

MASTEROPPGAVE

The influence of the Bis-EMA content on the sorption and solubility of dental composite resins

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Abstract

Several factors will have effect dental restorative materials in the oral environment that can affect the longevity of the material. Today dental composite resin-based materials (CRM) used to a major extent. The monomer mixture is of importance in CRMs and efforts are made to improve the materials by changing the monomer content. The present study investigated the effect of an increasing amount of Ethoxylated Bisphenol-A-Dimethacrylate (Bis-EMA) in experimental composite resin-based materials for dental use on the sorption and solubility behavior. Four different polymer mixtures containing Urethane dimethacrylate (UEDMA), Triethyleneglycol dimethacrylate (TEGDMA), Bis-glycidyl-dimethacrylate (Bis-GMA) Bis-EMA were used. The amount of UEDMA and TEGDMA were stable, while the content of Bis-EMA and Bis-GMA varied. For each group, 6 samples of each material were made for the 3 different storage periods (24 H, 7 and 30 days). The procedure was made according to ISO standard (4049:2009). Water sorption and solubility were calculated and statistically analyzed using ANOVA test and Tukey as post hoc ($p < 0.05$). The results showed that water sorption increases with increasing content of Bis-GMA and decreasing content of Bis-EMA. The material containing less Bis-EMA, showed the lowest weight gain after the drying period. That may have a clinical effect on the degradation of the material.

Introduction

In the oral cavity, restorative dental materials are exposed to several factors, e.g. water, bacteria, pH-difference, temperature fluctuations, and enzymes in addition to physical wear that influence the longevity of the restoration. A dental material has to overcome these challenging conditions, and retain its mechanical and physical properties as long as possible. Today, the use of dental polymer resin-based materials as restorative treatment is common, and the development of new and improved monomer mixtures to overcome the mechanical and physical challenges (e.g. shrinkage stress, degradation wear etc.) continues [1].

Dental resin-based composites are considered as thermosetting polymers containing polymer chains linked together through cross linkage forming a three-dimensional network [2]. The cross-linked network results in an increased glass transition temperature, high strength and toughness of the material. The degree of molecular relaxation, which is important for the polymerization stress, is also depending on the density of cross linkage as well as sorption and solubility behavior [3].

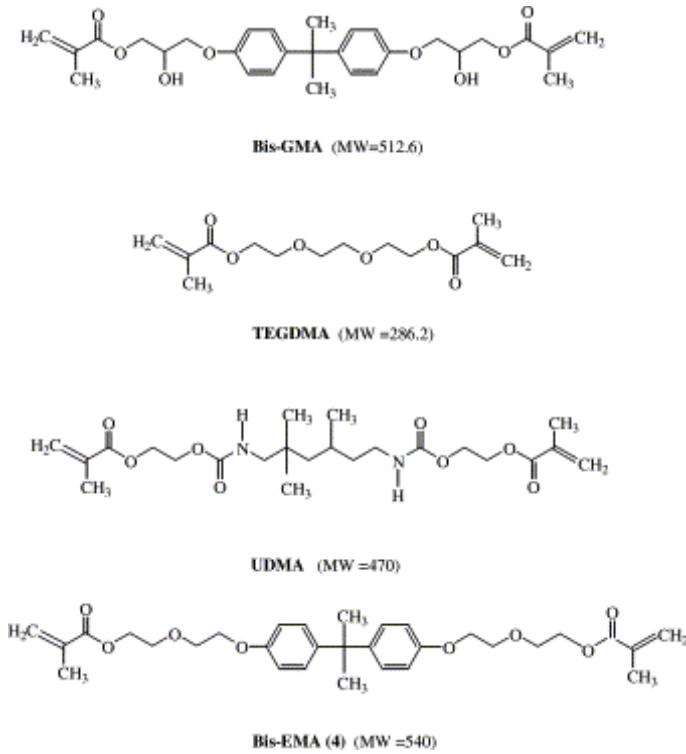
Most dental resin-based polymers are considered as amorphous networks formed by polar dimethacrylate monomers, leading to a certain degree of water sorption in the final product [4]. One model of sorption follows Henry's gas law, explaining that the amount of gas that dissolves in a liquid at a certain temperature is proportional to the pressure of the gas above the liquid [5]. The other model of water sorption follows Langmuir adsorption equation, relating the adsorption of a molecule on a surface to the gas pressure or concentration of the medium that is above this surface [6]. The sorption can to a certain degree have a positive effect on the material decreasing the

polymerization stress within the material due to swelling [7]. Still the sorption process will also have a negative effect due to degradation of the polymer cleaving the monomers leading to auto-degradation [8] Water is a very effective solute, due to its polar nature and relatively small molecules compared with the size of the polymer chains. The diffusion of water molecules into the polymer matrix is time dependent [7]. The water molecules have the ability to saturate the polar polymer matrix in a lot of methacrylates and weaken the intermolecular forces between the polymer chains, thereby increasing the plasticity of the matrix [3]. This leads to three dimensional changes of the polymer chain such as straightening of chains, resulting in the swelling of the material. The extent of these effects in the cross-linked network is determined by the type of the inter-polymer forces within the material and the hydrophilic properties of the monomers used [4]. As a positive effect, it has been suggested as written, that water uptake within the polymer chains reduces the post polymerization stresses within the matrix and thereby reduces the marginal leakage of dental restorations [9].

The structure of the monomer will give different physical and mechanical properties of the monomer and the polymer, e.g. the viscosity, hydrophilicity, polymerization shrinkage, resistant to mechanical wear and pH- and temperature fluctuations in the polymerized material [10]. By changing the amount of one monomer in a copolymer system, the properties of the matrix may be changed, and thereby the properties of the dental material.

In the present study, the content of Ethoxylated Bisphenol-A-Dimethacrylate (Bis-EMA) was investigated concerning the effect on water sorption and solubility of four different mixtures of experimental dental composite resin-based material.

The monomers Urethane dimethacrylate (UEDMA), Triethyleneglycol dimethacrylate (TEGDMA), Bis-glycidyl-dimethacrylate (Bis-GMA) and Bis-EMA was used in the experimental composite mixtures.



Graphic 1: molecular structure of monomers, Sideridou [4]

Bis-GMA was one of the first multifunctional methacrylates used in dentistry and is a common used monomer in the dental resin composite [1, 11]. Bis-EMA has a similar molecule structure as Bis-GMA, except for the hydroxyl groups and higher molecule weight.

Due to the high viscosity of Bis-GMA, monomers of lower molar mass, such as UEDMA and TEGDMA, are added to the resin to lower the viscosity. UEDMA and TEGDMA are more flexible molecules than Bis-GMA. The flexibility increases the degree of conversion in the resultant matrix and increases the density of the network [1].

Compared to Bis-GMA these monomers have more hydrophobic properties. There are several isomeric structures of the monomers, which may affect their properties, e.g. size and structure.

Since sorption and solubility are important features for the longevity of polymer based materials used in dentistry the hypothesis of the present study was that difference in water sorption and solubility in composite resin-based material was dependent on the amount and type of used monomers (i.e. Bis-GMA, Bis-EMA).

The aim of the present study was to investigate the effect of an increasing amount of Bis-EMA in experimental composite resin-based materials for dental use on the sorption and solubility behavior.

Materials and methods

Samples

The composite samples were made and prepared according to ISO 4049:2009 [12]. For each group (Table 1), 6 samples of each material for the 3 different storage periods (24 hours, 7 and 30 days) were made. Great care was taken to avoid contamination of the samples.

Table 1

Groups	Monomers (wt %)			
	Bis-EMA	Bis-GMA	UEDMA	TEGDMA
Group1	60	-	20	20
Group 2	45	15	20	20
Group 3	30	30	20	20
Control group	-	60	20	20

Initiator: Camphorquinone (wt%: 0,1)/Dimethylaminoethylbenzoate (wt%: 0,2)

Inhibitor: Butylhydroxytoluene (wt%: 0.05)

Fillers: Size: 0,7 μm ; Total (wt%: 72,8) [Dental glass (wt%: 66,4); Fumed silica (wt%: 6,4)]

The mould used for the making of the samples, was made in polytetra fluoroethen (Teflon). The material was inserted in the mould and then covered by a polyester film (GC 6000, 3M Comp. St. Paul US) and a glass plate was pressed at the top to evenly distribute the composite material in the mould. The glass plate was removed, and then the mixtures were light cured directly at the top of the samples, according to previous study [13]. After cured, the edges of the samples were trimmed and grinded with a polishing paper (600 grit).

The polymerization was performed in overlapping sections, as described in the standard, by a LED light (Celalux 2, VOCO GmbH, Cuxhaven, Germany) for 20 seconds with an average power density of 760 mW/cm². The power density was checked before start curing each sample by a radiometer (Ivoclar/Vivadent, AG, FL-9494, Schaan, Liechtenstein).

Sorption and solubility determination

The volume of the samples was calculated from the mean value of the diameter measured on 2 different angles, and the mean thickness from 5 different parts (middle, and 4 different parts of the periphery) of the sample, according to the standard.

The samples were then put into a desiccator at 37±1 °C and the weight controlled until the change in mass of the sample was less than 0,1mg in a 24 hours period. The mass was then recorded as M₁. The samples were then placed in individual water containers with 10 ml of double distilled water at an angle making the sample to be subjected to the water at all sites. The storage temperature was kept constant at 37±1 °C through the test period (24 H, 7 and 30 days).

At the end of the immersion time, the samples were retrieved from the water. The surfaces of the specimens were blown free of visible moisture by 15 seconds of waving the sample in the air and weighted 1 minute after removal from water. This mass was recorded as M₂.

The samples were then dried again, by the same procedure as in the determination of M₁. The end mass was then recorded as M₃ [12].

Water sorption (W_{sp}) was then calculated for each sample, by the equation:

$$W_{sp} (\mu\text{g}/\text{mm}^3) = (M_2 - M_3)/V$$

Solubility (W_{sl}) calculated by the following equation:

$$W_{sl} (\mu\text{g}/\text{mm}^3) = (M_1 - M_3)/V$$

V is the volume of the specimen, in cubic millimeters.

Statistic

Mean and standard deviation was calculated for, and the results were statistically analyzed using ANOVA test and Tukey as post hoc. Level of significance was set to $P < 0.05$.

Results

Table 2

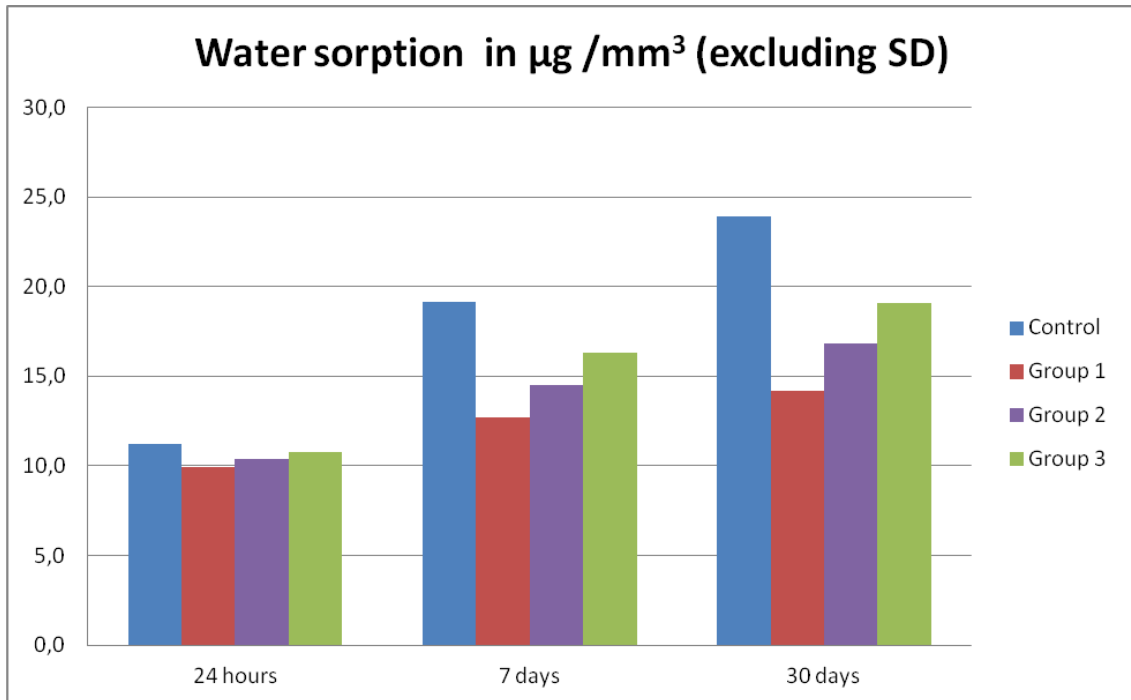
Comparison of the values for sorption and solubility ($\mu\text{g}/\text{mm}^3$) among the mixtures at different storage times. Same symbol = no significant difference.

	Sorption			Solubility		
	24h	7d	30d	24h	7d	30d
Control	11.2 (0.5) [*]	19.1 (0.3) [°]	23.9 (0.6) [¢]	1.6 (0.1) [‡]	-4.2 (0.4) [‡]	-4.2 (0.3) [‡]
Group 1	9.9 (1.0) [#]	12.7 (0.4) ^µ	14.2 (0.7) ^a	1.3 (0.2) [§]	-2.2 (0.1) ^Ω	-2.3 (0.3) ^Ω
Group 2	10.4 (0.1) ^{*#}	14.5 (0.3) [§]	16.8 (0.6) ^ϕ	1.5 (0.1) ^{‡§}	-2.5 (0.4) ^{ΩΔ}	-2.8 (0.2) ^Δ
Group 3	10.8 (0.3) ^{*#}	16.3 (0.3) [∞]	19.1 (0.5) ^π	1.5 (0.1) ^{‡§}	-3.1 (0.1) ^â	-3.0 (0.3) ^â

Sorption

For all storage periods, group 1 (containing the highest amount of Bis-EMA) had the lowest sorption, followed by group 2, group 3 (Table 2). The control group with no Bis-EMA showed the highest sorption value (Table 2). The difference was significant ($p < 0.05$). The sorption values increased with increase in the content of Bis-GMA for all storage periods except 24 hours.

After 24 hours, the sorption showed a tendency of leveling off and there was no significant difference of the sorption values among the groups, except between group 1 and the control group (Figure 1). At 7 days and 30 days storage periods, all groups were significant different from each other.



Graph 1: Water sorption in $\mu\text{g}/\text{mm}^3$. It is only a relative presentation, as standard deviation has not been included in the graphic calculations.

Solubility

The groups in the 24 hours test had all a decrease in weight (i.e. solubility).

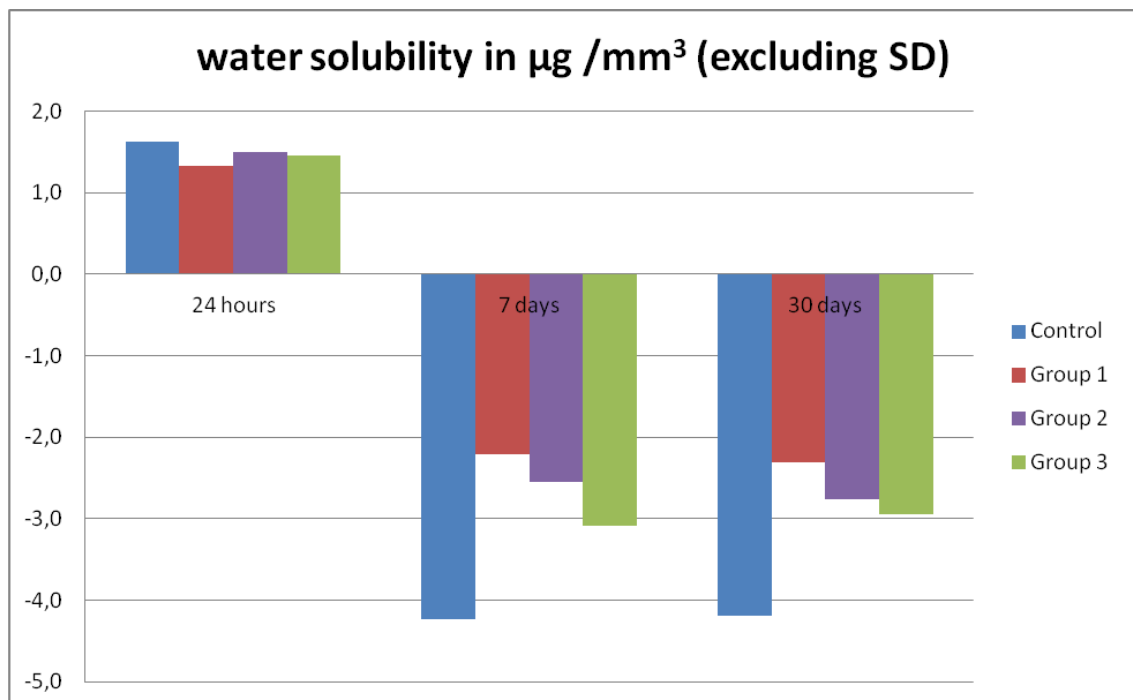
There was a significant difference only between the control group and group 1.

In the 7 days immersion time test, all groups had an increase in mass (i.e. negative solubility), with the control group presenting the highest gained value, followed by Group 3, that were the mixtures containing none and lower amount of Bis-EMA monomer (Table 2, Figure 2).

There was no significant difference ($p > 0.05$) between the values of solubility between 7 days and 30 days storage periods for all mixture groups tested (Table 3).

The greatest change in the solubility values, represented by the mass gain, happened between 24 hours and 7 days (Table 3). The change in weight from 7 days to 30 days storage periods was not significant. From 24 hours to 7 days storage period, there was a significant change in mass. This indicates that the samples reached closer to an equilibrium between 24 hours and 7 days.

After 24 hours the control group, that did not contain any Bis-EMA, showed significant higher negative solubility (i.e. weight gain). With an increased Bis-EMA content in the composite mixture, the negative solubility decreased.



Graph 2: Water solubility in $\mu\text{g}/\text{mm}^3$. It is only a relative presentation, as standard deviation has not been included in the graphic calculations.

Discussion

The hypothesis for the present study was that difference in water sorption and solubility for composite resin-based material was dependent on the amount and type of used monomers (i.e. Bis-GMA, Bis-EMA). The results of the present study showed a significant difference in the water sorption and solubility between the composite tested based on Bis-GMA and Bis-EMA. The hypothesis was therefore confirmed. The time the samples were exposed to water was also of importance.

The setup of this study aimed at making the results from the different groups comparable. By keeping the other components in the composite mixture equal in all groups (i.e. amount of filler particles, initiators, UEDMA and TEGDMA), the differences in results will reflect the changes in amount of Bis-GMA and Bis-EMA. The advantage of making an in vitro study to analyse changes in monomer content of composite resin-based materials for dental use is the ability to lower the risk of bias. In addition the study was to a major extent following a standard (i.e. ISO 4049). By controlling as many of the factors (e.g. temperature, amount of water, stability of temperature and environment) as possible, the effect of changes in the factors to be study as monomer content and time will be easier to analyse. The clinical interpretation is on the other hand difficult to achieve, as a clinical situation represents an additional set of factors (saliva proteins, temperature fluctuations, abrasion) not taken into account in this study.

The present study reflects that the composite materials for dental use based on the monomers Bis-GMA and Bis-EMA will show different properties when it comes to water sorption and solubility depending on type of monomer and amount. To

understand why, the monomer structure and the type of polymer network formed have to be looked upon.

One explanation could be by the type of secondary forces between the polymer chains (i.e. intermolecular bonds). The secondary forces provide the material several physical properties, e.g. glass transition temperature, sorption and solubility [3]. The strongest intermolecular force is the hydrogen bond [3]. While the Bis-GMA monomer has the ability to form hydrogen bonds with water its –OH group, Bis-EMA will form weaker bonds with water because of its ether group [14]. Water may act as a plasticizer increasing the distance between the polymer chains. In addition, Goncales et al showed the importance of the hydrogen bond making polymers based on Bis-GMA less favorable of molecular packing and consequently higher free volume that may increase sorption [10]. That could partly explain the results achieved in the present study where materials with high amount of Bis-GMA showed an increased sorption.

Another explanation could be the rate (i.e. speed) of the polymerization process. Sideridou et al found that materials with Bis-GMA showed a faster polymerization speed than materials containing Bis-EMA during the first few seconds of photopolymerization [15]. The polymerization also follows a steadier rate the first 30 seconds. If Bis-GMA has a more rapid polymerization than Bis-EMA relative to the other monomers in the mixture, the conclusion would be that the heterogeneity and free volume of the matrix would be increasing with increased amount of Bis-GMA in the composite mixture. The results were, however, based on monomers polymerized in homogenous solutions. Whether the polymerization process in a monomer mixture would be affected in the same manner can only be speculated upon but the results from

the present study may be partly explained by the fact of differences in rate of polymerization. The different monomers have distinct reactivity and polymerization rates in homogenous solutions [10]. Whether these differences in reaction rate have any significant effect on the matrix formation is unknown to the authors of the present study, as no research on this was found. It does however seem like a plausible theory that the monomers within the gel like micro-clusters with the highest polymerization rate, in this case Bis-GMA, would be polymerized to a greater extent in the early onset than the monomers with lower polymerization rate, thereby creating more homogenous areas within a heterogenic matrix. More like a salad bowl compared to a melting pot. Results from previous study showed that materials with a high amount of Bis-EMA showed a high degree of conversion [13].

Even if it is not quite clear whether the rate (i.e. speed) of the polymerization process could affect the 3-dimensional structure of the matrix, related to homogeneity of monomer distribution and “free volume” generated it can be hypothesized that the more tightly the matrix is bonded together by intermolecular forces locally in some areas of the material, the more heterogenic the total matrix formation. The result will be shown as increased sorption within the material.

Composite resin-based materials for dental use do often show a solubility (i.e. organic/inorganic substances are eluted from the material). The solubility is often highest within the first 24H to 7 days after the restoration is made [16]. If a material shows negative solubility over time (i.e. weight increase) the material has an ability to keep the water inside the structure. In addition, chemical reactions can occur that increase the weight of the material [8, 17].

In the present study the samples with high content of Bis-EMA incorporated less water, compared to the samples of made with more Bis-GMA and a decrease content of Bis-EMA. According to Ferracane et al [18] water molecules weaken the inter-polymer forces and increase the leakage of unreacted monomers. Sideridou et al found that Bis-EMA absorb less water, but released the greatest amount of unreacted monomers compared to Bis-GMA [19]. This is in contradiction to results found in vivo experiments by Michelsen et al. They found a large leakage of Bis-GMA in saliva and no trace of Bis-EMA [20]. As the present study did not look upon leakage the question in that respect cannot be answered.

The present study found that the experimental composite resin-based materials tested displayed a higher negative solubility the more Bis-GMA that was included in the mixture. As earlier mentioned, the hydrogen bonds between Bis-GMA and the water molecules are stronger than that of Bis-EMA and water. Due to the polar hydroxyl groups on Bis-GMA, the material is likely to have more hydrophilic properties than materials with higher amounts of Bis-EMA. The mass gain after drying time (M_3) in relation to the pre-immersed mass (M_1) reflect the intermolecular forces within the matrix that locks the water within. This interlocking takes time to occur as the water needs to infiltrate into the matrix, as reflected in the results of the present with solubility at 24 H and then an increased negative solubility over time. During the first few days, the water starts affecting the internal forces and filling the gaps in the matrix between the polymer filaments. Because of its large molecular size and chemical structure, Bis-GMA provides lower volatility, lower polymerization shrinkage, more rapid hardening, and stronger and stiffer resins [1]. As mentioned, studies done on leakage of monomers

from dental composites in water have shown that the leaching of unreacted monomers happens almost exclusively during the first 24 hours after placement in water [9, 21].

In the present study, 3 different evaluation times were used. There was only a significant difference in sorption between the groups in the 7 days and 30 days test, but not in the 24 hours test. Water sorption is a process that depends on many factors, such as temperature and surface size. It seems that the samples exposed to water in 24 hours had lesser differences in water sorption simply because other factors (than the small changes in monomer composition) have a greater impact on the rate of sorption initially. Since all the samples were subjected to the same temperature, the same amount of water (pressure), relatively uniform size and surface area, the initial sorption during the first 24 hours had no significant differences intergroup.

In addition, the sorption process is as shown by the present study, also depending on the monomers used. The relative increase in sorption between the different time periods analyzed was largest in the control group (containing no Bis-EMA), and lowest in group 1 (with no Bis-GMA) showing that the difference was least with the highest content of Bis-EMA. With a decreasing content of Bis-EMA the sorption values increased. Materials with a high amount of Bis-EMA may therefore show a lower saturation point than materials based on Bis-GMA. The uptake of water will then decrease faster compared to the other groups tested.

The weight loss in the 24 hours test, compared to a weight gain in the 7 days and 30 days test, could be due to that the process of complete water incorporation takes more than 24 hours to occur. The weight loss during the first 24 hours reflects a solubility of components of the composite. Due to the possibility of a simultaneous

water incorporation in the matrix, it is in this case not possible to determine the amount of solubility.

The results showed that solubility will appear in the material tested at the first 24 hours. That will probably result in an elution of substances from the material [13]. When stored longer a negative solubility will occur due to water uptake, with water bond to the chemical structure, affecting both polymer and fillers due to degradation [8, 22]. As an effect the longevity of the material may be reduced.

However, it is not certain whether the change in mass is due to only intake of water or also leakage of monomers or other substances, since the weight of the samples are not lower than the starting weight (M_1), and because the water used in the tests have not yet been tested for content. More research has, though, to be done to clarify the process.

Within the limitations of the present study the following conclusion were drawn

- The hypothesis was confirmed; a significant difference in sorption and solubility due to the different amounts of Bis-GMA and Bis-EMA in the composite mixture were shown.
- Water sorption increases with increasing content of Bis-GMA and decreasing content of Bis-EMA.
- The experimental composite- resin-based material containing the highest amount of Bis-EMA, showed the lowest weight gain after the drying period.

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References

1. Peutzfeldt, A., *Resin composites in dentistry: the monomer systems*. Eur J Oral Sci, 1997. **105**(2): p. 97-116.
2. Leksikon, S.N. *Herdeplast*. 2011 [cited 2011 21/12].
3. Terselius, b., *Polymerteknologi*, S. Kungliga tekniska Högskolan, Editor 1989, Kungliga Tekniska Högskolan, Sweden.
4. Sideridou, I., V. Tserki, and G. Papanastasiou, *Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins*. Biomaterials, 2003. **24**(4): p. 655-65.
5. Leksikon, S.n. *Henrys Lov*. [cited 2012 23/5].
6. Carr, R., et al., *Microscopic Perspective on the Adsorption Isotherm of a Heterogeneous Surface*. The Journal of Physical Chemistry Letters, 2011. **2**(14): p. 1804-1807.
7. Braden, M., *Water absorption characteristics of dental microfine composite filling materials. II. Experimental materials*. Biomaterials, 1984. **5**(6): p. 373-5.
8. Gopferich, A., *Mechanisms of polymer degradation and erosion*. Biomaterials, 1996. **17**(2): p. 103-14.
9. Asmussen, E. and K.D. Jorgensen, *A microscopic investigation of the adaptation of some plastic filling materials to dental cavity walls*. Acta Odontol Scand, 1972. **30**(1): p. 3-21.
10. Goncalves, F., et al., *Influence of BisGMA, TEGDMA, and BisEMA contents on viscosity, conversion, and flexural strength of experimental resins and composites*. Eur J Oral Sci, 2009. **117**(4): p. 442-6.
11. Anusavice, K., *Phillips' science of dental materials*, in *Phillips' science of dental materials* 2003, Saunders.
12. *Dentistry - Polymer-based restorative materials ISO 4049:2009*, 2009, International Organization for Standardization.
13. Roberto B Cornelio, H.K., Johan Haasum, Ulf W Gjedde, Ulf Ørtengren, *the influence of bisEMA on the degree of conversion and water sorption/solubility properties of dental composite resins*. Submitted to *Brazilian Journal of Oral Science* 2012.
14. Sideridou, I.D. and M.M. Karabela, *Sorption of water, ethanol or ethanol/water solutions by light-cured dental dimethacrylate resins*. Dent Mater, 2011. **27**(10): p. 1003-10.
15. Sideridou, I., V. Tserki, and G. Papanastasiou, *Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins*. Biomaterials, 2002. **23**(8): p. 1819-1829.
16. Ferracane, J.L., *Elution of leachable components from composites*. J Oral Rehabil, 1994. **21**(4): p. 441-52.
17. Ørtengren, U., Wellendorf H, Karlsson S, Ruyter IE, *water sorption and solubility of dental composites and identification of monomers released in an aqueous environment*. Oral Rehabil 2000.
18. Ferracane, J.L., H.X. Berge, and J.R. Condon, *In vitro aging of dental composites in water--effect of degree of conversion, filler volume, and filler/matrix coupling*. J Biomed Mater Res, 1998. **42**(3): p. 465-72.
19. Sideridou, I.D. and D.S. Achilias, *Elution study of unreacted Bis-GMA, TEGDMA, UDMA, and Bis-EMA from light-cured dental resins and resin composites using HPLC*. Journal of Biomedical Materials Research Part B: Applied Biomaterials, 2005. **74B**(1): p. 617-626.



20. Michelsen, V.B., et al., *Detection and quantification of monomers in unstimulated whole saliva after treatment with resin-based composite fillings in vivo*. Eur J Oral Sci, 2012. **120**(1): p. 89-95.
21. Ortengren, U., et al., *Water sorption and solubility of dental composites and identification of monomers released in an aqueous environment*. J Oral Rehabil, 2001. **28**(12): p. 1106-15.
22. Soderholm, K.J., et al., *Hydrolytic degradation of dental composites*. J Dent Res, 1984. **63**(10): p. 1248-54.