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Experimental investigation of dental composites degradation after early water exposure

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Abstract:

While dental composite long-term aging has already been studied in the past, no data exist about the early aging while it might be detrimental regarding the composites' longevity. This study aims to better understand the effects of early water exposure on dental composites. Dental resin composites with different fillers ratio were subjected to water exposure during 24h, 1 week, or 1 month. After photopolymerization, the samples were stored different conditions, whether in wet or dry condition (W, D, respectively) and in wet conditions after a first 24h storage in dry conditions (DW). Three-point bending tests were performed to measure the flexural modulus. The samples were then subjected to a sorption/desorption protocol. While the matrix alone did not undergo any mechanical degradation with exposure time, the composites matrices presented a decrease in elastic modulus. This decrease was the highest for the matrix with non-silanized fillers. Interestingly, the DW condition was detrimental for all the samples. Regarding the sample with non-silanized fillers in DW for 1 month presented an elastic modulus lower than the matrix alone. These results were assigned to the sorption capacity of the polymer matrix, suggesting that the diffusion mechanisms and the nature of water molecules are determinant in the composite degradation. This study showed that dental composite early degradation mechanisms after water exposure are involved in the polymer matrix post-polymerization process as soon as after 24h. Such mechanisms are detrimental in terms of the dental composite efficiency and have to be understood.

1. Introduction

The placement of dental composites has become a standard method in restorative dentistry for years. They are easy to manipulate and have suitable mechanical and esthetic properties [1]. Despite these advantages, dental composites also undergo a high degradation rate, which increases the risk for restoration failure [2]. Tremendous efforts have thus been made to maintain the properties of composite materials while increasing their longevity.

To improve the longevity of dental composites, the critical oral environment in which they evolve must be considered [3]. Throughout its lifespan, a dental restoration is subjected to complex physicochemical solicitations such as masticatory loads or acidic beverages, which alter the composite material properties promoting its early failure [2]. Among these, water aging is known to have a detrimental influence on the mechanical properties of different types of biomedical composites [4–6].

The mechanism of water degradation in polymer-based composites is somehow complex, involving both the organic matrix, the inorganic phase, and their interface. On one hand, water acts as a plasticizer for the matrix, promoting mobility between polymer chains, thus decreasing its elastic modulus [7]. On the other hand, water modifies the organic – inorganic interactions [8]. This may lead to a debonding between the matrix and the filler or a decrease in their interface properties, thus decreasing the composite's mechanical properties [8–10].

Due to the large variety of dental composite types, understanding the mechanisms of dental composite degradation through water aging is challenging. Composite water sorption depends on the composition of the matrix [6,11,12], or filler content [13], or silanization [14,15], while no apparent influence of water has been observed on the degree of conversion of the polymeric matrix [16,17],

More than 20 years ago, Ferracane et al. performed an interesting study involving a single matrix composition with different filler contents, curing time, and amount of silane coupling agent [18]. Interestingly, they observed that long-term water aging (up to 1 year) only had little effect on the elastic properties of the different samples. While these results provide relevant insights concerning water aging of dental composites, they do not elucidate the influence of water exposure on the early time of dental composites commissioning. Only few is known whether or not an abnormal initial composite water exposure has an influence on its further aging degradation.

The current study therefore aimed to investigate the influence of early water exposure on the elastic properties of dental composites with a defined matrix composition but different filler ratios. The effect of early water exposure was also investigated on a resin composite with non-silanized filler and one with unfilled resin.

2. Methods

2.1. Materials

The resin used in the present study is a non-commercial mixture of 40.3 wt% bisphenol A-glycidyl methacrylate (Bis-GMA), 19.9 wt% triethylene glycol dimethacrylate (TEGDMA), 19.9 wt% urethan dimethacrylate (UDMA), and 19.9 wt% ethoxylated bisphenol A dimethacrylate (EBPADMA). Camphorquinone and 2,4,6-Trimethylbenzodiphenylphosphine oxide were used as photoinitiators, and stabilizers were embedded in the mixture.

Random-shape silanized barium glass particles with an average size of 7 μm and pyrogenic silica particles with an average size of 0.04 μm were added to the monomer mixture. The barium glass accounts for 98.6 wt% of the total content of inorganic fillers and were silanized, if applicable, using 3-Methacryloxypropyltrimethoxysilane.

The materials were supplied by DMG Chemisch-Pharmazeutische Fabrik (Hamburg, Germany). The exact same materials have been used in previous studies [19,20].

To investigate the influence of the filler ratio, an unfilled resin (DMG0), and composite resins filled with 30 wt% (DMG30), and 50 wt% (DMG50) were prepared. Furthermore, to study the influence of the silane coupling agent, a composite resin filled with 30 wt% of non-silanized inorganic filler (DMG30ns) was also prepared.

2.2. Sample preparation

The sample preparation protocol used in the present study has been described previously [19] and is summarized below. The uncured filled matrix was poured in a custom-made mold in a dark room, in order to prepare 2 x 2 x 25 mm³ rectangular samples. The photopolymerization was performed by using a blue light lamp (DeepCure-S, 3M ESPE, Saint-Paul, USA), with a wavelength between 430 and 480 nm and a light intensity of 1470 mW / cm². The entire uncured composite resin was exposed to light through a 1 cm hole, so that each 1 cm section on one side and the other were exposed for 40 s, as explained previously [19]. The exposure used was longer than that recommended by the manufacturer (10 s) in order to ensure a homogeneous curing of the sample and limit potential variabilities due to a polymerization gradient. All the curing procedures were performed at the same controlled room temperature, to limit variations due to the influence of temperature on the polymerization of dental resin composites, but without any control of the relative humidity [21,22].

The cured samples were then subjected to different exposure conditions. A first group was exposed to an excess of distilled water at 37 °C (W, for wet samples), directly after curing as recommended in the ISO 4049. In a second group, samples were stored in dry conditions at 37 °C (D, for dry samples). In a third group, the samples were exposed to an excess of deionized water at 37°C after 24h of aging in dry conditions at 37 °C (DW, for dry wet samples). The water exposure lasted for 24h (24), 1 week (1W), or 1 month (1M). As an example, the sample DW1W was stored for 24h in dry conditions before being exposed to water during 1 week.

For each composition, exposure condition, and exposure time, 7 samples were prepared, resulting in a total of 252 samples categorized in 36 groups. A summary of the conditions, aging times, and the number of samples and their designations are given in the Table 1 of supplementary materials.

2.3. Mechanical experiments

Samples were tested on a three-point bending experimental setup, with a 20 mm supporting span, on an electromechanical testing machine (Adamel Lhomargy DY34, France). A displacement rate of 0.8 mm.min⁻¹ was applied. All the experiments were performed at controlled room temperature [23].

After testing, load-displacement curves were processed to obtain the maximum stress and strain at the bottom of the rectangular samples. The flexural stress σ (MPa) was calculated as follows:

$$\sigma = \frac{3FL}{2bh^2} \quad (1)$$

Where F (N) is the load of the load-displacement curve, L is the span (20 mm), and b and h are sample width (mm) and thickness (mm), respectively, measured using a numerical caliper.

The flexural strain, ε , was calculated as follows:

$$\varepsilon = \frac{6Dh}{L^2} \quad (2)$$

Where D (mm) is the displacement of the load-displacement curve.

The flexural modulus, E_F (MPa), was calculated from the linear part of the processed strain-stress curve and is associated with the pure linear elastic behavior of the sample and was calculated as follows:

$$E_F = \frac{L^3}{4bh^3} \left(\frac{dF}{dD} \right)_{el} \quad (3)$$

To investigate the filler ratio effect with respect to the different exposure conditions and times, the values of the different parameters obtained for DMG30 and DMG30ns were normalized with those of DMG0, as the reference for the unfilled resin, and DMG50, as the reference for the highly filled resin.

After mechanical experiments, the samples were stored at 4 °C in a dry state to limit further water diffusion within the composite.

2.4. Acetone sorption / desorption

In order to assess the structural and chemical degradation of the different composites, the samples were immersed in a solvent able to easily penetrate inside the samples. This solvent is able to swell the polymer network and elute the unreacted monomers while the silica fillers are not soluble by acetone. Due to water exposure, some water may still be retained in the polymer matrix [24]. The solvent also elutes some of this loosely bound water during desorption. Using this protocol, it was not possible to distinguish between monomers or water elution during the desorption process. However, for the dry condition, since there is no water only monomers were eluted from the sample.

After mechanical experiments, the samples were broken into two parts. One of these parts was weighed and immersed in acetone under agitation to promote the penetration of the solvent within the sample. After 72h of immersion, the samples were weighed again and placed in an oven at 40 °C for 48h before being weighed one last time. As the elution of monomers and swelling occurs in the polymer matrix, the parameters were expressed in terms of the resin mass instead of the composite mass. Thus, the mass of fillers (based on the filler ratios) was subtracted from the measured mass.

The mass gained due to acetone diffusion within the matrix (m_{Ac} in %) was calculated as follows:

$$m_{Ac} = \frac{(m_1 - p_{filler} \times m_0) - (m_f - p_{filler} \times m_0)}{(m_f - p_{filler} \times m_0)} \times 100 = \frac{m_1 - m_f}{(m_f - p_{filler} \times m_0)} \times 100, \quad (5)$$

where m_1 (g) is the mass of the sample after sorption and p_{filler} is the mass fraction of fillers (0 for DMG0, 0.3 for DMG30 and DMG30ns, and 0.5 for DMG50)..

The weight percentage of extracted materials with respect to the sample's mass (m_{EI} in wt%) was determined as follows:

$$m_{EI} = \frac{(m_0 - p_{filler} \times m_0) - (m_f - p_{filler} \times m_0)}{(m_0 - p_{filler} \times m_0)} \times 100 = \frac{m_0 - m_f}{(m_0 - p_{filler} \times m_0)} \times 100, \quad (4)$$

where m_0 (g) and m_f (g) are the sample's initial mass and mass after desorption, respectively.

Acetone was chosen because its solubility parameter ($20.1 \text{ J}^{1/2}.\text{cm}^{-3/2}$) is close to that of BIS-GMA and the other monomers that compose the resin and is thus able to solve them [25]. Furthermore, acetone is a highly volatile solvent, which allows easy drying of the sample.

Four samples of each composition and exposure condition, exposed during 24h or 1 month, were used for this sorption/desorption protocol.

As for the mechanical tests, the ratios between DMG30 or DMG30ns over DMG0 or DMG50 were measured.

2.5. Statistical test

Due to the low number of samples per condition, the results were analyzed by applying the non-parametric Mann-Whitney test using R[®] (The R foundation for Statistical Computing, Austria). As several statistical tests were applied, only results with a p-value < 0.01 were considered as significant to limit the risk of statistical error due to multiple testing and thus strengthen the conclusions. For the acetone sorption experiments, the low number of samples did not allow to have a p-value lower than 0.02. Hence, for this measurement, a p-value < 0.05 was considered significant.

3. Results

3.1. Mechanical experiments

For DMG0, the D samples had a higher modulus than the W and DW samples after 24h of water exposure. After 1 week, the flexural modulus was lower in the DW samples compared to the D and W samples. After 1 month, the D samples had a higher modulus than the W and DW samples. Exposure time did not significantly influence the flexural modulus of the DMG0 samples.

For DMG30, the D samples had a higher modulus compared to the W and DW samples, after 24h exposure. After 1 week and 1 month, a significant difference was observed between the 3 different exposure conditions, the D and the DW samples showing the highest and lowest modulus, respectively. There was a significant influence of exposure time on the D and W samples. After 1 week compared to 24h exposure, the flexural modulus increased by 26 % and 16 % for the D and W samples, respectively. After 1-month exposure, compared to 1 week, a 17 % and 7 % decrease in the modulus was observed for the D and W samples, respectively.

For DMG30ns, a significant difference was observed between all conditions, whatever the exposure time, the D and the DW samples showing the highest and lowest modulus, respectively. Aging time had an influence on all exposure conditions. After 1-week exposure, compared to 24h, an increase of 19 % was observed for the D samples and a decrease of 17 % was observed for the W samples. After 1 month, compared to 24h, an increase of 9 % was

measured for the D samples, whereas the modulus decreased by 33 % and 44 % for the W and DW samples, respectively. After 1-month exposure, compared to 1 week, the modulus decreased by 8 %, 20 %, and 24 %, for the D, W, and DW samples, respectively.

For DMG50, the DW samples had a lower modulus than the D and W samples after 24h of aging. A significant difference was observed between all aging conditions, after 1 week and 1-month exposure, the D and DW samples having the highest and lowest modulus, respectively. Exposure time had an influence on the D and W samples. The modulus of the W samples decreased by 20 % after 1-month exposure compared to 24h. A 19 % and 20 % decrease for the D and W samples, respectively, was observed after 1-month exposure, compared to 1 week (Fig. 1 and Table 1).

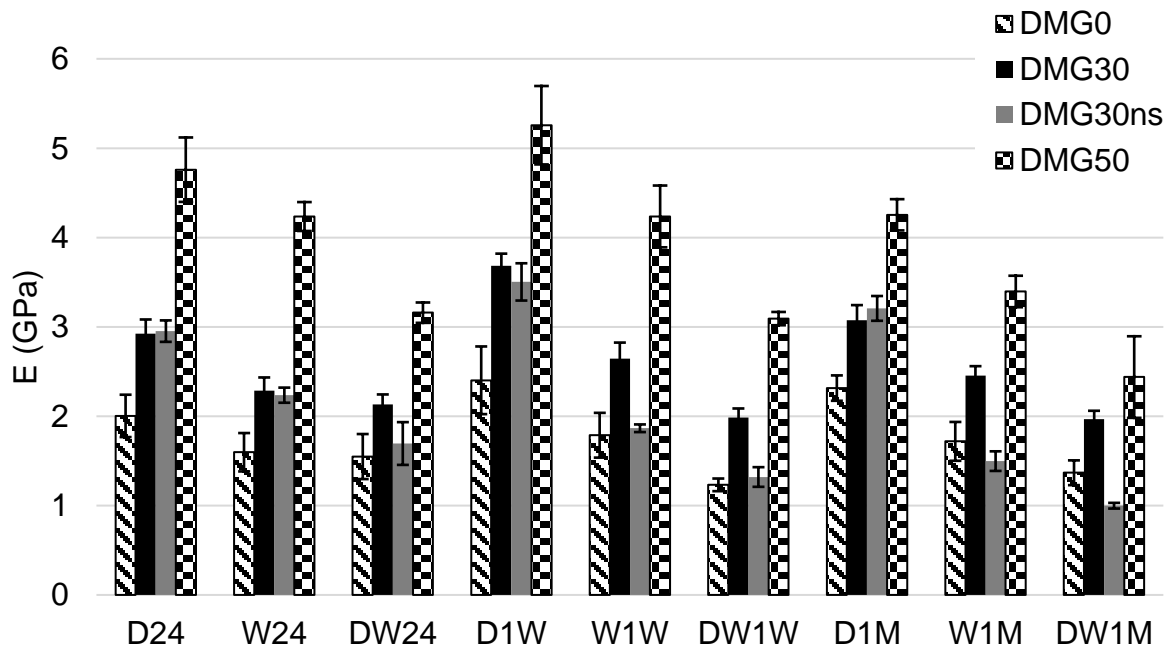


Fig. 1 Histogram of flexural modulus E_F for all samples. D24, D1W, and D1M: Dry for 24h, 1 week, and 1 month. W24, W1W, and W1M: Wet for 24h, 1 week, and 1 month. DW24, DW1W, and DW1M: Dry for 24h, and wet for 24h, 1 week, and 1 month.

E_F (MPa)		Aging condition		
Aging time	Composition	D	W	DW
24	DMG0	2.0 (0.2) ^{W,DW}	1.6 (0.2) ^D	1.6 (0.2) ^D
	DMG30	2.9 (0.2) ^{W,DW} _{1W}	2.3 (0.2) ^D _{1W}	2.1 (0.1) ^D
	DMG30ns	3.0 (0.1) ^{W,DW} _{1W,1M}	2.2 (0.1) ^{D,DW} _{1W,1M}	1.7 (0.2) ^{D,W} _{1M}
	DMG50	4.8 (0.4) ^{DW}	4.2 (0.2) ^{DW} _{1M}	3.5 (0.1) ^{D,W}
1W	DMG0	2.4 (0.4) ^{DW}	1.8 (0.3) ^{DW}	1.2 (0.1) ^{D,W}
	DMG30	3.7 (0.1) ^{W,DW} _{24,1M}	2.6 (0.2) ^{D,DW} _{24,1M}	2.0 (0.1) ^{D,W}
	DMG30ns	3.5 (0.2) ^{W,DW} _{24,1M}	1.9 (0.1) ^{D,DW} _{24,1M}	1.3 (0.1) ^{D,W} _{1M}
	DMG50	5.3 (0.4) ^{W,DW} _{1M}	4.2 (0.4) ^{D,DW} _{1M}	3.1 (0.1) ^{D,W}
1M	DMG0	2.3 (0.1) ^{W,DW}	1.7 (0.2) ^D	1.4 (0.1) ^D
	DMG30	3.1 (0.2) ^{W,DW} _{1W}	2.5 (0.1) ^{D,DW} _{1W}	2.0 (0.1) ^{D,W}
	DMG30ns	3.2 (0.1) ^{W,DW} _{24,1W}	1.5 (0.1) ^{D,DW} _{24,1W}	1.00 (0.1) ^{D,W} _{24,1W}
	DMG50	4.3 (0.2) ^{W,DW} _{1W}	3.4 (0.2) ^{D,DW} _{24,1W}	2.4 (0.5) ^{D,W}

Table 1 Means and standard deviations of flexural modulus (GPa). D24, D1W, and D1M: Dry for 24h, 1 week, and 1 month. W24, W1W, and W1M: Wet for 24h, 1 week, and 1 month. DW24, DW1W, and DW1M: Dry for 24h, and wet for 24h, 1 week, and 1 month. D, W, or DW upper subscripts signify a significant difference with the dry, the wet, and the dry wet groups, respectively, with same exposure time and condition. 24, 1W, or 1M lower subscripts signify a significant difference with the 24h, 1 week, or 1-month groups, respectively, with the same composition and exposure condition.

The flexural modulus of the DMG30 samples was always significantly higher than that of the DMG0, whatever the exposure time and condition. The modulus of DMG30 samples was consistently lower than that of DMG50, except for the DW conditions after 1-month exposure.

After 24h exposure, the DMG30ns modulus was higher than that of the DMG0 for the D and W conditions. After 1 week, the modulus of DGM30ns was higher than that of DMG0 only for the D condition. After 1 month, the modulus of DMG30ns was higher for the D condition, but lower for the DW condition, compared to DMG0. The modulus of DMG30ns samples were consistently lower than that of DMG50 samples, whatever the exposure time and condition (Fig. 2).

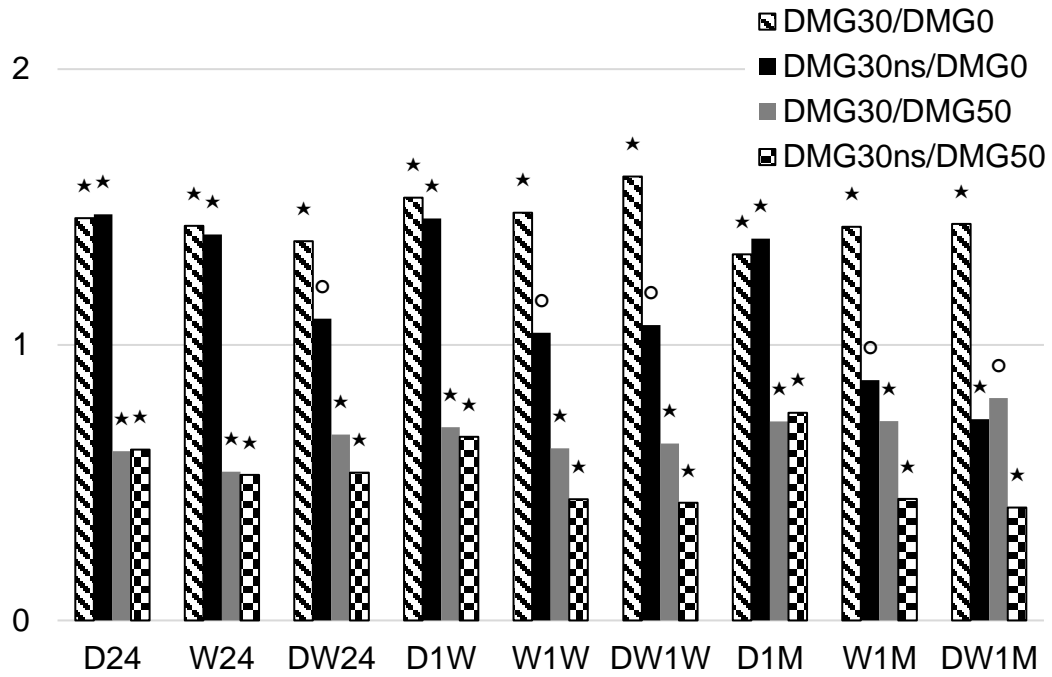


Fig. 2 Ratios of flexural modulus of DMG30 or DMG30ns over DMG0 or DMG50. ★ indicates a significant difference; ○ indicates a non-significant result. D24, D1W, and D1M: Dry for 24h, 1 week, and 1 month. W24, W1W, and W1M: Wet for 24h, 1 week, and 1 month. DW24, DW1W, and DW1M: Dry for 24h, and wet for 24h, 1 week, and 1 month.

3.2. Acetone sorption / desorption

For DMG0, D samples showed a larger acetone uptake than W and DW samples, after both 24h and 1-month exposure. No significant influence of exposure time was measured for the 3 exposure conditions.

For DMG30, after 24h exposure, D samples showed a larger acetone uptake compared to W samples. No significant difference was observed between the D and DW conditions, and between the W and the DW conditions. After 1 month, there was a significant difference between all exposure conditions, the D and W conditions showing the highest and lowest acetone uptake, respectively. Exposure time had an influence on the W samples, as shown by the 12 % decrease in m_{Ac} after 1-month exposure compared to 24h.

For DMG30ns, no significant difference was observed between the exposure conditions after 24h of aging. The W samples showed a lower acetone uptake than the D and DW samples after 1 month of aging. Exposure time had a significant influence on D samples, with a 10 % increase of m_{Ac} after 1 month compared to 24h.

For DMG50, no significant difference was observed between the exposure conditions after 24h of aging. The D samples showed a larger acetone uptake than the W and DW samples after 1-month exposure. After 1 month compared to 24h, there was a 6 % increase in m_{Ac} for D samples, and a 23 % and 15 % decrease in m_{Ac} for W and DW samples, respectively (Table 2).

m_{Ac} (%) mass of uptake Acetone		Aging condition		
Aging time	Composition	D	W	DW
24	DMG0	19.9 (0.5) ^{W,DW}	17.4 (0.9) ^D	18.1 (0.4) ^D
	DMG30	17.2 (0.4) ^W	15.2 (0.5) ^{D_{1M}}	15.8 (0.7)
	DMG30ns	23.9 (0.5) _{1M}	22.6 (1.0)	24.7 (1.6)
	DMG50	15.8 (0.1) _{1M}	16.2 (1.1) _{1M}	15.9 (0.6) _{1M}
1M	DMG0	21.8 (1.2) ^{W,DW}	18.8 (0.8) ^D	18.8 (0.6) ^D
	DMG30	16.8 (0.6) ^{W,DW}	13.4 (0.6) ^{D,DW₂₄}	14.9 (0.3) ^{D,W}
	DMG30ns	26.1 (0.7) ^{W₂₄}	22.1 (1.1) ^{D,DW}	24.9 (0.7) ^W
	DMG50	16.8 (0.5) ^{W,DW₂₄}	12.4 (0.6) ^{D₂₄}	13.5 (0.8) ^{D₂₄}

Table 2 Means (and standard deviation) of m_{Ac} (%). D24 and D1M: Dry for 24h and 1 month. W24 and W1M: Wet for 24h and 1 month. DW24 and DW1M: Dry for 24h, and wet for 24h and 1 month. D, W, or DW upper subscripts signify significant difference with the dry, the wet, and the dry wet groups, respectively, with same exposure time and condition. 24 or 1M lower subscripts signify significant difference with the 24h or 1-month groups, respectively, with the same composition and exposure condition.

The mass of acetone uptake was consistently lower in DMG30 compared to DMG0, whatever the exposure time and condition, but there was no significant difference between DMG30 and DMG50.

Conversely, the mass of acetone uptake was always higher in DMG30ns compared to DMG0 or DMG50, whatever the exposure time and condition (Fig. 3).

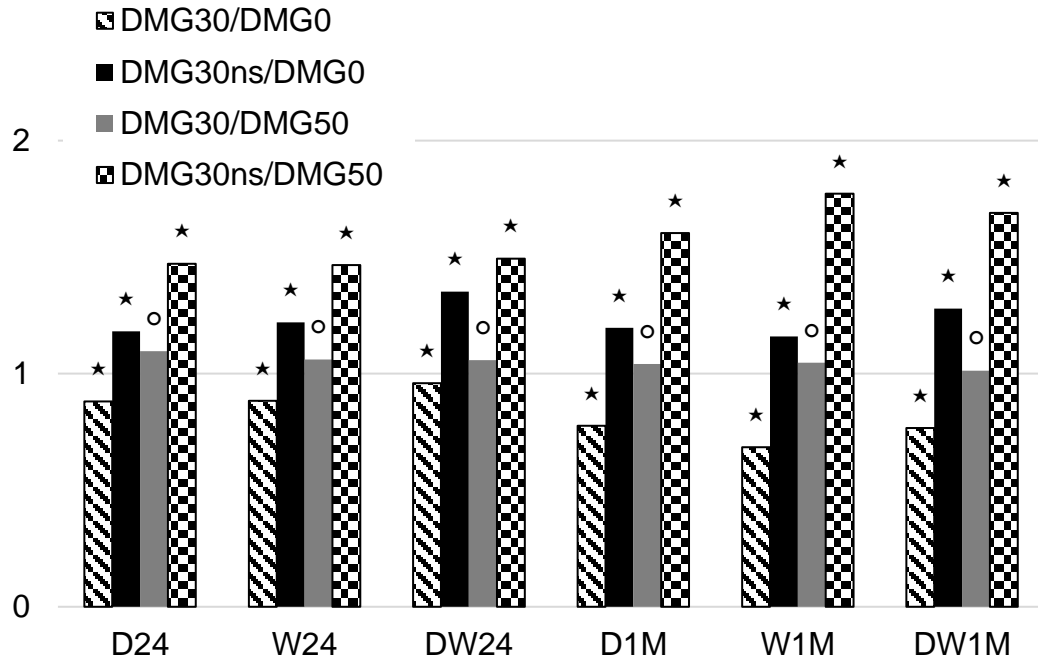


Fig. 3 Ratios of mass of uptake Acetone (m_{Ac}) of DMG30 or DMG30ns over DMG0 or DMG50. ★ means that the difference between DMG30/DMG30ns and DMG0/DMG50 is significant, whereas ○ means non-significant. D24 and D1M: Dry for 24h and 1 month. W24 and W1M: Wet for 24h and 1 month. DW24 and DW1M: Dry for 24h, and wet for 24h and 1 month.

For DMG0, D samples showed a larger mass of eluted monomers than the W and DW samples, after 24h and 1-month exposure. No significant influence of exposure time was measured.

For DMG30 after 24h exposure, D samples showed a larger mass of eluted monomers than the W and DW samples. After 1 month, W samples had a lower mass of eluted monomers than the D and DW samples. No significant influence of exposure time was measured.

For DMG30ns, after 24h exposure, W samples showed a lower mass of eluted monomers than the D and DW samples. After 1-month exposure, W samples had a lower m_{El} than D samples. After 1 month compared to 24h, there was a 30 %, 24 %, and 25 % increase in the mass of eluted monomers for the D, W, and DW conditions, respectively.

For DMG50, there was no significant difference between all exposure conditions after 24h exposure. After 1-month exposure, there was a significant difference between all exposure conditions, the D and W samples showing the highest and lowest m_{El} , respectively. exposure time had an influence on the D and W conditions, as shown by the 37 % increase in m_{El} for D samples, and 44 % decrease for W samples, after 1 month of aging compared to 24h (Table 3).

m _{El} (wt %)		Aging condition		
Mass of eluted material				
Aging time	Composition	D	W	DW
24	DMG0	8.5 (1.3) ^{W,DW}	3.4 (1.0) ^D	4.4 (0.8) ^D
	DMG30	4.1 (0.3) ^{W,DW}	2.2 (0.2) ^D	2.9 (0.5) ^D
	DMG30ns	6.9 (0.6) ^{W_{1M}}	5.4 (0.3) ^{D,DW_{1M}}	6.6 (0.2) ^{W_{1M}}
	DMG50	4.6 (0.2) _{1M}	4.4 (0.9) _{1M}	4.6 (0.3)
1M	DMG0	8.3 (1.0) ^{W,DW}	4.0 (0.3) ^D	5.4 (0.9) ^D
	DMG30	4.7 (0.6) ^W	2.2 (0.5) ^{D,DW}	3.9 (0.6) ^W
	DMG30ns	9.0 (0.4) ^{W₂₄}	6.8 (0.7) ^{D₂₄}	8.2 (0.4) ₂₄
	DMG50	6.3 (0.3) ^{W,DW₂₄}	2.5 (0.5) ^{D,DW₂₄}	4.2 (0.6) ^{D,W}

Table 3 Means (and standard deviation) of m_{El} (wt %). D24 and D1M: Dry for 24h and 1 month. W24 and W1M: Wet for 24h and 1 month. DW24 and DW1M: Dry for 24h, and wet for 24h and 1 month. D, W, or DW upper subscripts signify a significant difference with the dry, the wet, and the dry wet groups, respectively, with same aging time and condition. 24 or 1M lower subscripts signify a significant difference with the 24h or 1-month groups, respectively, with the same composition and aging condition.

After 24h exposure, DMG30 showed a lower mass of eluted monomers compared to DMG0 for the D condition. After 1 month, this mass was lower for both the D and W conditions compared to DMG0. Compared to DMG50, DMG30 samples had a lower mass of eluted monomers for the W and DW conditions after 24h exposure. After 1 month, only the DMG30 samples in D condition had a smaller mass of eluted monomers compared to DMG50.

The DMG30ns samples in W and DW conditions had a larger mass of eluted monomers compared to DMG0 at both 24h and 1-month exposure. The mass of eluted monomers from DMG30ns samples was significantly higher than that of DMG50 samples for all exposure conditions and times, except after 24h of in W conditions (Fig. 4).

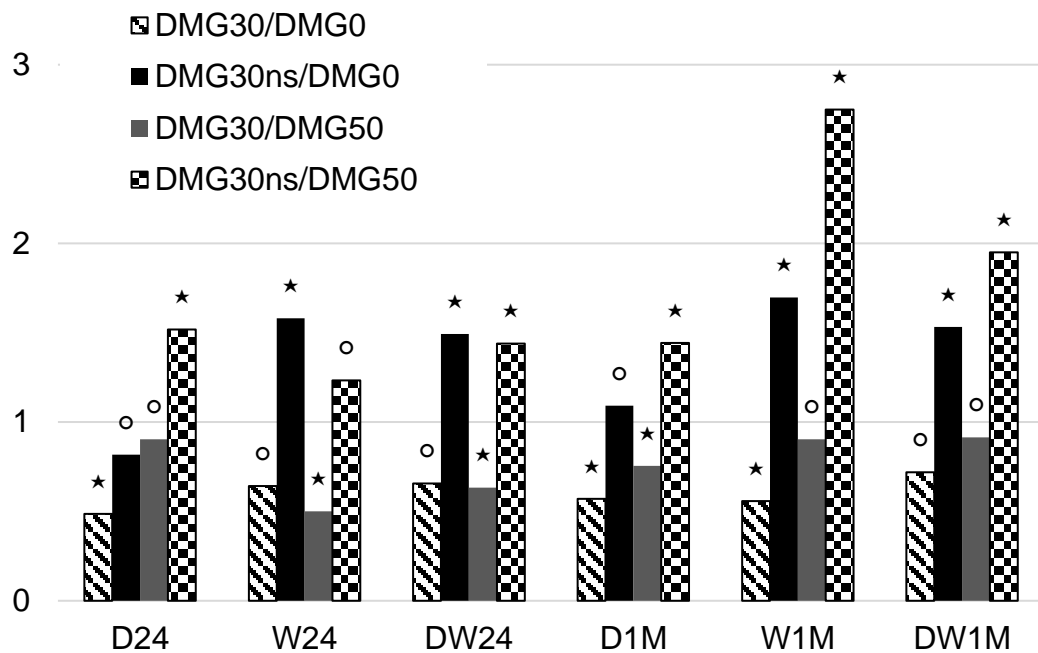


Fig. 4 Ratios of mass of eluted material (m_{EI}) of DMG30 or DMG30ns over DMG0 or DMG50. ★ means that the difference between DMG30/DMG30ns and DMG0/DMG50 is significant, whereas ○ means non-significant. D24 and D1M: Dry for 24h and 1 month. W24 and W1M: Wet for 24h and 1 month. DW24 and DW1M: Dry for 24h, and wet for 24h and 1 month.

4. Discussion

Dental composites water degradation is determinant to ensure their longevity within the oral environment. In the current study, it is shown that water can degrade the composite as soon as 1-week storage depending on its composition. Long terms studies did also find that major variation in the composites elastic modulus happened in the first months of aging [18].

It is known that water can degrade composites by inducing matrix swelling, hydrolysis, and osmotic pressure which may promote physical damage to both the matrix and the interphase between the matrix and the fillers [10,26,27]. In addition, water acts as a plasticizer and increases the material's compliance by interacting with the polymer chains [7,28]. In their work, Musto et al. defined three types of water species depending on the type of interactions between the water molecules and the polymeric matrix [29]. Matrix plasticization is thought to be associated with strongly bound water which breaks hydrogen bonds between polymer chains, compared to free water or loosely bound water [29,30]. The water-based degradation of dental composites thus involves both structural and chemical mechanisms.

Interestingly, the DW condition was the most affected in terms of elastic modulus, for all compositions and exposure times. The results presented in the current study are therefore intriguing: a sample that has been aged for 24h under dry conditions is more prone to water degradation. This result suggests that during the first 24h of post-polymerization, the structure and chemistry of the resin evolve differently, depending on whether it is stored in wet or dry conditions, and that the way the structure evolves will have a major influence on the water-based matrix degradation. Such results are of major interest both regarding the clinical conditions in which the composite is polymerized and for the patient life-style sometimes after the composite placement. To provide the right advised to the clinicians, the early degradation mechanisms have to be understood.

The contribution of the filler content on the type of water species developing within the matrix appears to be an important feature in the current study. On one hand, the unfilled resin, DMG0, had a higher m_{Ac} – the mass of acetone gained - compared to the resins filled with silanized fillers (DMG30 and DMG50), highlighting an easier acetone diffusion within the matrix. This also suggests that the water that has diffused within the DMG0 matrix during the early exposure experiments was loosely bound to the polymeric chains, as strongly bound water is less easily removed by acetone. The other hypothesis explaining this higher acetone uptake for the matrix alone is that acetone diffusion is influenced by the presence the fillers. Still, it has to be noticed that such mechanism depends on the presence of the organo-silane bonds at the matrix-filler interface. The current results have shown a higher acetone uptake within DMG30ns with non-silanized fillers compare to the matrix alone (Fig. 3).

Furthermore, the DMG50 composite was the only silane-based composite for which the DW samples showed a lower flexural modulus than the W samples, after only 24h exposure. Considering that DMG50 showed a similar mass of acetone uptake between the W and DW conditions (after both 24h and 1-month exposure), the filler-based degradation cannot be explained only by the diffusion kinetics of water through the matrix. It is also interesting to note that the flexural modulus of DMG30 was similar to that of the DMG50 after 1 month in DW conditions. With a higher filler ratio, DMG50 undergoes a more detrimental decrease in elastic mechanical properties compared to DMG30. Together, these results suggest a major influence of the fillers on the type of water diffusion pathway and within the matrix.

It is also known that dental resin mechanical properties are associated with its degree of conversion [4]. In Ferracane et al. study, the higher degree of conversion was observed for the composite with 37 % of filler [18]. A too high filler content can result in a lower degree of conversion. This results in a higher content of unreacted monomers act as a pathway for water diffusion [31]. It seems that when the first 24h post-polymerization occurs in dry conditions; the matrix degrade faster in water if the filler content is higher. Accordingly, Palin et al. observed a large variation in dental composite mechanical properties during the first 24h of water exposure [32]. In the present study, m_{EI} - the mass of eluted material - is related to this degree of conversion as it is usually calculated based on the ratio between monomer and polymer content [33]. According to Ferracane et al. study, in the current study, the mass of eluted material is sometimes significantly lower for DMG30 (Figure 4) [18]. Still, in their study, Ferracane et al. did not investigate the degree of conversion of the matrix alone. As water may already have eluted some of these monomers [34,35], the D samples are the ones that reflect the real mass of monomers present in the resin after curing. It is worth noting that the eluted monomer mass for the D samples obtained in the present study are in agreement with previous studies [25]. Furthermore, it is known that the silanization of the fillers has an influence on the degree of conversion of the matrix, with an increased conversion when the fillers are silanized [18,36]. Accordingly, the present results found a difference in the mass of eluted monomers between the DMG30 and DMG30ns composites in D conditions. Furthermore, the elution of monomers from the unfilled resin was the highest, which is in agreement with previous studies [14]. Surprisingly, for DMG30ns and DMG50 aged in D conditions, the mass of eluted monomers increased after 1-month exposure compared to 24h, whereas increasing time is generally associated with a higher degree of conversion due to post-polymerization.

The results obtained in the present study do not allow to determine whether the m_{EI} parameters for the W and DW conditions represent the mass of eluted monomers, the mass of eluted loosely bound water, or the sum of the two. The mass of eluted material increased between 24h and 1-month exposure for the DMG30ns. This signifies that

there is a time-dependent increase in the amount of material easily solubilized by acetone in the non-silanized based composites. Along with this result, the mass of acetone that was able to diffuse within the matrix showed no difference between 24h and 1-month exposure. This suggests that the excess of eluted material in DMG30ns after 1-month exposure compared to 24h is mainly due to free water that penetrates through the porosity with time. This is in accordance with the non-silanized matrix-filler interface that acts as a preferential pathway for water diffusion. Inversely, the nano-porosity of the matrix alone limits the possibility for the water to diffuse increasingly with time. Water diffusion within these nano-porosity may have limited interactions with the matrix, thus limiting its degradation [17]. It is worth noting that the matrix filler interface is often considered as a preferential zone for the mechanical degradation of dental composite associated with the fillers leaching [32,37]. Still, previous studies on the topic mainly work with long ageing time (> 1 month, 26 weeks in [32]). Previous studies have shown that the filler leaching was minimal at 1 month with a large increased as time increases [38,39]. Hence, in the current study, it is hypothesized that the leaching of fillers during water exposure is not involved in the composite mechanical degradation. Furthermore, the water solubility of the matrix-fillers organo-silane bonds using 3-Methacryloxypropyltrimethoxysilane has been shown to be low after 1 month exposure [40]. Such previous results suggest that the filler-matrix bonds, in the case of silanized fillers, may not be involved in the composites after early water exposure. The water diffusion is known to occurs preferentially in the resin phase [41]. Nevertheless, no results can allow to confirm the hypothesis, hence the influence of filler leaching can not be excluded.

Conversely, one can notice that the mass of eluted material from DM30 showed no difference between 24h and 1-month exposure whereas the mass of diffused acetone was decreased after 1 month. This implies less space for acetone to penetrate within the DMG30 matrix after 1 month. This result suggests that the amount of strongly bound water, that is not easily solubilized by acetone, increases with exposure time [42].

While very simple, the analyses performed in the current study show the relevance of investigating the early mechanisms involved during water exposure and their effects on the polymer matrix of dental composites. Defining the relationship between the water species present in the composite, whether free or strongly bound water, might be of great interest to better understand the structural and chemical reorganization of the matrix during the early time of water exposure. This reorganization might be a major factor to explain the decrease in elastic properties of the composite.

The present investigation has different limitations. First, the low content of fillers used does not represent what is used in clinical practice. Practical issues arose when mixing non-silanized fillers with the resin. It was not possible to mix more than 30 wt% of non-silanized fillers, due to particle agglomeration. Therefore, the higher filler ratio used, for silanized based fillers, was set at 50 wt% to limit the difference with the 30 wt% composite. Another limitation was the use of distilled water rather than artificial saliva. It is known that composite behavior during exposure is different whether water or saliva is used as solvent, due to the ionic composition of artificial saliva [43–45]. Understanding the influence of saliva on the degradation of dental composite is undoubtedly clinically relevant. Nevertheless, reproducing human saliva is very difficult, and the compositions used in the literature differ from one another [46]. Due to this reason, and because of the different resin compositions and filler types used herein, it would have been even more difficult to compare the results of this study with those of the literature. Finally, the present study was limited to the study of short-term exposure (up to 1 month) whereas the longevity of restorative composites can exceed several years [47,48]. Nevertheless, the present study shows that the initial

condition in which the dental composites are handling have a major influence on their further water-based degradation. This strongly suggest to rigorously control the environmental condition in which the dental composites are prepared, both experimentally and in clinics, to further control the degradation kinetics. As an example, if the DW condition appears to have a faster degradation kinetics, this suggests that, after being placed, the dental composite needs to be exposed to water quickly in order to prevent a detrimental degradation. This study shows the importance to investigate the early water-based degradation of dental composite as it will have an influence on the composite long-term decrease in materials properties. Future studies have to be done to understand the early water diffusion mechanisms and the nature of water molecules within the polymer matrix depending on the condition of post-polymerization. Such investigations could be done using spectroscopic methods [29,30].

5. Conclusions

In summary, early water exposure has an influence on the mechanical properties of dental composites which is dependent on exposure time and conditions, filler content, and silanization. No degradation of the matrix alone has been observed, while the composite with non-silanized filler underwent the higher degradation both in W and DW conditions. It is suggested that the non-silanized interface between the matrix and the fillers act as a porous preferential pathway for water diffusion, increasing the specific surface in contact with water, and thus promoting the matrix degradation. Inversely, in the matrix alone, the pores are mainly nanopores, limiting the diffusion of water with time. The first storage in 24h before water exposure (DW conditions) appeared as the most detrimental, even for the matrix alone. Interestingly, while the composite with 30 % of filler had a lower modulus in DW during the first week compared to the composite with 50 %, there was no more difference after 1 month. Furthermore, the samples stored in dry conditions presented a higher capacity for acetone diffusion, suggesting a different arrangement of the organic molecules. These results strongly suggest that water plays a major role in the polymer matrix post-polymerization. The initial handling condition (dry or wet) in which the matrix structural and chemical reorganization occurs in the early time after photopolymerization, is likely to greatly influence the water-based diffusion and interactions with the polymer matrix. Depending on this initial handling, a higher amount of filler may not be an advantage in terms of elastic modulus. A clinical significance would be to rigorously control the environment in which the composite is stored and polymerized to promote the suitable post-polymerization during the first 24h. As well as long-term degradation, the early degradation of dental composites after water exposure is critical in regard to its mechanical properties.

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7. Conflicts of interest

The authors declare no conflicts of interest.

8. References

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