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► **To cite this version:**

Rémy Gauthier, Hazem Abouellei, Yoan Boussès, Nathalie Brulat-Bouchard, Pierre Colon, et al..  
Experimental Investigation of Dental Composites Degradation After Early Water Exposure. *Journal of Biomechanical Engineering*, 2022, pp.1-18. 10.1115/1.4056197 . hal-03851084

**HAL Id: hal-03851084**

**<https://hal.science/hal-03851084>**

Submitted on 14 Nov 2022

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# Experimental investigation of dental composites degradation after early water exposure

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Keywords: Dental composites, early water degradation, elastic modulus

## 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.

## 34 **1. Introduction**

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

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

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

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

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

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

## 62 **2. Methods**

### 63 **2.1. Materials**

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

69 Random-shape silanized barium glass particles with an average size of 7  $\mu\text{m}$  and pyrogenic silica particles with an  
70 average size of 0.04  $\mu\text{m}$  were added to the monomer mixture. The barium glass accounts for 98.6 wt% of the total  
71 content of inorganic fillers and were silanized, if applicable, using 3-Methacryloxypropyltrimethoxysilane.

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

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

## 77 2.2. Sample preparation

78 The sample preparation protocol used in the present study has been described previously [19] and is summarized  
79 below. The uncured filled matrix was poured in a custom-made mold in a dark room, in order to prepare 2 x 2 x  
80 25 mm<sup>3</sup> rectangular samples. The photopolymerization was performed by using a blue light lamp (DeepCure-S,  
81 3M ESPE, Saint-Paul, USA), with a wavelength between 430 and 480 nm and a light intensity of 1470 mW / cm<sup>2</sup>.  
82 The entire uncured composite resin was exposed to light through a 1 cm hole, so that each 1 cm section on one  
83 side and the other were exposed for 40 s, as explained previously [19]. The exposure used was longer than that  
84 recommended by the manufacturer (10 s) in order to ensure a homogeneous curing of the sample and limit potential  
85 variabilities due to a polymerization gradient. All the curing procedures were performed at the same controlled  
86 room temperature, to limit variations due to the influence of temperature on the polymerization of dental resin  
87 composites, but without any control of the relative humidity [21,22].

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

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

## 97 2.3. Mechanical experiments

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

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

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

103 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)  
104 and thickness (mm), respectively, measured using a numerical caliper.

105 The flexural strain,  $\varepsilon$ , was calculated as follows:

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

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

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

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

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

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

#### 114 2.4. Acetone sorption / desorption

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

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

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

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

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

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

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

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

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

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

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

## 140 2.5. Statistical test

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

## 147 3. Results

### 148 3.1. Mechanical experiments

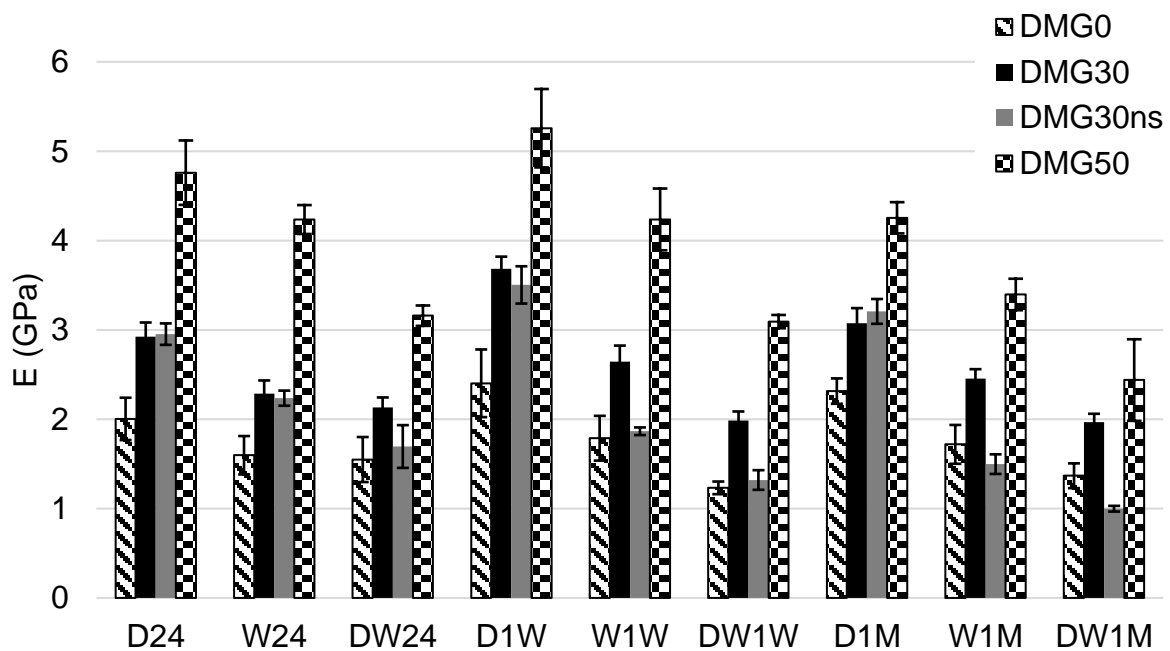
149 For DMG0, the D samples had a higher modulus than the W and DW samples after 24h of water exposure. After  
150 1 week, the flexural modulus was lower in the DW samples compared to the D and W samples. After 1 month, the  
151 D samples had a higher modulus than the W and DW samples. Exposure time did not significantly influence the  
152 flexural modulus of the DMG0 samples.

153 For DMG30, the D samples had a higher modulus compared to the W and DW samples, after 24h exposure. After  
154 1 week and 1 month, a significant difference was observed between the 3 different exposure conditions, the D and  
155 the DW samples showing the highest and lowest modulus, respectively. There was a significant influence of  
156 exposure time on the D and W samples. After 1 week compared to 24h exposure, the flexural modulus increased  
157 by 26 % and 16 % for the D and W samples, respectively. After 1-month exposure, compared to 1 week, a 17 %  
158 and 7 % decrease in the modulus was observed for the D and W samples, respectively.

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

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

166 For DMG50, the DW samples had a lower modulus than the D and W samples after 24h of aging. A significant  
 167 difference was observed between all aging conditions, after 1 week and 1-month exposure, the D and DW samples  
 168 having the highest and lowest modulus, respectively. Exposure time had an influence on the D and W samples.  
 169 The modulus of the W samples decreased by 20 % after 1-month exposure compared to 24h. A 19 % and 20 %  
 170 decrease for the D and W samples, respectively, was observed after 1- month exposure, compared to 1 week (Fig.  
 171 1 and Table 1).



172 *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*  
 173 *for 24h, 1 week, and 1 month. DW24, DW1W, and DW1M: Dry for 24h, and wet for 24h, 1 week, and 1 month.*

174

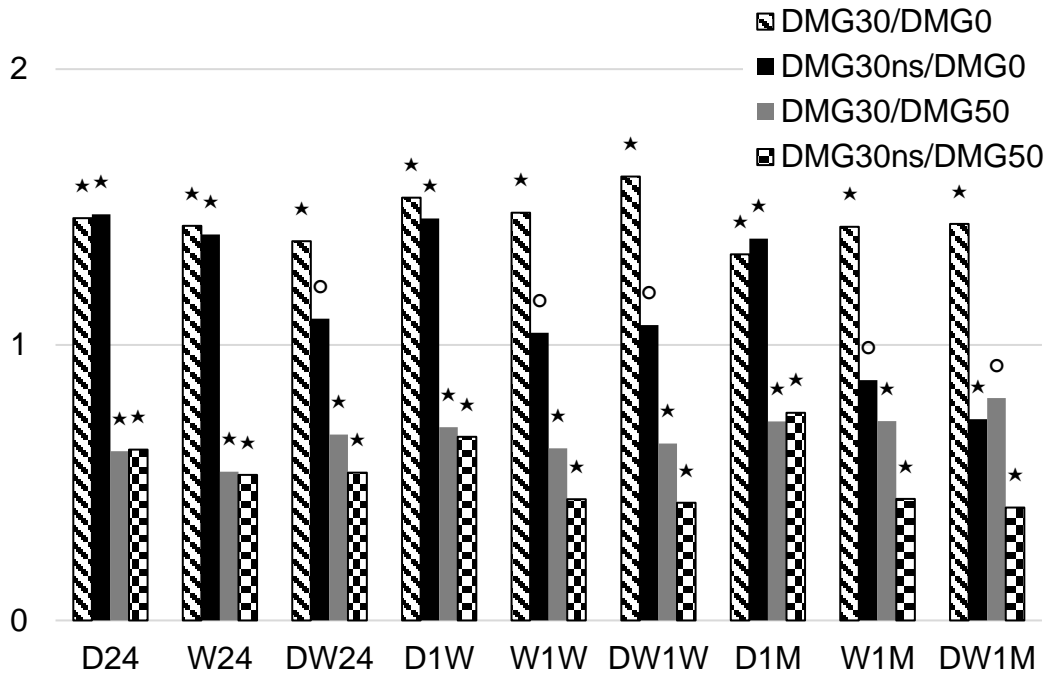
$E_F$ (MPa)		Aging condition		
Aging time	Composition	D	W	DW
24	DMG0	2.0 (0.2) <sup>W,DW</sup>	1.6 (0.2) <sup>D</sup>	1.6 (0.2) <sup>D</sup>
	DMG30	2.9 (0.2) <sup>W,DW</sup> <sub>1W</sub>	2.3 (0.2) <sup>D</sup> <sub>1W</sub>	2.1 (0.1) <sup>D</sup>
	DMG30ns	3.0 (0.1) <sup>W,DW</sup> <sub>1W,1M</sub>	2.2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

175 Table 1 Means and standard deviations of flexural modulus (GPa). D24, D1W, and DIM: Dry for 24h, 1 week, and 1 month. W24, W1W, and  
176 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  
177 subscripts signify a significant difference with the dry, the wet, and the dry wet groups, respectively, with same exposure time and condition.  
178 24, 1W, or 1M lower subscripts signify a significant difference with the 24h, 1 week, or 1-month groups, respectively, with the same composition  
179 and exposure condition.

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

183 After 24h exposure, the DMG30ns modulus was higher than that of the DMG0 for the D and W conditions. After  
184 1 week, the modulus of DGM30ns was higher than that of DMG0 only for the D condition. After 1 month, the  
185 modulus of DMG30ns was higher for the D condition, but lower for the DW condition, compared to DMG0. The  
186 modulus of DMG30ns samples were consistently lower than that of DMG50 samples, whatever the exposure time  
187 and condition (Fig. 2).





188

189 *Fig. 2 Ratios of flexural modulus of DMG30 or DMG30ns over DMG0 or DMG50. ★ indicates a significant difference; ○ indicates a non-*  
 190 *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,*  
 191 *DW1W, and DW1M: Dry for 24h, and wet for 24h, 1 week, and 1 month.*

### 192 3.2. Acetone sorption / desorption

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

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

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

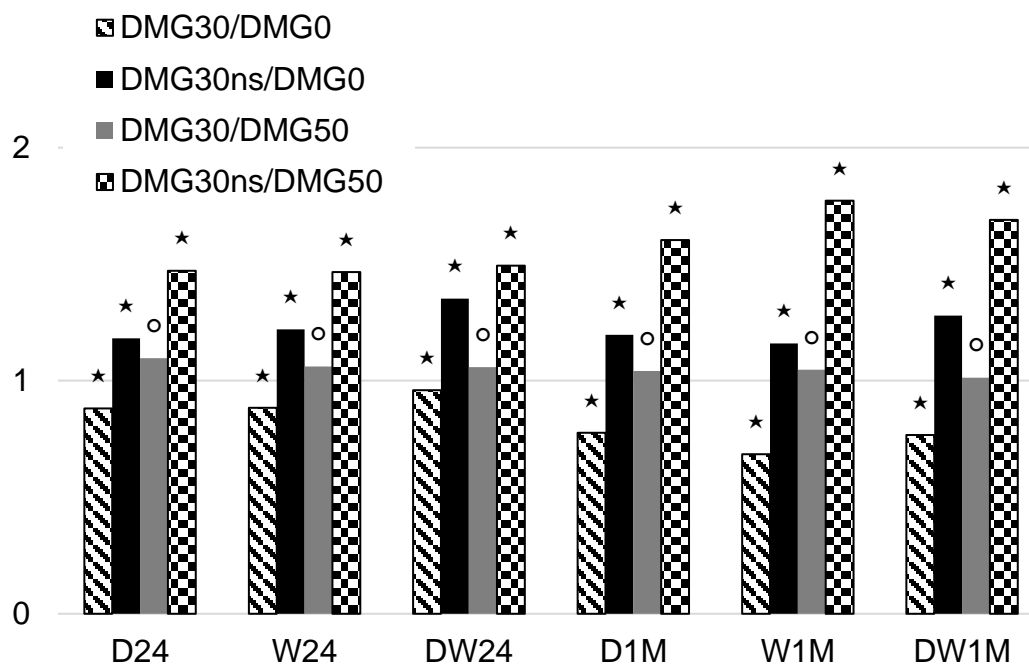
203 For DMG50, no significant difference was observed between the exposure conditions after 24h of aging. The D  
 204 samples showed a larger acetone uptake than the W and DW samples after 1-month exposure. After 1 month  
 205 compared to 24h, there was a 6 % increase in  $m_{Ac}$  for D samples, and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

<b>m<sub>Ac</sub> (%)</b> <b>mass of uptake Acetone</b>		<b>Aging condition</b>		
<b>Aging time</b>	<b>Composition</b>	<b>D</b>	<b>W</b>	<b>DW</b>
<b>24</b>	<b>DMG0</b>	19.9 (0.5) <sup>W,DW</sup>	17.4 (0.9) <sup>D</sup>	18.1 (0.4) <sup>D</sup>
	<b>DMG30</b>	17.2 (0.4) <sup>W</sup>	15.2 (0.5) <sub>1M</sub> <sup>D</sup>	15.8 (0.7)
	<b>DMG30ns</b>	23.9 (0.5) <sub>1M</sub>	22.6 (1.0)	24.7 (1.6)
	<b>DMG50</b>	15.8 (0.1) <sub>1M</sub>	16.2 (1.1) <sub>1M</sub>	15.9 (0.6) <sub>1M</sub>
<b>1M</b>	<b>DMG0</b>	21.8 (1.2) <sup>W,DW</sup>	18.8 (0.8) <sup>D</sup>	18.8 (0.6) <sup>D</sup>
	<b>DMG30</b>	16.8 (0.6) <sup>W,DW</sup>	13.4 (0.6) <sub>24</sub> <sup>D,DW</sup>	14.9 (0.3) <sub>24</sub> <sup>D,W</sup>
	<b>DMG30ns</b>	26.1 (0.7) <sub>24</sub> <sup>W</sup>	22.1 (1.1) <sup>D,DW</sup>	24.9 (0.7) <sup>W</sup>
	<b>DMG50</b>	16.8 (0.5) <sub>24</sub> <sup>W,DW</sup>	12.4 (0.6) <sub>24</sub> <sup>D</sup>	13.5 (0.8) <sub>24</sub> <sup>D</sup>

207 Table 2 Means (and standard deviation) of m<sub>Ac</sub> (%). D24 and D1M: Dry for 24h and 1 month. W24 and W1M: Wet for 24h and 1 month. DW24  
208 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  
209 the dry wet groups, respectively, with same exposure time and condition. 24 or 1M lower subscripts signify significant difference with the 24h  
210 or 1-month groups, respectively, with the same composition and exposure condition.

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

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



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

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

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

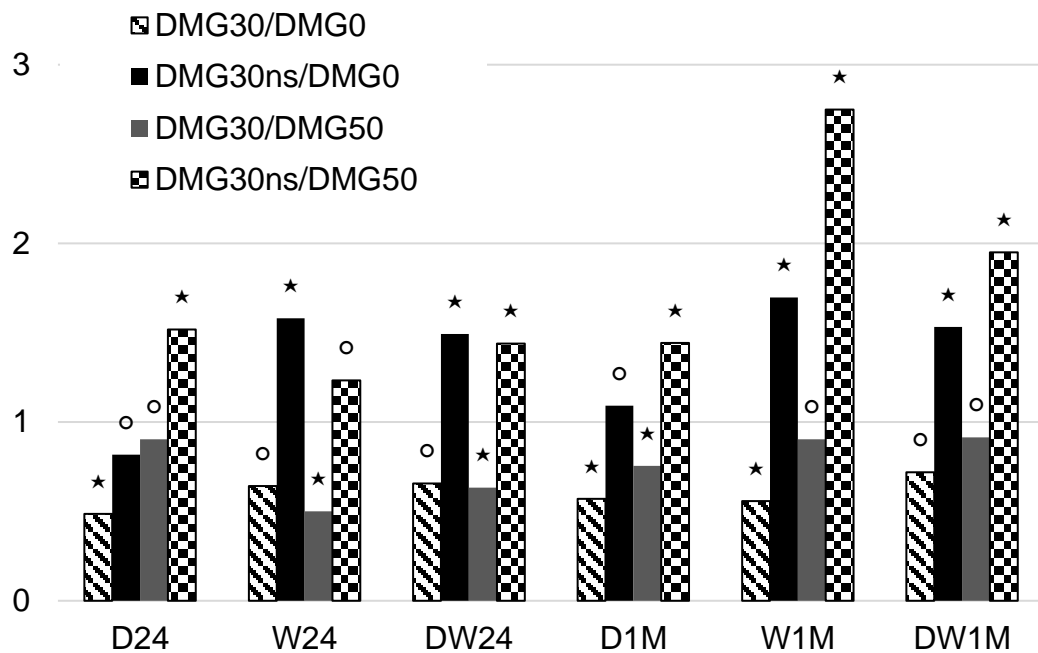
223 For DMG30ns, after 24h exposure, W samples showed a lower mass of eluted monomers than the D and DW  
 224 samples. After 1-month exposure, W samples had a lower  $m_{EI}$  than D samples. After 1 month compared to 24h,  
 225 there was a 30 %, 24 %, and 25 % increase in the mass of eluted monomers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

227 For DMG50, there was no significant difference between all exposure conditions after 24h exposure. After 1-  
 228 month exposure, there was a significant difference between all exposure conditions, the D and W samples showing  
 229 the highest and lowest  $m_{EI}$ , respectively. exposure time had an influence on the D and W conditions, as shown by  
 230 the 37 % increase in  $m_{EI}$  for D samples, and 44 % decrease for W samples, after 1 month of aging compared to  
 231 24h (Table 3).

$m_{EI}$ (wt %)		Aging condition		
Mass of eluted material				
Aging time	Composition	D	W	DW
24	DMG0	8.5 (1.3) <sup>W,DW</sup>	3.4 (1.0) <sup>D</sup>	4.4 (0.8) <sup>D</sup>
	DMG30	4.1 (0.3) <sup>W,DW</sup>	2.2 (0.2) <sup>D</sup>	2.9 (0.5) <sup>D</sup>
	DMG30ns	6.9 (0.6) <sup>W<sub>1M</sub></sup>	5.4 (0.3) <sup>D,DW<sub>1M</sub></sup>	6.6 (0.2) <sup>W<sub>1M</sub></sup>
	DMG50	4.6 (0.2) <sub>1M</sub>	4.4 (0.9) <sub>1M</sub>	4.6 (0.3)
1M	DMG0	8.3 (1.0) <sup>W,DW</sup>	4.0 (0.3) <sup>D</sup>	5.4 (0.9) <sup>D</sup>
	DMG30	4.7 (0.6) <sup>W</sup>	2.2 (0.5) <sup>D,DW</sup>	3.9 (0.6) <sup>W</sup>
	DMG30ns	9.0 (0.4) <sup>W<sub>24</sub></sup>	6.8 (0.7) <sup>D<sub>24</sub></sup>	8.2 (0.4) <sub>24</sub>
	DMG50	6.3 (0.3) <sup>W,DW<sub>24</sub></sup>	2.5 (0.5) <sup>D,DW<sub>24</sub></sup>	4.2 (0.6) <sup>D,W</sup>

232 Table 3 Means (and standard deviation) of  $m_{EI}$  (wt %). D24 and D1M: Dry for 24h and 1 month. W24 and W1M: Wet for 24h and 1 month.  
233 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  
234 wet, and the dry wet groups, respectively, with same aging time and condition. 24 or 1M lower subscripts signify a significant difference with  
235 the 24h or 1-month groups, respectively, with the same composition and aging condition.

236 After 24h exposure, DMG30 showed a lower mass of eluted monomers compared to DMG0 for the D condition.  
237 After 1 month, this mass was lower for both the D and W conditions compared to DMG0. Compared to DMG50,  
238 DMG30 samples had a lower mass of eluted monomers for the W and DW conditions after 24h exposure. After 1  
239 month, only the DMG30 samples in D condition had a smaller mass of eluted monomers compared to DMG50.  
240 The DMG30ns samples in W and DW conditions had a larger mass of eluted monomers compared to DMG0 at  
241 both 24h and 1-month exposure. The mass of eluted monomers from DMG30ns samples was significantly higher  
242 than that of DMG50 samples for all exposure conditions and times, except after 24h of in W conditions (Fig. 4).



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

#### 246 4. Discussion

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

251 It is known that water can degrade composites by inducing matrix swelling, hydrolysis, and osmotic pressure  
 252 which may promote physical damage to both the matrix and the interphase between the matrix and the fillers  
 253 [10,26,27]. In addition, water acts as a plasticizer and increases the material's compliance by interacting with the  
 254 polymer chains [7,28]. In their work, Musto et al. defined three types of water species depending on the type of  
 255 interactions between the water molecules and the polymeric matrix [29]. Matrix plasticization is thought to be  
 256 associated with strongly bound water which breaks hydrogen bonds between polymer chains, compared to free  
 257 water or loosely bound water [29,30]. The water-based degradation of dental composites thus involves both  
 258 structural and chemical mechanisms.

259 Interestingly, the DW condition was the most affected in terms of elastic modulus, for all compositions and  
 260 exposure times. The results presented in the current study are therefore intriguing: a sample that has been aged for  
 261 24h under dry conditions is more prone to water degradation. This result suggests that during the first 24h of post-  
 262 polymerization, the structure and chemistry of the resin evolve differently, depending on whether it is stored in  
 263 wet or dry conditions, and that the way the structure evolves will have a major influence on the water-based matrix  
 264 degradation. Such results are of major interest both regarding the clinical conditions in which the composite is  
 265 polymerized and for the patient life-style sometimes after the composite placement. To provide the right advised  
 266 to the clinicians, the early degradation mechanisms have to be understood.

267 The contribution of the filler content on the type of water species developing within the matrix appears to be an  
268 important feature in the current study. On one hand, the unfilled resin, DMG0, had a higher  $m_{Ac}$  – the mass of  
269 acetone gained - compared to the resins filled with silanized fillers (DMG30 and DMG50), highlighting an easier  
270 acetone diffusion within the matrix. This also suggests that the water that has diffused within the DMG0 matrix  
271 during the early exposure experiments was loosely bound to the polymeric chains, as strongly bound water is less  
272 easily removed by acetone. The other hypothesis explaining this higher acetone uptake for the matrix alone is that  
273 acetone diffusion is influenced by the presence the fillers. Still, it has to be noticed that such mechanism depends  
274 on the presence of the organo-silane bonds at the matrix-filler interface. The current results have shown a higher  
275 acetone uptake within DM30ns with non-silanized fillers compare to the matrix alone (Fig. 3).

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

284 It is also known that dental resin mechanical properties are associated with its degree of conversion [4]. In  
285 Ferracane et al. study, the higher degree of conversion was observed for the composite with 37 % of filler [18]. A  
286 too high filler content can result in a lower degree of conversion. This results in a higher content of unreacted  
287 monomers act as a pathway for water diffusion [31]. It seems that when the first 24h post-polymerization occurs  
288 in dry conditions; the matrix degrade faster in water if the filler content is higher. Accordingly, Palin et al. observed  
289 a large variation in dental composite mechanical properties during the first 24h of water exposure [32]. In the  
290 present study,  $m_{EI}$ - the mass of eluted material - is related to this degree of conversion as it is usually calculated  
291 based on the ratio between monomer and polymer content [33]. According to Ferracane et al. study, in the current  
292 study, the mass of eluted material is sometimes significantly lower for DMG30 (Figure 4) [18]. Still, in their study,  
293 Ferracane et al. did not investigate the degree of conversion of the matrix alone. As water may already have eluted  
294 some of these monomers [34,35], the D samples are the ones that reflect the real mass of monomers present in the  
295 resin after curing. It is worth noting that the eluted monomer mass for the D samples obtained in the present study  
296 are in agreement with previous studies [25]. Furthermore, it is known that the silanization of the fillers has an  
297 influence on the degree of conversion of the matrix, with an increased conversion when the fillers are silanized  
298 [18,36]. Accordingly, the present results found a difference in the mass of eluted monomers between the DMG30  
299 and DMG30ns composites in D conditions. Furthermore, the elution of monomers from the unfilled resin was the  
300 highest, which is in agreement with previous studies [14]. Surprisingly, for DMG30ns and DMG50 aged in D  
301 conditions, the mass of eluted monomers increased after 1-month exposure compared to 24h, whereas increasing  
302 time is generally associated with a higher degree of conversion due to post-polymerization.

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

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

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

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

333 The present investigation has different limitations. First, the low content of fillers used does not represent what is  
334 used in clinical practice. Practical issues arose when mixing non-silanized fillers with the resin. It was not possible  
335 to mix more than 30 wt% of non-silanized fillers, due to particle agglomeration. Therefore, the higher filler ratio  
336 used, for silanized based fillers, was set at 50 wt% to limit the difference with the 30 wt% composite. Another  
337 limitation was the use of distilled water rather than artificial saliva. It is known that composite behavior during  
338 exposure is different whether water or saliva is used as solvent, due to the ionic composition of artificial saliva  
339 [43–45]. Understanding the influence of saliva on the degradation of dental composite is undoubtedly clinically  
340 relevant. Nevertheless, reproducing human saliva is very difficult, and the compositions used in the literature differ  
341 from one another [46]. Due to this reason, and because of the different resin compositions and filler types used  
342 herein, it would have been even more difficult to compare the results of this study with those of the literature.  
343 Finally, the present study was limited to the study of short-term exposure (up to 1 month) whereas the longevity  
344 of restorative composites can exceed several years [47,48]. Nevertheless, the present study shows that the initial

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

## 354 **5. Conclusions**

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

## 373 **6. Acknowledgments**

374 The authors wish to thank DMG Chemisch-PharmazeutischeFabrik (Hamburg, Germany) for the materials supply.  
375 This work was funded by the ANR project Toothbox (ANR 16-CE08-0024). The authors wish to thank Véréna  
376 Landel, from the Département de la Recherche Clinique et de l'Innovation of the Hospices Civils de Lyon, for her  
377 careful English reviewing and editing.

## 378 **7. Conflicts of interest**

379 The authors declare no conflicts of interest.



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