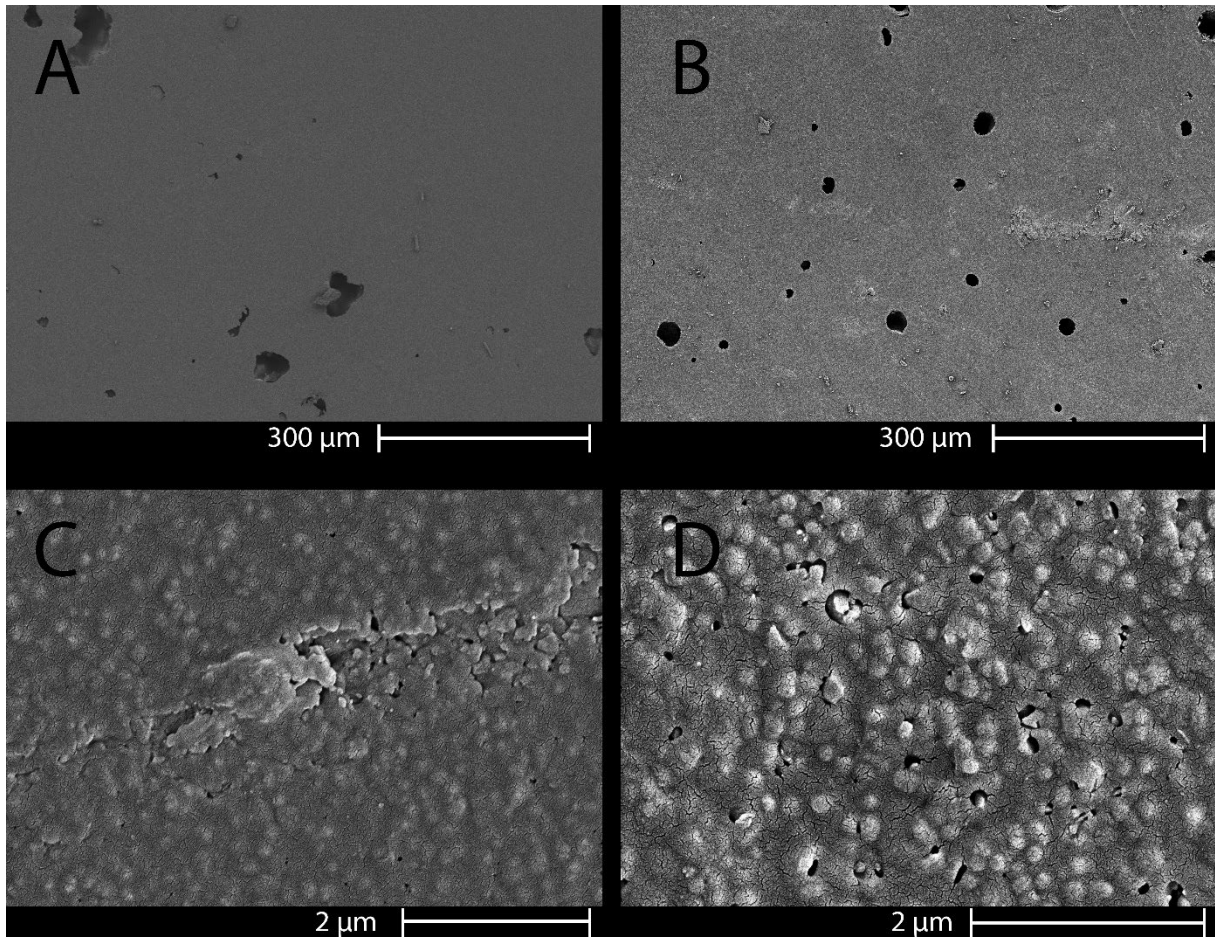


Figure 5: The sample surface of TEC samples exposed to water. Image A and C are of the surface of the HC sample group after 90 d of water, while B and D are from the LC group (also after 90 d of water exposure). The lower magnifications (5A and 5B) show a smooth surface with gas pockets formed during light-curing, probably due to air caught under the mylar sheet. Images 5C and 5D display a higher magnification of the surface, revealing that the integration of the filler particles is failing for the LC group. Furthermore, the polymer matrix between the filler particles has eroded, making the filler particles protrude more clearly from the surface.

The fracture surfaces also differed between the material groups. For both materials, the fracture surfaces of the LC groups had more cracks and pits when compared to the HC groups, irrespective of the medium they had been stored in (i.e., water or air).

For the GR material, the fracture surface of the LC groups stored in water (Fig. 6C) showed multiple crack lines and appeared rougher than the HC in water storage (Fig. 6A) as well as the LC sample stored in air (Fig. 6B). Fracture lines emerging from the surface and propagating into the bulk of the material were observed, and larger dislodged particles were visible along the fracture lines (Fig. 6C). On the fracture surface close to the top of the sample (where it had been exposed to the highest initial tensile forces during bi-axial flexure testing), the polymer matrix appeared stretched (Fig. 6C and 6D). This feature was not observed in the other samples.

The GR fracture surfaces showed both fractured and partially stripped inorganic filler particles (Fig. 7) in all groups. Large filler particles with smooth fracture surfaces that appear to be well embedded into the polymer matrix are observed in the fracture surface (Fig. 7 red arrows). Also, unfractured particles partially covered in the polymer matrix (Fig. 7 blue arrows), as well as imprints of filler particles that had been pulled out from the polymer matrix, were visible (Fig. 6E and Fig. 7 turquoise outlines).

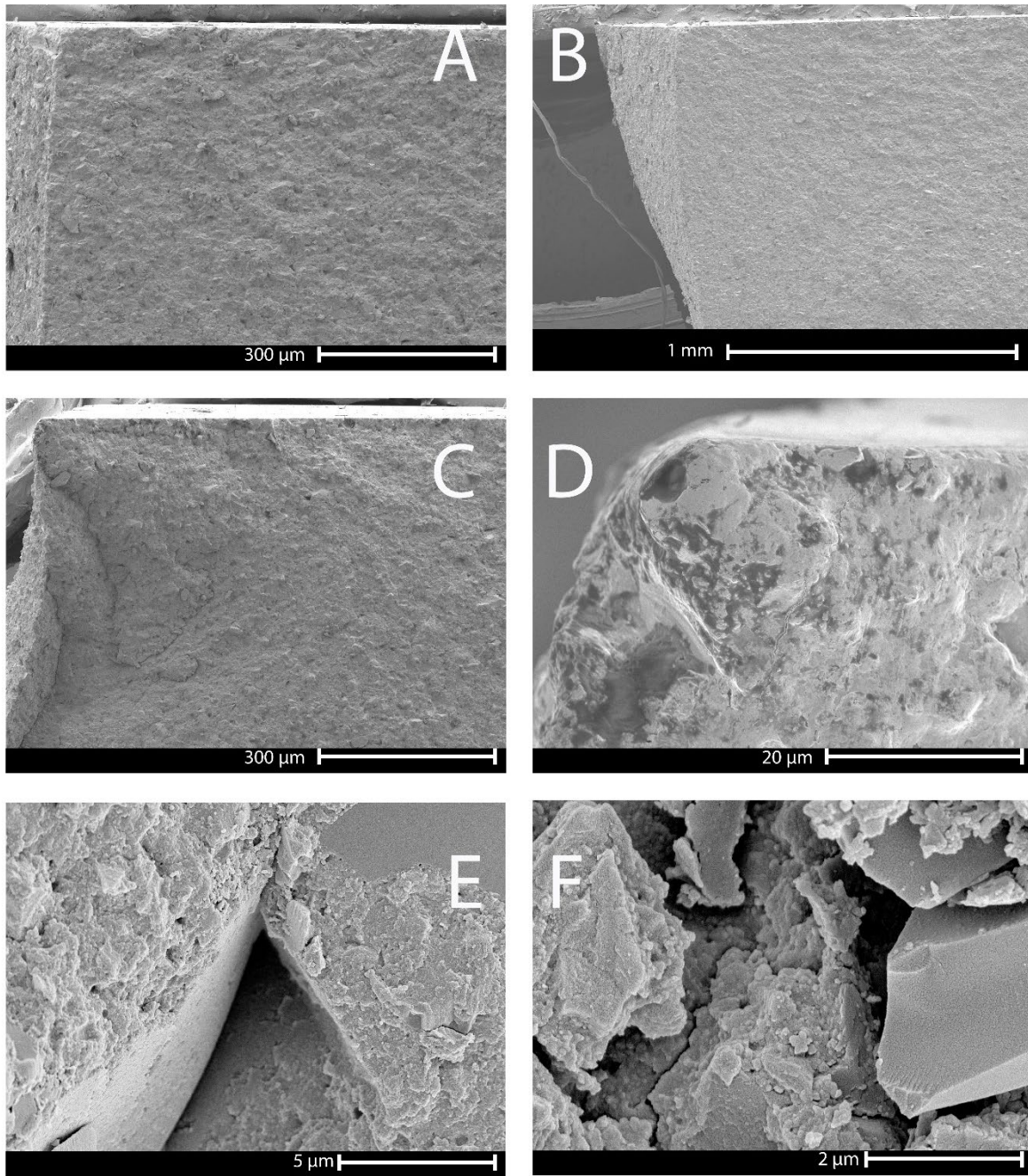


Figure 6: Fracture surfaces of GR. Image A shows an LC sample stored in air after 90 d, while B is the HC group stored in water. Note the intact singular straight vertical fracture edge. C is the LC group stored in water for 90 days, showing a more complex vertical fracture edge, with multiple cracks and dislodged particles. D shows the left upper tip of the same sample depicted in C, showing an irregular structure. E illustrates a typical «imprint» from a dislodged (or “plucked”) filler particle. F shows the «stripped» filler particles observed in LC samples stored in air, where the polymer matrix appears to have been pulled free from the filler particle.

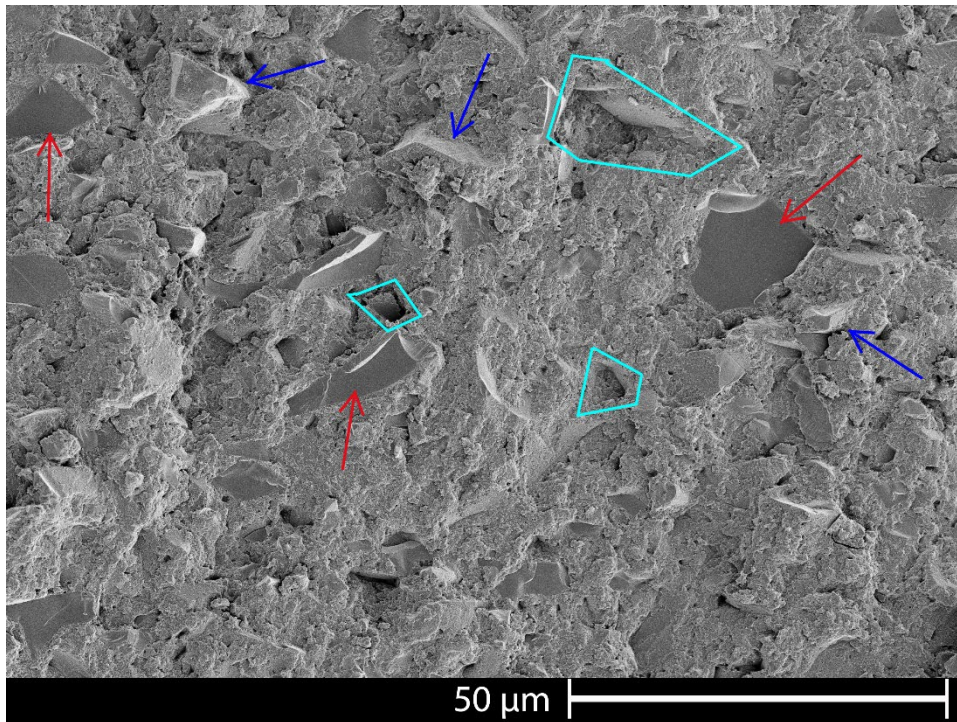


Figure 7: GR fracture surface with typical features found in all groups. Blue arrows indicate partially stripped inorganic filler particles embedded into the polymer matrix. The red arrows point to fractured filler particles, while the turquoise outlines are located around "imprints" made from fully dislodged filler particles.

The GR material low-cure samples stored in air showed stripped filler particles that seemed to have fractured into multiple fragments (Fig. 6F). Zones on the polymer matrix appeared to have suffered from multiple minor fractures, with dislocated filler particles that appeared to be completely stripped off from the polymer matrix. Fewer "stripped" filler particles were observed for the LC samples stored in water. For the samples stored in water, the integration of the fractured filler particles appeared intact (for the magnifications used). The inorganic filler particles were either fully dislodged (Fig. 6E) or partially fractured, and only a few of the fragments observed had any gaps along the borders. "Imprints" after dislodged filler particles or pieces of such particles were visible in the matrix (Fig. 6E). However, in the LC groups stored in air, "stripping" of filler particles and gap formation along the filler particles were observed (Fig. 6F).

For TEC, the (relatively) large filler particles were pre-polymerized composite particles making it more difficult to identify any fractured filler particles as they would appear very similar to the polymer matrix (Fig. 8A and B). In both HC and LC sample groups exposed to water, stripped filler particles were observed (Fig. 8A-D). Indications of failure in integrating the organic filler particles were observed in the HC (Fig. 8C) and LC (Fig. 8D) sample groups. The gap formation along the filler particle observed in the LC water storage group (fig. 5D and 8D) suggests erosion along the filler particles within the polymer matrix and the surface.

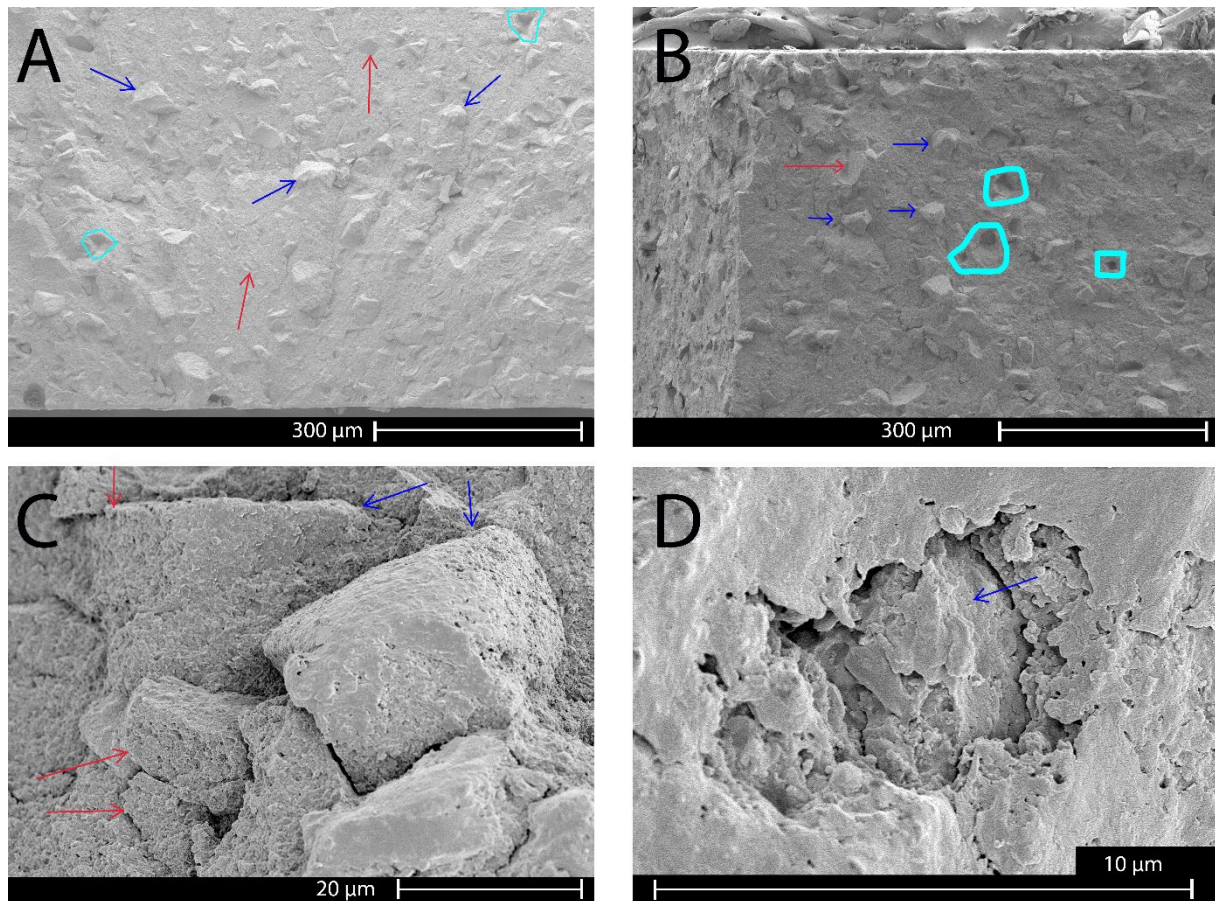


Figure 8: Fracture surfaces of TEC samples: HC (A) and LC (B) show relatively similar fracture surfaces, with protruding filler organic filler particles (blue arrows) and fractured filler fragments (red arrows). «imprints» of dislodged particles are also observed (turquoise outlines). C shows stripped filler particles (blue arrows) in the HC samples stored in water. The red arrows point to rough surfaces caused by fractured particles. D shows an organic pre-polymerized filler particle surrounded by polymer matrix in an LC sample stored in water. An apparent gap between the filler particle and the polymer matrix indicates that the particle's integration is incomplete.

4. Discussion:

Q_{max} was generally lower TEC than for GR samples. Samples stored in water always had lower Q_{max} than corresponding samples stored in air. For most of the samples, Q_{max} decreased with storage time and increased with radiant exposure. Since several of these trends were statistically significant, the null hypothesis of the study (e.g., no statistical change in Q_{max} or T_g) was rejected.

4.1. Discussion about the methods used

The current project was motivated by the findings presented in an earlier paper, revealing that the solubility increased and the Knoop surface hardness decreased over time when the radiant exposure was reduced. By using the same commercial dental RCM products and keeping the sample parameters identical (i.e., the same light-cure protocols and light-curing unit, sample mould, same storage temperature) as in the earlier paper, the water sorption and solubility of the samples in the current project was expected to be in line with the results reported in the former paper. The rationale was to further investigate the mechanical properties of the materials in question by keeping as many of the test parameters identical to the previous work.

The radiant energy needed to achieve sufficient curing in an RCM depends on factors such as type of initiator system, material colour/shade and material translucency. In the scientific literature, intra-

material comparison of surface hardness is often used to evaluate the curing level. To achieve similar surface hardness on both sides of a 2 mm thick polymer disc (top and bottom, where the bottom surface has approx. 80 % of the top value), a radiant exposure (irradiance/ light intensity * duration) of 16-24 J/cm² is required, depending on the shade/colour of the material (Anusavice, 2003; Schattenberg et al., 2008). The HC group was set to be somewhat higher than the reported requirements (26.6 J/cm²) for the current project to assure the materials' "adequate" curing state. The LC light-curing setup was chosen as it produced a clinically indistinguishable material from the HC setup while still only providing a radiant exposure (of 3.7J/cm²) less than ¼ of the reported requirement. This level of radiant exposure was also easily reproducible, as the light-curing unit used (Ivoclar/Vivadent Bluephase G2) had these settings pre-programmed. The argument can be made that the LC radiant exposure might be considered high with a relatively high irradiance of more than 700mW/cm² for 5 s, as reports of curing units used in clinics internationally report mean irradiance values far lower (Hao et al., 2015; Maghaireh et al., 2013; Miyazaki et al., 1998).

The water sorption and solubility values reported by others and in earlier papers indicate that most of the elution and water absorption occurs within the first weeks of water exposure; however, some authors report even longer (Alshali et al., 2015; Braden, 1984; Braden et al., 1976; Örtengren et al., 2001). For this project, the initial elution and absorption were less of interest, as it has been well documented to the authors' knowledge. Despite the reported equilibrium of absorption occurring within these initial weeks, the water sorption and solubility seems to continue at a lower rate for several months post-cure (Alshali et al., 2015; Pearson, 1979; Wikant et al., 2020). The cause of these long-term effects has been linked to an increase in water absorption, but any concurrent effects of low radiant exposure at these stages seem, to the knowledge of the authors, to be less scrutinised (Ferracane, 2006). Therefore, the duration of the water exposure was set from 30 to 90 days.

The 3-point-bending or 4-point-bending setups for flexural tests of dental composites are more commonly used than the bi-axial test setup. However, a piston-on-ring bi-axial flexural test setup was chosen for this project to accommodate the use of an identical sample shape used in an earlier paper with the same materials tested (Wikant et al., 2020). This also excluded the need for light-curing in overlapping sections to produce the samples, keeping the variability within and between samples to a minimum (Palin et al., 2003).

The TGA was performed to investigate the water content within the samples after drying and determine the inorganic filler content within the two materials tested to verify the reported values presented by the manufacturers. As for water content, the TGA did not confirm the presence of water within the dried samples. However, due to the strong coherence between water molecules and the hydrophilic groups in the material, it cannot be excluded that minor quantities of water were present within the material bulk.

The inorganic filler content reported by the manufacturer of the TEC material seemed to be somewhat high compared to the results presented here. The TGA showed an inorganic filler content of approx. 72 wt.%, while the value reported by the manufacturer was 75-76 wt.%. The discrepancy might be the inclusion of the silane coupling agent, which most likely will account for some additional mass because of the high filler surface caused by the nano-metre-sized inorganic filler particles included in the TEC material. For GR, the discrepancy appears to be smaller (within 1-2 wt.%), which is within the expected range of variability.

The mechanical properties of glassy polymers such as dental RCMs are usually described as a function of temperature, as temperature changes significantly impact the material properties (Gedde and Hedenqvist, 2019). The fictive temperature is the temperature at which glass would be in equilibrium if brought to it from its given state. In contrast to the glass transition temperature (the midpoint in the temperature range where a glass turns from a solid to a rubber/liquid), the fictive temperature is not affected by the test parameters used in the analysis (Gedde and Hedenqvist, 2019). The estimation of the fictive temperature was performed to evaluate the polymerisation and the state of cure of the materials.

The differential scanning calorimetric analysis showed that the samples stored in water underwent plasticisation (a lowering of the transition temperature), which prohibited physical ageing observed as a lowering of the fictive temperature. The samples stored in water at 37°C showed a fictive temperature of 37°C, confirming that complete equilibrium of the glassy structure had occurred. After drying, the samples stored in water showed a surface structure of increased free volume with a significant effect on the maximal stress at fracture.

4.2. General discussion

Possible pathways of hydrolytic and hygroscopic degradation of dental composites have been reported (Ferracane, 2006; Göpferich, 1996; Santerre et al., 2001). Despite the well documented pathways for degradation, the results reported are conflicting. For example, Ferracane and Marker, 1992 and Drummond and Savers, 1993 reported no significant difference in mean flexural strength after two years of water exposure when using a 3-point bending test setup. However, the results presented in the present paper are in line with findings done by Curtis et al., 2008, who reported a significant reduction in mean bi-axial flexural strength in dental composites exposed to water for up to 1 year. Furthermore, other investigators have reported a decrease in the mean flexure strength of dental composites after immersion in water up to 6 months using a three-point bending flexure test methodology (ARIKAWA et al., 1995; Øysæd and Ruyter, 1986; Pegoretti and Migliaresi, 2002).

As water diffuses into the bulk of the material, it acts as a plasticiser, reducing the strength of inter-polymer forces (Ortengren, 2000). The DSC results of the present study indicate that physical ageing did not occur in the sample groups stored in water, as water reduced the viscosity and allowed for further movement of the free monomers and radicals within the bulk of the material. The reduction in viscosity combined with the presence of water may lead to propagation rather than crosslink formation, as water alters the conditions for physical ageing and diffusion. Therefore, direct water exposure after finalised light-curing is essential for evaluating this effect. Any extended duration of storage in temperatures close to the polymerisation temperature would allow for the onset of physical ageing (and further crosslink formation). The influence of water on methacrylate-based materials would be most prominent on and close to the sample surface, as the diffusion into the material bulk is time-dependent (Braden, 1984; Braden et al., 1976; Braden and Davy, 1986). Water absorption would be most prominent in bis-GMA-based monomers due to the hydroxyl groups. The relatively rigid monomer structure and high viscosity cause a more abrupt reduction in polymerisation rate compared to bis-EMA (Dickens et al., 2003). The SEM images of the samples surface from the LC GR material after 90 days illustrate the effects of water exposure (fig. 5D). The combination of low radiant exposure and early onset water immersion seems to make the hygroscopic and hydrolytic degradation effects more visible (Ferracane, 2006).

The globular structures observed may be the gel-clusters formed during polymerization, which were initially surrounded by a polymer matrix with a lower crosslink density (Krasowska and Barszczewska-Rybarek, 2016). The polymer matrix surrounding the gel-cluster structures has a low concentration of crosslinks, making it more susceptible to water degradation (Barszczewska-Rybarek and Jurczyk, 2015; Krasowska and Barszczewska-Rybarek, 2016; Rey et al., 2002).

The monomer content will affect the water absorption of the resultant polymer matrix, and materials containing bis-GMA have shown higher water sorption compared to than polymers made from UDMA or bis-EMA (Cornelio et al., 2014; Gajewski et al., 2012). The suggested reason is that the hydroxyl groups of bis-GMA form hydrogen bonds, reducing both the DC and increasing the water absorption (Cornelio et al., 2014). The GR also contains TEGDMA, a monomer more prone to cyclization, which reduces the crosslink density of the material (Elliott et al., 2001). For the material TEC, the inclusion of bis-EMA will most likely reduce the intermolecular forces (i.e., reduces the viscosity and increase the DC) because of the lack of hydroxyl groups, compared to bis-GMA (Gajewski et al., 2012; Kalachandra et al., 1997; Lemon et al., 2007). UDMA can form hydrogen bonds; however, the flexibility of the monomer allows for the formation of intramolecular hydrogen bonds that strongly reduce the viscosity of the material. Therefore, bis-EMA and UDMA allow polymerisation to continue further despite becoming diffusion dependent (Dickens et al., 2003).

The Biaxial flexure test revealed that the Q_{max} of both materials tested were affected by the duration of storage/exposure. For GR, the GLM statistical test indicated that water exposure further reduced the mechanical properties. The results suggest that the hydrophilic nature of the monomers and the polymer matrix structure in GR increased the rate of the water effects. The LC group had already reached a more stable state within the first 30 days of exposure/storage. For the more hydrophobic TEC material, the effects of water exposure seem to be less prominent, and therefore other degradative processes are more influential within the storage duration tested.

The difference in filler particles can further explain the difference in Q_{max} between the materials tested. As the TEC material contained composite-based filler particles (i.e., prepolymers), the integration of these fillers may be weaker than the inorganic fillers used in GR. Cured composite materials tend to lose the ability to form covalent bonds with polymer radicals in new composite materials over time, as the available, free monomers are reduced. According to research on repair of dental composite restorations, the bond strength between cured and uncured material start to decrease if the cured material has been stored for more than 14 days (i.e., dry storage) before the repair attempt (Eliasson and Dahl, 2017; Mjör and Gordan, 2002; Valente et al., 2016). For pre-polymerized filler particles, such reduction could be affected by the production process and the shelf-life of the composite materials. Therefore, organic composite filler particles may not provide the same ability to form covalent bonds with the polymer matrix as inorganic filler particles treated with a silane coupling agent. It is unclear from the information provided by the manufacturer of the material TEC whether the composite filler has been treated with any form of coupling agent before incorporation. However, the addition of a silane coupling agent would only be relevant on the surfaces of the smaller, exposed inorganic filler particles within the composite filler, making up a significantly lower surface area than a coated inorganic filler particle.

The SEM study showed structural features suggesting degradation induced by water between the constituents of the composites tested. For both materials tested, the erosive degradation observed indicates an erosion of the polymer matrix surrounding the nanometre-sized inorganic filler particles and/or on the filler particles themselves (see fig. 7D and fig.8D). The images of TEC illustrate erosion of the organic filler particles or the polymer matrix surrounding them, as there are apparent differences between the LC samples stored in water to the samples stored in air. Elution and degradation of pyrogenic silica have been reported by Söderholm et al., 1984, 2000 among others, and the osmotic forces caused by ion elutes have been suggested as the cause of fractures in the composite material (as seen in fig. 7D).

The SEM images for TEC indicate that the integration of the organic filler particles was weaker than the polymer matrix, as stripped composite particles with larger smooth surfaces were detected in both curing setups of the TEC material stored in water for 90 days (see Figs. 8C, 8D, 11C, and 11D). For the GR HC material samples, the inorganic filler particles observed appeared to be covered in polymer matrix remnants to a much larger extent. Furthermore, fracture lines along the outline of the organic filler particles were observed in TEC. In contrast, the inorganic particles in GR were often fractured/split, and fracture lines/gap formation along the circumference of the embedded particles were rarely observed. The differences observed between the two tested materials suggest that using a silane coupling agent produced a better and more stable integration of the filler particles within the limited observation timeframe.

On both the TEC LC and HC samples exposed to water for 90 days (Fig. 8C and D), openings of $\varnothing < 200$ nm appear on the surface. To the knowledge of the authors, the forming of these openings is unclear, but they appear in higher concentrations on the LC sample surface exposed to water. The openings are irregular in outline and larger in diameter than the ones observed on the surface of the HC group.

Moreover, on the LC group, the openings appear to be located around partly exposed filler particles where the filler-polymer matrix integration is incomplete or outright absent (fig 8C and 8D). Similar voids have been described as “filler pluck-out effect” by others; however, it is not apparent to the authors if the current findings are of the same type (Ferracane and Condon, 1992; Sidhu et al., 1997; Wang et al., 2013). It may be hypothesised that these structures are pores/free volume created during the polymerisation process, as the low radiant exposure may cause an increase in the mean polymer segment length between crosslinks. As water facilitates the elution of unbound constituents, further volume loss may occur.

As the light-curing of the dental RCMs samples was performed at room temperature, with the material at the corresponding temperature before the polymerisation, the vitrification would be determined by the ambient temperature (Cook, 1992). The polymerisation was significantly reduced as the viscosity of the forming material led to an upward shift in the glass transition temperature to the point where the T_g was equivalent to the polymerisation temperature. The results presented suggest that the polymerisation temperature does not exceed the ambient temperature. Any increase in temperature caused by the exotherm polymerisation has minimal effect on the fictive temperature for the resultant composite material. In a dental composite with high filler content, the temperature increase caused by the exotherm polymerisation process will be dissipated into the surrounding filler particles. Others have observed and discussed this, and the results presented here correlate with this theory (Cook, 1992).

For the samples exposed to water, the plasticising effect of the water allows further polymerisation and rearrangement of the polymer segments compared to the samples stored in air, as the water lowers the T_g . As the samples were removed from water storage to undergo bi-axial flexure tests and stored in dry dram glasses after fracture, some of the water content within these samples were lost before the DSC analysis. The loss of the plasticising water content increased the fictive temperature, as seen in fig 1b. The unintended drying of the water-stored samples prior to the DSC analysis provided additional insight as the increase in fictive temperature became apparent.

5. Conclusion

Within the limitations of the present study, the following conclusions can be drawn: Reducing the radiant exposure reduced the mechanical properties tested. The monomer constituents affect the water sensitivity of the materials and reducing the radiant exposure will make the materials more sensitive to water degradation. The material based on a combination of bis-GMA and TEGDMA appeared to be more susceptible to water degradation than the material that contained more hydrophobic monomers such as bis-EMA and UDMA within the exposure duration tested.

The integration of organic filler particles within the TEC material tested appeared to be further weakened by water exposure. Crack formation along the filler particles was observed after 90 days of water exposure for both curing setups.

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