

ORIGINAL ARTICLE

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

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### Abstract

**Objective.** The aim of this work was to assess the influence of the bis-EMA content on the degree of conversion (DC) and its effect on the water sorption and solubility. **Materials and methods.** In a polytetrafluorethylene (PTFE) mould, 30 samples ( $\varnothing = 5$  mm, height = 2 mm) of four experimental dental composite resins were cured for 10 s, 20 s and 40 s. The DC was analysed by Fourier Transform (FT)-Raman spectroscopy. To analyse sorption and solubility, six samples ( $\varnothing = 15$  mm and thickness = 1 mm) of each composite ( $n = 72$ ) were stored in water at 37°C for different storage periods: 24 h, 7 days and 30 days. **Results.** When cured for 20 or 40 s the DC increased with the increasing content of bis-EMA. However, the presence of 15 wt% of bis-GMA did not affect the DC, except when cured with 10 s irradiation time. This study also found a correlation between the content of bis-EMA and the reduced values for sorption and solubility, for all storage times used, when the materials were cured with 20 s. **Conclusions.** 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.

**Key Words:** dental composites, bis-EMA, hydrogen bonds, energy density, FT-Raman spectroscopy

### Introduction

To achieve a proper longevity with dental composite resin-based materials (CRM), factors such as irradiation time, light intensity and the chemical characteristics of the monomers (e.g. type of co-monomers, molar mass and amount of hydrogen bonding) will influence the curing process [1–4]. The hydrogen bonds have been brought to attention, due to their intrinsic correlation with the viscosity of the CRMs and the final degree of conversion (DC) [5,6]. Dental resin monomers are typically mono-, di- or trimethacrylates of various chemical structures, where the polymerization sites are the vinyl bonds of the methacrylate groups [7]. Conversion of the vinyl bonds is responsible for the polymer chain growth and the formation of a three-dimensional covalent network [8]. It is well known that not all vinyl bonds are

converted during the free-radical polymerization process, resulting in residual monomers and the presence of functional groups trapped inside the polymer network [9–11].

One of the first dimethacrylate monomers developed for CRMs, and still most often used, is bisphenol-A glycidyl dimethacrylate (bis-GMA) (Figure 1A) [12]. bis-GMA contains two aromatic groups in its structure that increase its viscosity and make it less flexible compared to the other monomers used in dental materials. Thus, a lower degree of conversion is achieved, as shown in studies on bis-GMA [13,14]. Generally, a lower viscosity of the composite resins and a higher flexibility of the monomer molecules lead to a higher degree of conversion, due to mobility of the monomers themselves and of the free radicals of the growing polymer chain [13,14]. In order to decrease the viscosity of the composite

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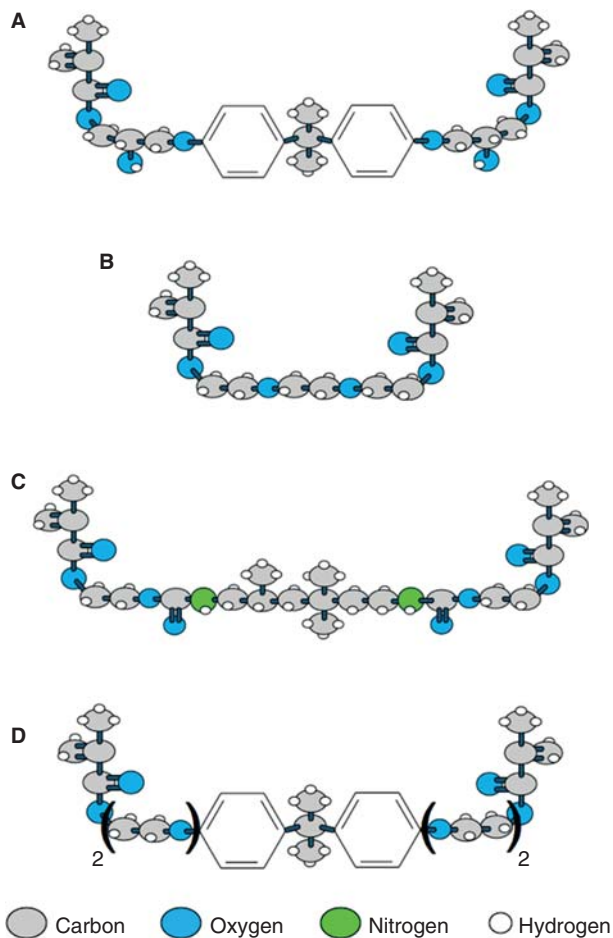


Figure 1. Chemical structure of the monomers often used in dental composite resins. (A) Bis-GMA; (B) TEGDMA; (C) UDMA; (D) Bis-EMA.

materials, increase the DC and allow a higher incorporation of fillers, bis-GMA is diluted with less viscous monomers [3,4,7,15]. Triethyleneglycol dimethacrylate (TEGDMA) (Figure 1B) and urethane-dimethacrylate (UDMA) (Figure 1C) are commonly used diluting monomers, due to their aliphatic, flexible structures and low viscosity [3,4,7,13–15]. Thus, with the increased cross-link density of the formed network resulting from the dilution, DC was found to be influenced by the ratio between high viscous monomers, with a large and stiff structure, and low viscous monomers, with smaller and flexible structure [13]. However, diluting monomers resulted in a brittle composite [3,14].

Ethoxylated bisphenol-A dimethacrylate (bis-EMA) (Figure 1D) has been introduced in combination with the aforementioned monomers [7,16–18]. bis-EMA is a monomer analogous to bis-GMA (Figure 1A), also containing two aromatic groups in its structure, but without the two hydroxyl groups (-OH). Lack of the -OH in bis-EMA has been suggested to increase its flexibility, due to the lack of ability to form strong intermolecular hydrogen bonds leading to an increased DC [18]. However, instead of

forming a highly cross-linked network, bis-EMA has been found highly capable to form primary cycles [19]. Despite bis-EMA being extensively used in composite resin-based materials at present, its role in co-polymerization with bis-GMA and the effect of the tendency of the type of double bond conversion (i.e. cross-linking or cyclization) on properties such as sorption/solubility seems to be insufficiently studied. The hypothesis for the present study was that, despite the ability of bis-EMA to form primary cycles, increased content of bis-EMA vs bis-GMA in experimental composite resin-based materials would yield higher DC, independently of the curing time. In addition, a higher content of bis-EMA vs bis-GMA would result in CRMs with lower water susceptibility. The aim of the present work was to assess the influence of the bis-EMA content on the degree of conversion in experimental composites cured with different irradiation times and its effect on the water sorption and solubility at different storage times.

## Materials and methods

### Materials

Experimental composite resin-based materials were used in four mixtures varying the content of bis-EMA in their composition (Table I). The CRM materials were made and provided by VOCO GmbH (Cuxhaven, Germany).

### Degree of conversion

One sample of each uncured composite was used as a reference for the assessment of the total amount of vinyl bonds within the material. Thirty samples ( $\varnothing = 5$  mm, height = 2 mm) of each composite were made in a mould of polytetrafluorethylene (PTFE) and the DC was analysed at the top and bottom of each sample. The choice of the mould material was based on the results of a previous study showing no differences in the DC values for composites cured in various moulds [20]. The composite was inserted in the mould with a slight excess of the material. A polyethylene terephthalate sheet (PETP

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

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

Initiator: Camphorquinone (0.1%) and Dimethylaminoethylbenzoate (0.2%); Inhibitor: Butylhydroxytoluene (0.05%). The filler content is 72.8 wt% with 66.4% of dental glass (0.7  $\mu\text{m}$ ) and 6.4% of fumed silica.

thickness = 0.50  $\mu\text{m}$ ) was placed on top of each sample and a glass-plate was used to press the material. The plate was removed and the material was polymerized through the PETP sheet directly with a fully charged LED light (Celalux 2, VOOCO). The samples were cured for 10 s, 20 s both at 850  $\text{mW}/\text{cm}^2$  and 40 s. The latter irradiation had a soft start cycle of 5 s (310  $\text{mW}/\text{cm}^2$ ) followed by 35 s at high intensity (850  $\text{mW}/\text{cm}^2$ ). The power density was measured before each curing by a radiometer (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein). The samples were taken from the mould and the excess of the material was removed by using a paper with grit no 600. Each individual sample was stored in a dark container for 24 h at 23°C  $\pm$  1 prior to the FT-Raman spectroscopy analysis.

Degree of conversion was analysed by Fourier Transform (FT)-Raman spectroscopy (Spectrum 2000R NIR-Raman, PerkinElmer, Waltham, Massachusetts, US) by using the reflection mode to calculate the area of the peaks representing the aliphatic (1639  $\text{cm}^{-1}$ ) and the aromatic (1608  $\text{cm}^{-1}$ ) double bonds. The analysis was performed with 32 scans at resolution of 4  $\text{cm}^{-1}$  in the spectral region 2000–1000  $\text{cm}^{-1}$  and laser power of 1 W and the peaks of the aliphatic double bonds were determined before and after curing each composite. The degree of conversion of each sample was determined according to:

$$\text{DC} = (1 - [A_{\text{cured}} / A_{\text{Uncured}}]) \times 100$$

where  $A_{\text{Cured}}$  is the ratio of aliphatic (1639  $\text{cm}^{-1}$ ) to aromatic (1608  $\text{cm}^{-1}$ ) carbon-carbon double bond peak areas of the cured samples, and  $A_{\text{Uncured}}$  is the equivalent ratio for the material before the polymerization process.

#### *Sorption and solubility*

The sample preparation and analysis of water sorption and solubility were performed according to ISO 4049:2009 [21]. In a PTFE mould, six samples ( $\varnothing = 15$  mm and thickness = 1 mm) of each composite ( $n = 72$ ) were made. The samples were cured only from the top, based on the results from the analysis of the degree of conversion. The samples were cured in overlapping sections by a LED light (Celalux 2) with 20 s irradiation time. The time was set according to the manufacturer's instructions and the results from the analysis of the degree of conversion. The power density was similar to the irradiation used for the DC measurements and was controlled before curing by a radiometer (Bluephase, Ivoclar Vivadent). After curing, the samples of each composite were individually dried according to the protocol described in the standard [21]. After a constant mass for each

specimen was obtained, the samples were individually stored in containers filled with 10 mL of double distilled water for the storage periods groups of 24 h, 7 days and 30 days, at 37°C  $\pm$  1, including two extra exposure times compared to the method described in ISO 4049, giving the possibility to analyse the water susceptibility as a function of time. The water sorption ( $W_{\text{sp}}$ ) and solubility ( $W_{\text{sl}}$ ) were calculated in micrograms per cubic millimetres from the following equations:

$$W_{\text{sp}} = (M_2 - M_3) / V$$

$$W_{\text{sl}} = (M_1 - M_3) / V$$

where  $M_1$  is the mass of the specimen after drying to constant weight prior to water immersion,  $M_2$  is the mass of the specimen after immersion in water for the specific time period,  $M_3$  is the mass of the re-conditioned specimen after last drying to constant weight and  $V$  is the volume ( $\text{mm}^3$ ) of the sample.

#### *Statistical analysis*

Data for the degree of conversion and the water sorption and solubility were analysed by one-way ANOVA and Tukey's Post Hoc tests. In addition, the independent 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 with the range 0.1–0.29 small, 0.3–0.49 moderate and 0.5–1.0 strong correlation [22]. All statistical analyses were made using the software IBM SPSS Statistics, version 19 (SPSS, Inc., IBM Company, Armonk, New York, US) with level of significance set at  $p < 0.05$ .

## **Results**

#### *Degree of conversion*

The results concerning degree of conversion are presented in Tables II and III. The composite 1, that contained the highest amount of bis-EMA, showed the highest degree of conversion, independent of the variation in irradiation time (Tables II and III).

There were no significant differences in the DC values at the bottom of all composite resins for each irradiation time tested, except for the composite 2, where 40 s irradiation resulted in a significantly higher DC than the 10 s irradiation ( $p < 0.05$ ) (Table II). With 10 s irradiation, the composite resin containing 15 wt% of bis-GMA (i.e. composite 2) had a similar DC value as the composite resin containing 60 wt% of

Table II. Comparison of the DC (%; mean (SD)) at the bottom of the samples of each composite resin cured with three different irradiation times.

Composites	Irradiation		
	10 s	20 s	40 s
Composite 1	71.5 (0.7) <sup>A a</sup>	69.0 (6.1) <sup>D a</sup>	72.5 (3.9) <sup>F a</sup>
Composite 2	64.4 (2.8) <sup>B b</sup>	66.2 (3.7) <sup>D b,c</sup>	68.3 (3.2) <sup>F c</sup>
Composite 3	56.7 (3.9) <sup>C d</sup>	60.4 (3.8) <sup>E d</sup>	60.8 (3.8) <sup>G d</sup>
Control	61.7 (4.4) <sup>B e</sup>	58.9 (2.5) <sup>E e</sup>	60.6 (3.9) <sup>G e</sup>

Same capital letter indicates no significant difference in DC values between each composite resin cured with the same irradiation time—one way ANOVA (columns).

Same lower case letter indicates no significant difference in DC values for one composite resin cured with different irradiation times—one way ANOVA (rows).

bis-GMA (i.e. control). In addition, equal amounts of bis-EMA and bis-GMA (Composite 3) yielded a cured material with the lowest DC value among all composites studied ( $p < 0.05$ ). With 20 s and 40 s irradiation, the composite resins containing the higher amount of bis-EMA (i.e. composites 1 and 2) showed significantly higher DC values than those containing a high amount of bis-GMA (i.e. composites 3 and control) ( $p < 0.05$ ).

The DC at the top of the samples (Table III) followed the same trend as the DC at the bottom, except for the samples cured with 10 s irradiation, when the composite 3 had similar DC value as the composites 2 and the control ( $p < 0.05$ ). There was no significant difference between the DC at the top and at the bottom of the samples for all composites tested (Tables II and III).

### Sorption

The water sorption data are displayed in Figure 2. All composite resins tested had a significant increase in the sorption values with increased storage period. The

Table III. Comparison of the DC (%; mean (SD)) at the top of the samples of each composite resin cured with three different irradiation times.

Composites	Irradiation		
	10 s	20 s	40 s
Composite 1	71.2 (4.6) <sup>A a</sup>	70.0 (6.2) <sup>C a</sup>	71.1 (4.4) <sup>E a</sup>
Composite 2	62.1 (3.2) <sup>B b</sup>	65.2 (4.0) <sup>C b,c</sup>	68.5 (3.6) <sup>E c</sup>
Composite 3	59.7 (3.3) <sup>B d</sup>	57.2 (4.5) <sup>D d</sup>	62.4 (2.0) <sup>F e</sup>
Control	58.8 (4.0) <sup>B f</sup>	60.1 (5.7) <sup>D f</sup>	61.9 (6.0) <sup>F f</sup>

Same capital letter indicates no significant difference in DC values between each composite resin cured with the same irradiation time—one way ANOVA (columns).

Same lower case letter indicates no significant difference in DC values for one composite resin cured with different irradiation times—one way ANOVA (rows).

composite 1, which contained the highest amount of bis-EMA, had the lowest sorption values, independent of the storage period. In addition, the analysis showed that, after a 24 h storage period, the composite 1 was the only composite resin with a significant lower sorption value than the control. At 7 days and 30 days of storage, the sorption values for each composite differed significantly from each other ( $p < 0.05$ ) and the sorption increased with increasing content of bis-GMA: Control > Composite 3 > Composite 2 > Composite 1. For 20 s of irradiation, at 24 h a moderate negative correlation between DC at the bottom and sorption ( $r = -0.41$ ) was shown, whereas there was a strong negative correlation ( $r = -0.69$ ) for 7 days and 30 days.

### Solubility

The results of the water solubility measurements are presented in Figure 3. The composite 1, which contained the highest amount of bis-EMA, had the lowest solubility values during the whole storage period. At 24 h storage period, the solubility values followed the same pattern as the sorption values. The composite 1 was the only composite with lower loss in weight (i.e.  $M_1 - M_3$ ) compared to the control, resulting in a significantly lower solubility value.

After 7 days of storage, an increase in dry weight ( $M_3$ ) was found for all the tested composites, resulting in significant differences ( $p < 0.05$ ) and negative values of solubility. For the composites containing a higher amount of bis-EMA (i.e. composites 1 and 2), the solubility did not differ from each other, but was significantly lower than the solubility of the composite 3 and the control.

After a 30 day storage period, the solubility was similar to that after 7 days of storage for all composites, revealing no further gain in dry weight of the materials. The comparison of solubility values of each composite showed a significant increase in  $M_3$  with the increased content of bis-GMA: Control > Composite 3 > Composite 2 > Composite 1. For 20 s of irradiation at 24 h there was a moderate negative correlation between DC at the bottom and solubility ( $r = -0.35$ ), whereas a strong positive correlation ( $r = 0.60$ ) was shown for 7 days and 30 days.

### Discussion

bis-EMA is today extensively used in CRMs. However, its role in the polymerization process and for sorption/solubility seems still to be further clarified. Other studies on the issue have been based on commercial composites or unfilled resins [13,18]. To further investigate the role of bis-EMA, the composite resin-based materials analysed in the present study were experimental grades and had a composition varying only in the content of bis-EMA vs bis-

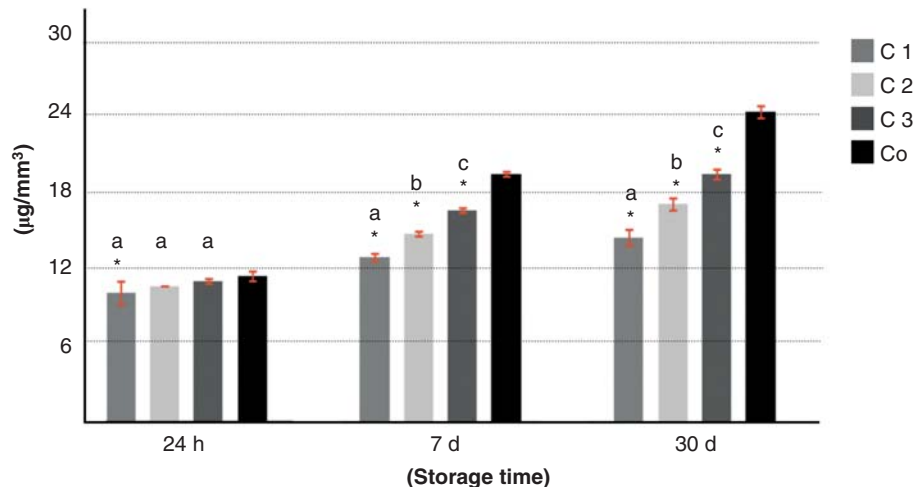


Figure 2. Comparison of the sorption values ( $\mu\text{g}/\text{mm}^3$ ) between each composite resin at the different storage periods. \* indicates a significant difference from the control. Same letter indicate no significant difference between each composite resin.

GMA. The content of the other monomers, as well as the content of filler and additives, were kept constant. By this procedure and through the production of the material by a manufacturer in a high quality process, the risk of uncontrolled factors influencing the results was reduced. Hence, the results presented can most probably be traced to differences in bis-EMA and bis-GMA contents between the materials studied.

The substitution (partly or completely) of bis-GMA monomer by bis-EMA in the experimental composite resin-based materials investigated resulted in an increased DC and decreased water sorption and low solubility. The hypothesis presented was, therefore, partly accepted. Concerning water susceptibility, the hypothesis could be accepted since a higher amount of bis-EMA vs bis-GMA resulted in lower water susceptibility. A correlation between the degree of conversion and the susceptibility was also shown.

The DC was assessed by FT-Raman spectroscopy, which has been proven an efficient method for measuring degree of conversion based on the fact that the

unwanted background fluorescence is often encountered in composites [23]. In addition, the samples could be investigated without any particular sample preparation [23]. The mixtures with higher content of bis-EMA vs bis-GMA expressed higher values of DC independent of the irradiation time used for polymerization (Tables II and III). This could be explained by the greater mobility of the bis-EMA molecule caused by its lower viscosity compared to that of bis-GMA.

The viscosity of the monomers used, defined by their chemical characteristics, has been found to influence the polymerization rate [13,24–26]. The rate of polymerization is intrinsically correlated with the initial viscosity, due to its influence on the mobility of the monomers and free radicals [13,24–27]. Further, the rate of polymerization is governed by the termination and propagation rates [13,14,26,27]. Even at low conversion, a cross-linked network will form when polymerizing these dimethacrylate and termination becomes diffusion controlled due to restrictions in the mobility of the free radicals, leading

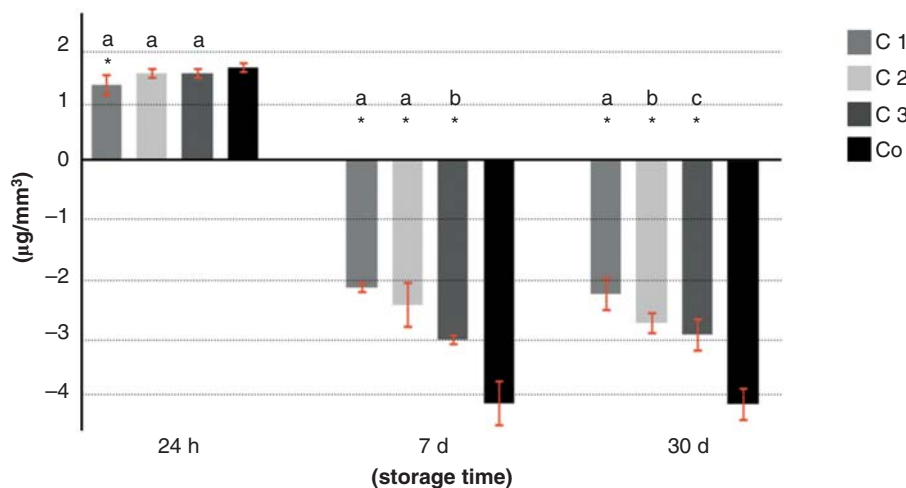


Figure 3. Comparison of the solubility values ( $\mu\text{g}/\text{mm}^3$ ) between each composite resin at the different storage periods. \* indicates a significant difference from the control. Same letter indicate no significant difference between each composite resin.

to the onset of an autoacceleration (i.e. a rapid increase in the polymerization rate). At higher conversions, a tighter network and more viscous material will induce a diffusion controlled propagation as well and lead to an autodeceleration (i.e. reduced propagation). These features have been found to directly affect the final conversion of the double bonds, resulting in unreacted monomers and functional groups 'trapped' into the final polymer [13,14,26,27]. This has been stated as the main reason for the shortcomings of thermosetting polymers based on chain reactions containing bis-GMA [13,27]. The higher viscosity of bis-GMA has been explained by the presence of two phenyl rings in the molecular structure and also by the ability to form strong intermolecular hydrogen bonds (HB) due to the hydroxyl (-OH) groups [5,6,16,26,27]

The bis-EMA monomer used in the present study has a molecular structure that also contains the two phenyl rings, but does not have the ability to form strong intermolecular hydrogen bonds, due to the lack of -OH groups. Gonçalves et al. [16] showed that the viscosity decreased and the degree of conversion increased when the content of bis-EMA was increased in experimental resins. In the present study, experimental composite resin-based materials, not only resins, were analysed, varying only in the content of bis-EMA vs bis-GMA. The results obtained on degree of conversion is in line with the results by Gonçalves et al. [16]. Consequently, it is likely to assume that the chemical structure of bis-EMA positively affected the degree of conversion of the composite resin-based materials tested due to reduction or absence of hydrogen bonds in the resin matrix. The increased DC found in the present study for composite resin-based materials with higher content of bis-EMA suggests that the rate of polymerization (i.e. the speed of the network formation) seemed to be slowed down in the beginning of the polymerisation process. That is, due to a lower initial viscosity of bis-EMA, that delays the onset of autoacceleration through increased mobility of the monomers.

To further investigate the behaviour of bis-EMA in the mixtures, the use of different light-curing times and modes was also performed. Sufficient energy density (i.e. number of photons) is an important factor for achieving higher values of DC and is calculated by the power density (PD)  $\times$  irradiation time [1,2]. The same power density was used for curing all the samples at 10 and 20 s, thus the energy density (8.5 vs 17 J/cm<sup>2</sup>, respectively) varied only with the irradiation time used. For 40 s of curing, the soft start mode was used with a total energy density of 31.2 J/cm<sup>2</sup>.

The composite resin-based materials tested presented different behaviours when cured with different energy densities (Tables II and III). When cured for 20 or 40 s there was a clear trend of the DC decreasing with the increasing the content of bis-GMA. Still, the

comparison between composites 1 and 2 (Table I) showed no significant difference in DC despite the bis-GMA content (15 wt% in composite 2). The -OH group in the bis-GMA molecule is capable to form strong intermolecular HB between two -OH groups and also weaker intra- and/or intermolecular hydrogen bonds with carbonyl groups (C = O) [6,28,29]. However, whereas in composite 1 there was no HB with -OH groups, due to the absence of bis-GMA, in composite 2, not only was there the presence of those types of HB cited above, but also the presence of weak HB between -OH and the ether groups in the bis-EMA molecule. This result suggests that with the presence of a low content of bis-GMA, formation of some hydrogen bonds can occur which can slow down the rate of polymerization, but the mixture still allowed a higher mobility of the free radicals. However, when the content of bis-GMA was increased to 30 wt% or above, the DC was affected due to more hydrogen bonding, leading to a significantly lower DC value. Based on the results obtained it is therefore likely to suppose that the presence of >15 wt% of bis-GMA in the composite resin-based materials studied could be a limiting factor when cured for >20 s with the power density used.

At 10 s irradiation, the energy density, however, was not sufficient for curing the composite with 15 wt % bis-GMA to reach the DC value of the composite with no bis-EMA (composite 1). This result suggests that the mobility of the monomers was still affected by the content of bis-GMA so that an energy density over 8.5 J/cm<sup>2</sup> seems necessary to overcome the initial limitations of the mobility caused by formation of hydrogen bonds, even for materials with low content of bis-GMA. Further studies on the impact of the hydrogen bond on polymerization rate at different energy densities seem, however, to be needed for further clarification.

The results of the present study on experimental composite resin-based materials support the theory that the hydrogen bond is an important feature for the degree of conversion, due to its effect on the different propagation and termination rates caused by increased mobility of the free radicals with reduction and/or absence of strong hydrogen bonds.

In addition to degree of conversion, water susceptibility of the experimental composite resin-based materials was also analysed. The results showed that both water sorption and solubility were affected by the content of bis-EMA vs bis-GMA and correlated to the degree of conversion. Water sorption and solubility measurements were performed based on the ISO 4049 standard [21], but using different storage times, already shown to be a valid method [30,31]. Since a levelling off after 7 days was expected [31–34], the final storage time was set to 30 days.

The substitution of bis-GMA by bis-EMA led to a similar positive trend for the values of water

susceptibility as that of the DC. The results of sorption of the materials tested are presented in Figure 2. The lower water sorption of the composite resin-based materials investigated with higher bis-EMA content could also be explained by the type of secondary forces between the polymer chains (i.e. intermolecular bonds).

While the bis-GMA monomer has the ability to form hydrogen bonds with water through its -OH group, bis-EMA can only form weaker bonds with water through its ether and carbonyl groups [35]. The present results correspond with the results from Sankarapandian et al. [36], who showed that the absence of the hydroxyl group in ethoxylated monomers (as for bis-EMA) resulted in lower water uptake.

Figure 3 shows that there were two patterns of solubility behaviour. Whereas at a 24 h storage period all the composite resins presented reductions in weight, after the final drying at 7 days and 30 days an opposite trend was found. The weight gain, shown as negative values of solubility in the present study, suggests that the water molecules have been kept inside the structure [31–35]. Dental composite resin-based materials often show variations in solubility behaviour. Still the solubility values have been found to be highest after 24 h to 7 days depending on the material [33,37]. In the present study, the materials containing a higher percentage of bis-EMA both displayed reduced sorption and reduced weight gain after a longer period of storage. That may be explained by the fact that materials with an increased amount of bis-EMA seemed to incorporate less water than did materials containing higher bis-GMA, probably due to the polar hydroxyl groups in bis-GMA. These OH-groups may have increased the attraction of the water molecules into the polymer network and, as a result, the water molecules diffuse within the polymer chains cleaving the intermolecular bonds and may induce the leakage of the unreacted monomers [33,37,38]. Recently, Michelsen et al. [39] measured amounts of bis-GMA, as well as UDMA and HEMA, in patient saliva 10 min after restorative treatment, but no bis-EMA could be detected although present in the used composite. In the present study no analysis of the eluate was made. Kalachandra and Kusy [40] found that, after the formation of the polymer network, the water uptake of the polymer based on bis-EMA was ~ 3-times lower than that of the polymer based on bis-GMA. Thus, the formation of a tight network seems to be, together with the reduced hydrogen bonds formation, an important feature in reducing the water uptake. This is in agreement with the findings of the present study, where the composites with higher content of bis-EMA achieved a significantly higher DC and lower sorption and solubility values, as shown in Figures 2 and 3. There was no significant difference in DC between the top and bottom of the samples tested, therefore the trends in correlation between DC at the bottom and

sorption/solubility seems likely to be valid for the complete composite resin-based samples tested. The correlation found between DC and sorption and solubility had similar trends of a moderate correlation between the values at 24 h storage period and a strong correlation at 7 day and 30 day storage periods. The positive correlation found between DC and solubility was due to the negative solubility values found, representing a gain in weight, indicating that the increase in DC led to less gain in weight.

Within the limitations of this study it could be concluded that the degree of conversion was positively affected (i.e. higher degree of conversion) for the experimental composites tested with higher content of bis-EMA, due to lower viscosity and disability to form hydrogen bonds compared to composites with higher content of bis-GMA. Depending on the energy density delivered from the curing device, even the presence of small amounts (15 wt%) of bis-GMA influenced the degree of conversion negatively. A correlation between the degree of conversion and water susceptibility for the experimental composite resin-based materials was found and was stronger for longer storage times.

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