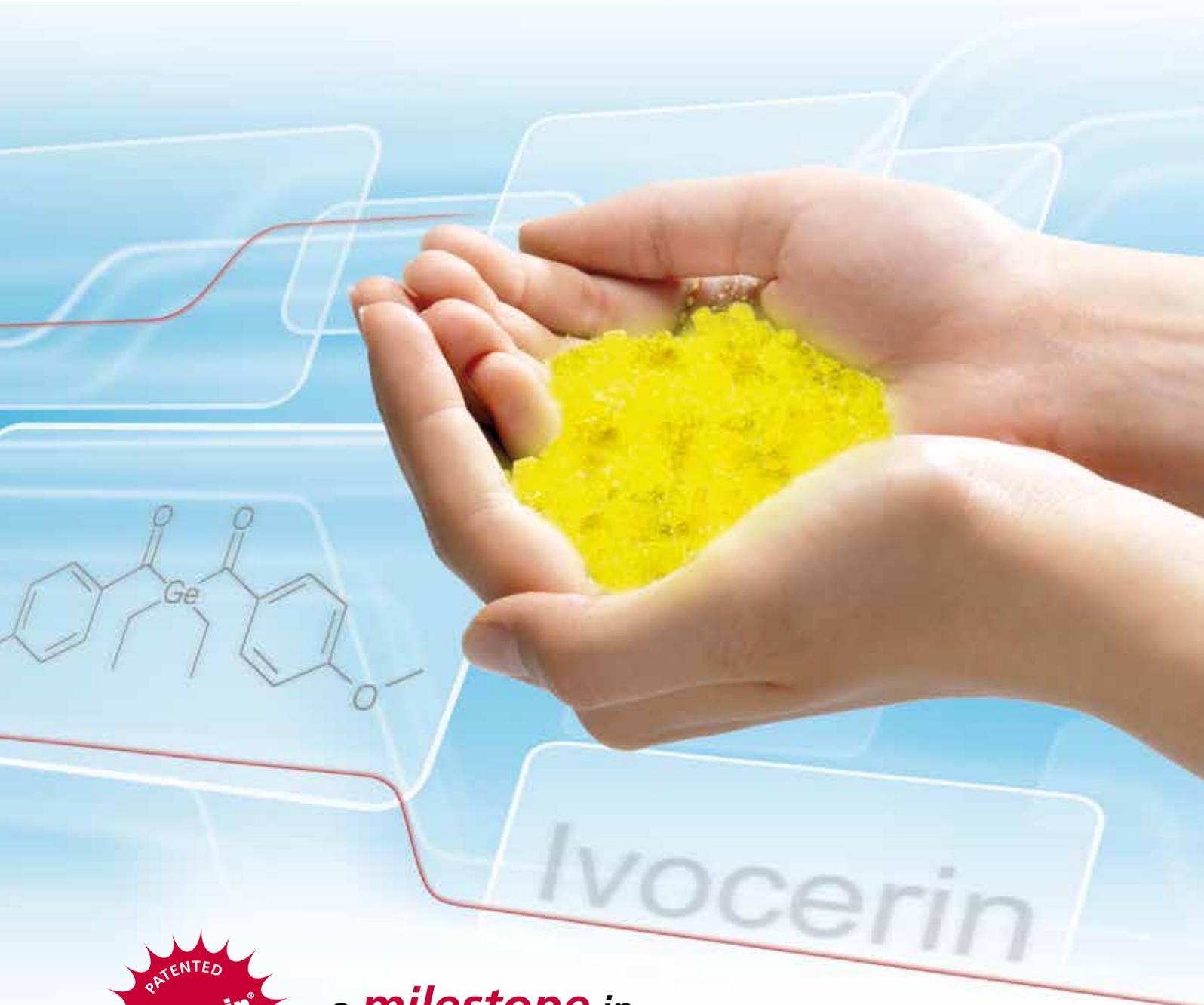


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July 2013

# REPORT

Research and Development Ivoclar Vivadent AG, 9494 Schaan / Liechtenstein



– a ***milestone*** in  
composite ***technology.***

ivoclar  
vivadent®  
passion vision innovation



Dr Thomas Hirt  
Chief Technology Officer

The 2-mm increment technique has been the standard application method for direct dental composites for many years. Over time, the properties of resin composites have been consistently improved and the bond strength of dental adhesives optimized. In contrast, the light initiators used in composite filling materials and the light-emitting efficiency of the photo-polymerization process remained unchanged for many years.

This edition of the R&D Report looks at the fundamentals of photo-polymerization and discusses our new photoinitiator Ivocerin®. In this publication, we describe the development, working mechanism and application of a new class of photoinitiators for the visible light spectrum and light polymerization in general. Ivocerin has enabled us to develop Tetric EvoCeram® Bulk Fill, a direct composite that can be applied and cured in 4-mm bulk increments. The use of Ivocerin is explained on the basis of this product.

Three technological developments of Ivoclar Vivadent have been incorporated into Tetric EvoCeram Bulk Fill:

- Ivocerin as a photoinitiator (polymerization booster)
- A light sensitivity filter patented by Ivoclar Vivadent
- Filler technology (shrinkage stress reliever) patented by Ivoclar Vivadent

The new Ivocerin photoinitiator is characterized by high quantum efficiency, high absorption capacity and very good bleaching properties. Following on from excellent theoretical findings, we examined different concentrations and combinations of light initiators in restorative composites. In the process, we established an ideal concentration level and an effective combination with other photoinitiators. From a commercial and strategic point of view, it was important for us to obtain patents for this new type of photoinitiator, to ensure exclusivity.

After obtaining very promising fundamental research data, we proceeded to optimize the synthesis of Ivocerin in order to reproduce the molecule in large amounts and at a high level of purity. At the same time, the first successes regarding a 4-mm

depth of cure were attained with experimental composites. Furthermore, *in vitro* studies showed excellent results in terms of marginal seal, retention and esthetics. The results were comparable to those of Tetric EvoCeram placed in 2-mm increments. Ultimately, Tetric EvoCeram Bulk Fill was produced on the basis of Tetric EvoCeram, with the addition of Ivocerin and other photoinitiators. The monomer-filler system was also optimized to enhance the esthetics of the material, to reduce shrinkage stress and increase depth of cure. In a short space of time, we succeeded in launching the esthetic 4-mm bulk-fill composite Tetric EvoCeram Bulk Fill.

Ivocerin represents a very interesting alternative to the established photoinitiators: camphorquinone-amine, phenyl propandione and acyl phosphine oxide (Lucirin TPO). Ivocerin is capable of absorbing light at a higher wavelength range than acyl phosphine oxide, and can therefore be activated by all commercially available (halogen, LED) polymerization lights. In contrast to the camphorquinone-amine initiators, Ivocerin can be used to produce amine-free composite resins, which are colour-stable under artificial sunlight and do not interact with acid monomers. For Tetric EvoCeram Bulk Fill however, the combination of Ivocerin plus camphorquinone-amine has proven to be most successful at ensuring excellent cure in increments of 4 mm.

In this R&D Report, Prof. Dr Moszner provides detailed information about the scientific fundamentals of photopolymerization and the synthesis and development of the new Ivocerin initiator. Dr Burtscher, Director of R&D Clinical, compares the properties of Ivocerin with those of camphorquinone. A description of the development of Tetric EvoCeram Bulk Fill based on Tetric EvoCeram is given by K. Vogel, a Senior Research Associate at Ivoclar Vivadent. J. Todd of Scientific Services provides a summary of the results of internal and external materials science studies on Tetric EvoCeram Bulk Fill and Ivocerin, whilst Dr Heintze and Dr Peschke discuss the clinical significance of simulation tests and the clinical performance of Tetric EvoCeram Bulk Fill respectively.

- 4** Prof. Dr Norbert Moszner  
**State of the art:  
Photopolymerization in dentistry**
- 11** Dr Peter Burtscher  
**Ivocerin® in comparison to camphorquinone**
- 16** Dipl. Ing. Karin Vogel  
**From Tetric EvoCeram® to  
Tetric EvoCeram® Bulk Fill**
- 21** Joanna-Claire Todd (BA, MPH)  
**Materials Science Investigations underpinning  
Tetric EvoCeram® Bulk Fill and Ivocerin®**
- 28** Dr Siegward Heintze  
**Laboratory simulation tests with  
Tetric EvoCeram® Bulk Fill and their clinical  
significance**
- 36** Dr Arnd Peschke  
**Tetric EvoCeram® Bulk Fill  
in clinical use**



Prof. Dr Norbert Moszner  
Head of Department: Basic Research – Polymer Chemistry

## State of the art: Photopolymerization in dentistry

### Introduction

Light-curing filling materials have been on the market since the 1970s. These materials are composed of monomers and fillers and additionally contain initiators, stabilizers and additives which are dissolved in the monomer. As the polymerization reaction can be initiated “on demand”, these materials give users sufficient time to apply them in the cavity.

Single-component materials offer decisive advantages over two-component materials. As no mixing is required, these materials usually feature a much higher consistency and thus have a lower monomer content. This results in a lower degree of polymerization shrinkage and improved stability. A vacuum during the production process ensures that the pastes are “evacuated”, eliminating any air, creating a pore-free material. The photoinitiators used are temperature-insensitive and do not require refrigeration. As light transmission through composite material is only limited, a cavity usually needs to be filled in several increments, each of which is cured separately. Normally, the thickness of each increment must not exceed 2 mm, as complete curing cannot be ensured with thicker layers. In order to increase the admissible maximum layer thickness, all factors influencing the depth of cure need to be taken into account, including translucency, shading, initiators and their concentration, exposure time and light intensity. The photoinitiator Ivocerin®, which was developed by Ivoclar Vivadent in cooperation with the Vienna University of Technology, has made a major contribution to increasing the admissible layer thickness without detrimentally affecting the optical properties of composite resin such as translucency and shade.

### The fundamentals of radical photopolymerization

Radical photopolymerization is an electromagnetic radiation (light)-induced process which results in the formation of a polymer. The radical  $R\cdot$  that triggers the process is formed by exposing a photo-unstable compound, the so-called photoinitiator (PI), to light (photolysis). Radicals are unstable (reactive) groups of atoms with at least one unpaired electron e.g.  $\cdot\text{CH}_3$ , a methyl radical. Photoinitiators can be classified according to the wavelength range of the light used for their activation ( $\lambda$  in nm) or according to the mechanism employed for the photolysis. The types of light most frequently used for photopolymerization are medium-wave ultraviolet light (UVB, 280–315 nm), long-wave ultraviolet light (UVA, 315–380 nm), visible light (VL, 400–780 nm) and short-wave infrared light (NIR, 780–1500 nm). Accordingly, we differentiate between UV, VL and NIR photoinitiators, which absorb light in the respective spectral region. As the light energy is inversely proportional to the wavelength, ultraviolet light has more energy than visible light or NIR radiation. The radicals that initiate the polymerization reaction are either formed by means of bond fission (cf. Fig. 1: **M-PI**) or by the transfer of a hydrogen atom H from a second compound, the so-called coinitiator DH (cf. Fig. 1: **B-PI**). Irrespective of the mechanism used, it is important that the photoinitiator (A or B) reaches an excited state ( $A^*$  or  $B^*$ ) due to the light energy absorbed, as in this state, radicals are formed through bond fission (**M-PI**) or hydrogen transfer (**B-PI**) [1].

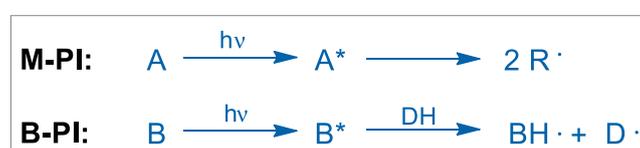


Fig. 1: The mechanism of radical formation in photoinitiators

Many photoinitiators contain carbonyl groups as light-absorbing groups ( $\text{>C=O}$ ). One example is the commercially available Lucirin TPO (2,4,6-trimethylbenzoyldiphenylphosphine oxide), which absorbs light in the transition area between the visible and the UVA range ( $\lambda_{\text{max}} = 385 \text{ nm}$ ) and forms radicals by bond fission (Fig. 2). An example of a carbonyl compound that requires hydrogen transfer to form radicals is camphorquinone (CQ,  $\lambda_{\text{max}} = 468 \text{ nm}$ ). It absorbs light in the visible spectrum and is used in combination with amine as the coinitiator (Fig. 3).

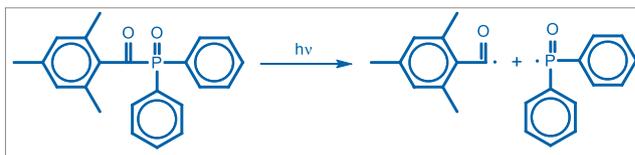


Fig. 2: Radical formation of Lucirin TPO (acylphosphine oxide)

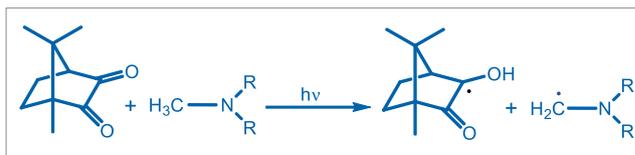


Fig. 3: Radical formation of CQ with amines

In dental materials, methacrylic acid esters, so-called methacrylates, are employed as radically polymerizable monomers [2-4]. Depending on their number  $n$  of polymerizable methacrylate groups, they are classified into monofunctional ( $n = 1$ ; e.g. methyl methacrylate), difunctional ( $n = 2$ ) and multifunctional ( $n = 2$ ) methacrylates (Fig. 4).

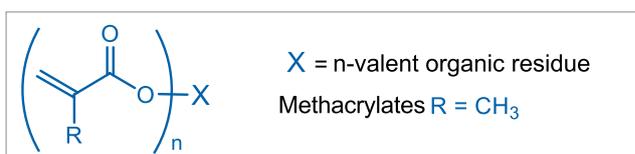


Fig. 4: Structural chemical formula of methacrylate

In the radical photopolymerization of monofunctional monomers  $M$ , linear polymers are formed. In the process, the speed of polymerization  $RP$  is directly proportional to the product of the monomer concentration  $[M]$  and the root extracted from the speed of the radical formation  $R_i$  [5]:  $RP \sim [M] \cdot R_i^{0.5}$ .

The speed of the radical formation  $R_i$  is dependent on the intensity of the incident light, the conversion quantum efficiency, the extinction coefficient, the concentration of the photoinitiator and the thickness of the layer through which the light needs to pass. Consequently, effective photoinitiators should be characterized by high quantum efficiency and a high extinction coefficient, i.e. show strong absorption of light in the wavelength range applied.

In the radical photopolymerization of dimethacrylates, a three-dimensional (3-D) polymer network is formed. Therefore, dimethacrylates are also called crosslinkers. If we look at the time-dependent turnover of e.g. dimethacrylates during photopolymerization, the following sequences can be distinguished [3, 6]: During the radiation phase, radicals are formed until the photoinitiator is used up. Within a split second, these radicals react with the stabilizer molecules until these are used up completely. Photopolymerizable materials contain stabilizers such as 2,6 di-tert. butyl-4-methyl-phenol (BHT) or hydroquinone monomethyl ether (MEHQ) in order to ensure storage stability for several years. Following the reaction with the stabilizer molecules, linear polymer radicals with lateral double bonds form. This is followed by the formation of branched radicals and micro-gel particles in quick succession (Fig. 5). When the so-called gelation point is reached (after approx. 1–2 s), a 3-D polymer network is formed, which leads to a considerable acceleration of the polymerization reaction. When customary light sources are used, approx. 5–10 s are required to achieve a nearly 100 % monomer conversion rate and a high rate of double bond formation. Even after the radiation phase, i.e.

when primary radicals are no longer formed, still any existing macro-radicals embedded in the polymer network can react with the remaining double bonds by means of a dark reaction [7].

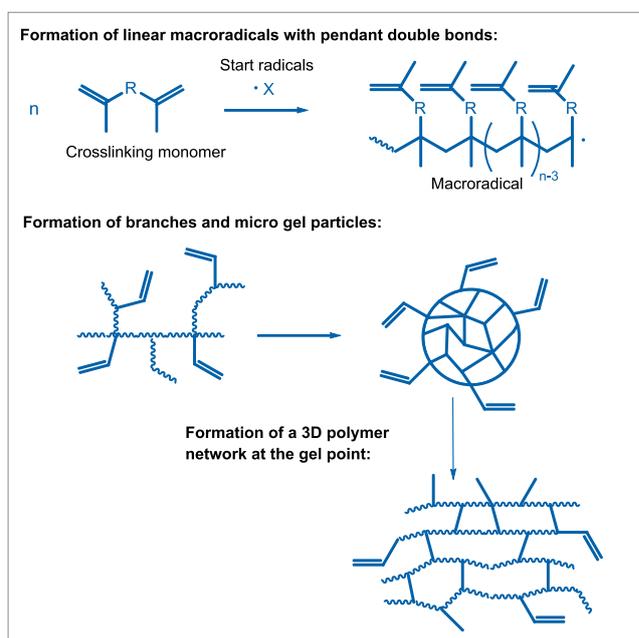


Fig. 5: The sequence of cross-linking radical polymerization

This crosslinking polymerization process results in the desired curing of the material while heat is released. Even if a 100 % monomer conversion rate is achieved (meaning that all the monomer molecules are linked to the network by at least one double bond), the 3-D polymer network still contains unconverted double bonds and polymer radicals. This is due to the fact that at room temperature, the network that forms is not flexible enough to allow all the double bonds or radicals to be accessed during the polymerization reaction. As the flexibility of a polymer network decreases with increasing network density, the remaining double bond content of the polymer network increases with the functionality of the primary monomers. During the photopolymerization process, the properties of the employed monomer mixture or the composite paste undergo a significant change: The initially viscous, non-crosslinked material becomes solid, insoluble and odourless. The exothermal polymerization reaction manifests itself through a temperature increase. At the same time, the monomer mixture which is in the state of being cured is reduced in volume. This phenomenon is also described as polymerization shrinkage.

## Photoinitiators in dental materials

Light-curing dental filling materials were mentioned for the first time in a patent [8] issued in 1970 and were introduced to the market a few years later [9, 10]. These materials, which also included fissure sealants, cavity liners and cements, typically contained UV initiators such as benzoin methyl ether ([11], Fig. 6) and were cured by irradiation with UV curing lights.

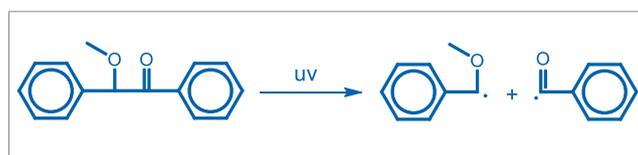


Fig. 6: Radical formation during UV cleavage of benzoin methyl ether

However, polymerization by means of ultraviolet light has several significant disadvantages. For example, ultraviolet radiation may damage the mucous membranes or harm the eyes of dentists and patients. The main disadvantage, however, is the fact that ultraviolet radiation is strongly scattered by the filler particles, so that in shaded composite resin a curing depth of less than 1 mm is achieved. To overcome these drawbacks, composite resins containing alpha diketones as photoinitiators have been developed, which are cured with light in the visible range. [12]. Alpha diketones are compounds that feature two neighbouring carbonyl groups.

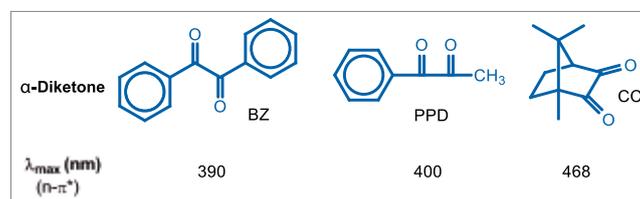


Fig. 7: Examples of alpha diketones and their absorption maximum in the long-wave range

Dibenzoyl (BZ), 1-phenyl-1,2-propanedione (PPD) or camphorquinone (CQ) are easily accessible alpha diketones that absorb light in the visible spectrum (Fig. 7). These compounds have an intensive yellow (CQ) to pale yellow (BZ) colour. This is due to the fact that they absorb light in the visible blue spectrum (400–500 nm). As mentioned earlier, they require a coinitiator to form polymerization-inducing radicals. Due to the relatively strong light absorption properties of CQ and its low toxicity/the low toxicity of its photolysis products, CQ-containing photoinitiators have been used in dentistry (mainly CQ-amine systems)

almost exclusively. As a result, the photochemistry of CQ is very well-researched; for a summary of related literature please refer to [13]. If CQ is exposed to blue light in the presence of amine  $R-N(CH_3)_2$ , a CQ radical anion and an amine radical cation are formed (Fig. 8). This is followed by the transfer of a hydrogen atom from the amine radical cation - the rate-determining step which results in the formation of a CQ radical and an aminoalkyl radical. Only the aminoalkyl radical can initiate the polymerization reaction. In the course of the reaction, the molecule group responsible for the yellow shade of CQ is destroyed. Thus in contrast to other visible light absorbing photoinitiators, CQ demonstrates an excellent photo-bleaching effect. In other words, it loses its colour almost completely when exposed to light in the visible range. Unfortunately, the quantum efficiency of CQ-based photoinitiator systems has been shown to be at a level of only 0.07, which is very low [14].

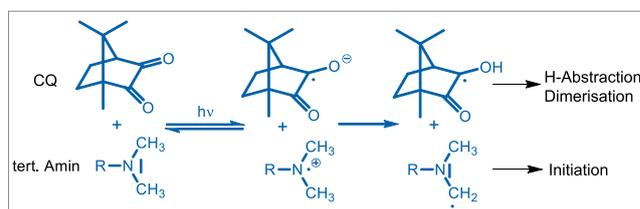


Fig. 8: Radical formation of CQ-amine systems

Several amines were examined regarding their suitability as coinitiators with CQ. In Figure 9, a selection of the most suitable amines is presented. They are characterized by optimum properties such as quick formation of radicals in combination with CQ, minimum propensity to discolour or release odours and low toxicity [13]. Amine-based coinitiators such as 4-(dimethylamino)benzoic acid ethyl ester (DMAB) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) tend to be found in combination with CQ in dental materials.

Due to various reasons, CQ-amine photoinitiators were combined with other photoinitiators [15]. By adding alpha diketone (PPD) (Fig. 7), for example, more reliable curing of composite resins containing CQ-amine mixtures was attained [16, 17]. Better curing results could also be achieved by combining CQ-amine systems with cationic photoinitiators [18, 19].

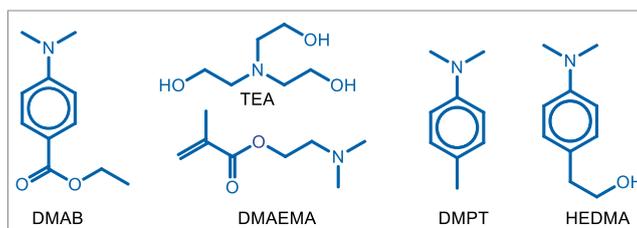


Fig. 9: Structures of effective amine-based coinitiators for CQ

CQ-amine photoinitiator systems have also been combined with the above-mentioned Lucirin TPO (Fig. 2,  $\lambda_{max} = 385$  nm) and Irgacure 819 (bis-(2,4,6-trimethylbenzoyl)phenylphosphine oxide), whose absorption spectrum maximum is in the range of 397 nm [20-23]. When exposed to light, these initiators disintegrate while forming radicals (Fig. 10).

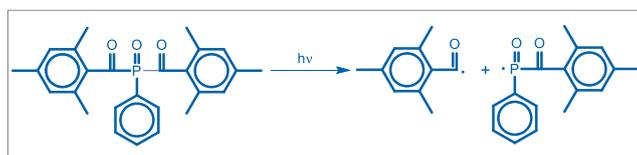


Fig. 10: Radical formation of Irgacure 819

CQ-amine photoinitiator systems have several drawbacks. They may cause discolouration of the composite resin due to the oxidation of the remaining amine component. In acidic compositions such as enamel-dentin adhesives or self-adhesive cements containing acidic monomers, another problem may occur: The acid-base reaction of the acidic monomers with the amine-based coinitiator may detrimentally affect the formation of radicals. In order to eliminate these disadvantages, various other substances were investigated with regard to their possible use as a substitute for amine. For literature on this topic please refer to [13]. In addition, CQ amine-free alternatives were evaluated. Apart from the above-mentioned Irgacure 819, these included visible light-absorbing photoinitiators such as titanocene or dye-borate systems [24].

## Ivocerin® – a new photoinitiator for dental materials

### The chemistry of Ivocerin®

Our search for an alternative visible light photoinitiator was crowned with success: in cooperation with Prof. R. Liska of the Vienna University of Technology we succeeded in developing tailor-made visible light photoinitiators based on germanium compounds. Even though it was known from the literature that radicals are formed [during light-induced cleavage of e.g. organic germanium compounds 25], the potential of these compounds as photoinitiators for the visible light spectrum had not yet been fully recognized when we started work in this field. We were able to show for the first time that germanium compounds such as benzoyltrimethylgermane (Ge-1) or dibenzoyldiethylgermane (Ge-2) (Fig. 11) represent very efficient visible light photoinitiators for methacrylate resins [26, 27]. In contrast to Lucirin TPO ( $\lambda_{\max} = 385$  nm) or Irgacure 819 ( $\lambda_{\max} = 379$  nm), Ge-1 ( $\lambda_{\max} = 411$  nm) and Ge-2 ( $\lambda_{\max} = 418$  nm) show a pronounced red shift in their absorption, which means that they absorb light more strongly within the visible region. Moreover, compared to CQ, Ge-1 and Ge-2 demonstrate much more intensive absorption in the visible region. The quantum efficiency of the light-induced cleavage for Ge-2 was determined to be 0.85, while that for Irgacure 819 was determined to be 0.59. As mentioned previously, the quantum efficiency for CQ-amine photoinitiators is below 0.10 and thus significantly lower. Moreover, quick decolouration of Ge-1 and Ge-2 was observed upon exposure to light. An analysis of dental composites containing Ge-1 or Ge-2 as photoinitiators [27, 28] also showed that they offer considerable advantages compared to CQ amine-based materials. Apart from demonstrating quicker curing and excellent bleaching behaviour, these materials require a much lower concentration of the photoinitiator to achieve comparable mechanical properties. Similar to CQ amine-based composite resins, Ge-1 or Ge-2-based materials also show high storage stability.

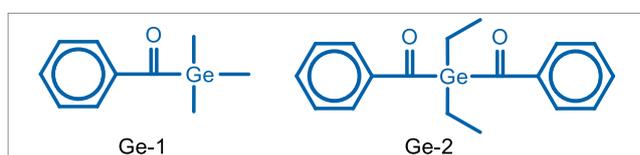


Fig. 11: Structure of the germanium photo-initiators Ge-1 and Ge-2

In cooperation with Prof. G. Gerscheidt and Prof. R. Saf of the Graz University of Technology as well as Prof. R. Liska of the Vienna University of Technology, the mechanism of photolysis in diacylgermanes exemplified by Ge-2 was studied using state-of-the-art methods [30]. In the study, light-induced cleavage of Ge-2 was investigated under various conditions. The examinations conducted confirmed that dibenzoyldiethylgermane Ge-2 forms benzoyl (B·) and germyl radicals (G·) as direct cleavage products (Fig. 12). It was established that benzaldehyde (BA) and a germane (GM) form as secondary photolysis products of the radicals B· and G· in the absence of a monomer, as well as the combination products B-B and G-G of the radicals (B·/G·) (Fig. 13 and 14).

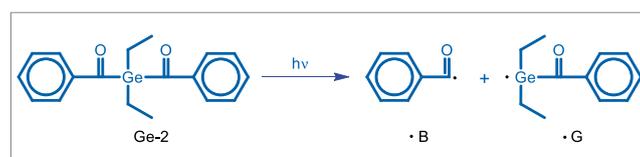


Fig. 12: Cleavage of the germanium compound Ge-2

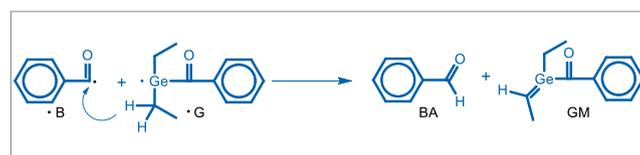


Fig. 13: Hydrogen transfer between the primary radicals B· and G·

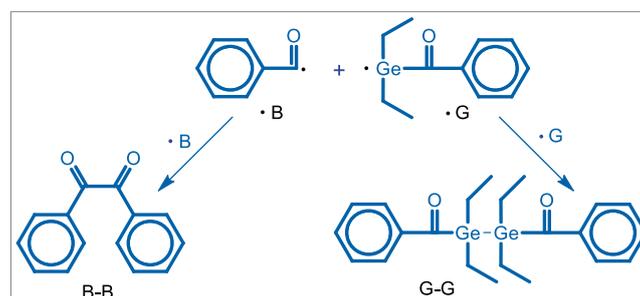


Fig. 14: Combination products of the primary radicals B· and G·

This also proved that when dibenzoyldiethylgermane Ge-2 is used as a photoinitiator, the benzoyl (B·) and germyl (G·) radicals produced by photolytic fission are the radicals that initiate the polymerization reaction.

Based on the results of these mechanistic investigations and the evaluation of different synthesis methods and structural variations of germanium compounds, bis-(4-methoxybenzoyl)diethyl-

germane Ge-3 was selected as the optimum photoinitiator and protected by a patent under the name of Ivocerin (Fig. 15). We were able to efficiently synthesize Ge-3 ( $\lambda_{\text{max}} = 408 \text{ nm}$ ) in two stages. It showed the strongest absorption in the visible region [30]. Ge-3 is a solid substance which is not soluble in water and has an intensive yellow colour. Its melting point is at approx.  $50^\circ\text{C}$ . The synthesis of Ge-3 is started by metallating protected 4-methoxybenzaldehyde using n-butyl lithium, which is then followed by a coupling reaction with dichlorodiethylgermane. In a second stage, the protecting group is split off (Fig. 15). The resulting Ivocerin is of high purity ( $> 96\%$  when determined by HPLC).

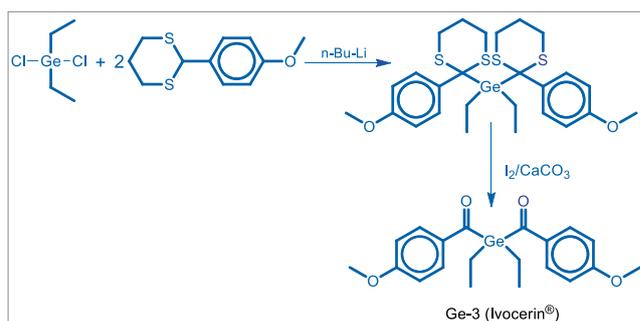


Fig. 15: Synthesis of the germanium photoinitiator Ivocerin

Apart from chemical characterization and application tests, toxicological investigations were conducted with Ivocerin and comprehensive patent protection measures were initiated.

While inorganic germanium compounds are usually toxic, organic germanium compounds are often characterized by very low toxicity. The LD50-value of tetraalkylgermanes ranges between 3000 and 5000 mg/kg, for example [31].

The cytotoxicity (XTT<sub>50</sub> value) of Ivocerin was investigated by means of an XTT assay. The initiator was found to be non-cytotoxic [32]. Moreover, two mutagenicity tests were conducted. Neither the Ames test (in vitro) [33] nor the Mouse Micronucleus Assay (in vivo) [34] revealed any mutagenic effects of Ivocerin.

We were able to obtain comprehensive patent protection for the germanium compounds. The US and EP patents were granted in 2009 [35].

## Summary

Compared to conventional camphorquinone/amine-based photoinitiator systems, the novel germanium photoinitiator Ivocerin is characterized by intensive absorption of light in the visible region and high photoreactivity. Furthermore, it imparts an excellent bleaching behaviour to composite resins. The radicals required to initiate the polymerization reaction are created by light-induced cleavage of Ivocerin. Additional co-initiators or accelerators are not required. The quantum efficiency of radical formation in conjunction with Ivocerin is many times higher than that in conjunction with camphorquinone.

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## Ivocerin® in comparison to camphorquinone

### Introduction

All customary composite filling materials are polymerized with blue light. Therefore, the light-absorbing initiators in the composites have an inherent yellow colour, as this is the complementary colour to blue light. When composites are cured, the colour of the initiator largely disappears, however a slight yellowish tinge always remains - meaning completely white restorations cannot be created with materials that cure with blue light. This light tinge is accepted by dental practitioners, as natural teeth also have a yellow hue.

### Photoinitiators

Figures 1a, 1b and 1c show the initiators in their pure form. Camphorquinone (CQ) and Ivocerin® in particular, exhibit a very strong yellow colour.

Figure 2 compares the absorption spectra of conventional initiators with that of Ivocerin. Of particular note is the strong absorption of Ivocerin in comparison to camphorquinone despite the fact that its concentration is considerably lower. Acyl phosphine oxide, e.g. Lucirin TPO, predominantly absorbs light in the UV range. Hence, its inherent yellowish colour is very light, as shown in Figure 1b.

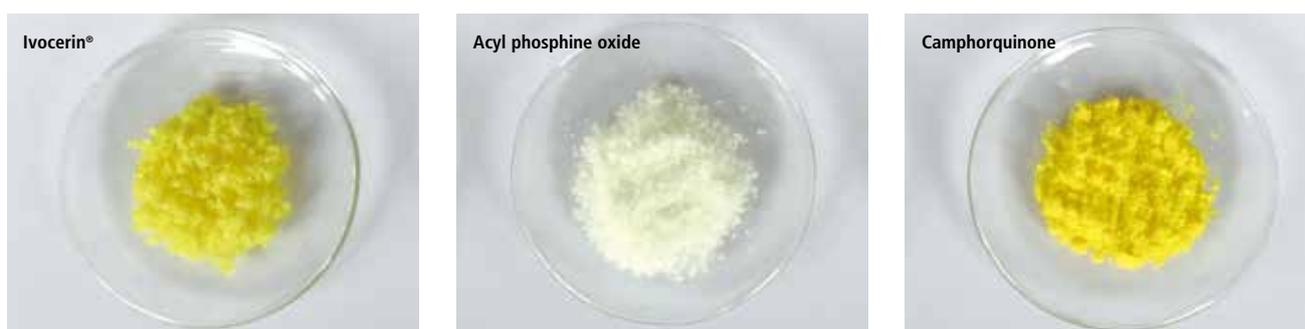


Fig. 1a-c: Photoinitiators in their pure form

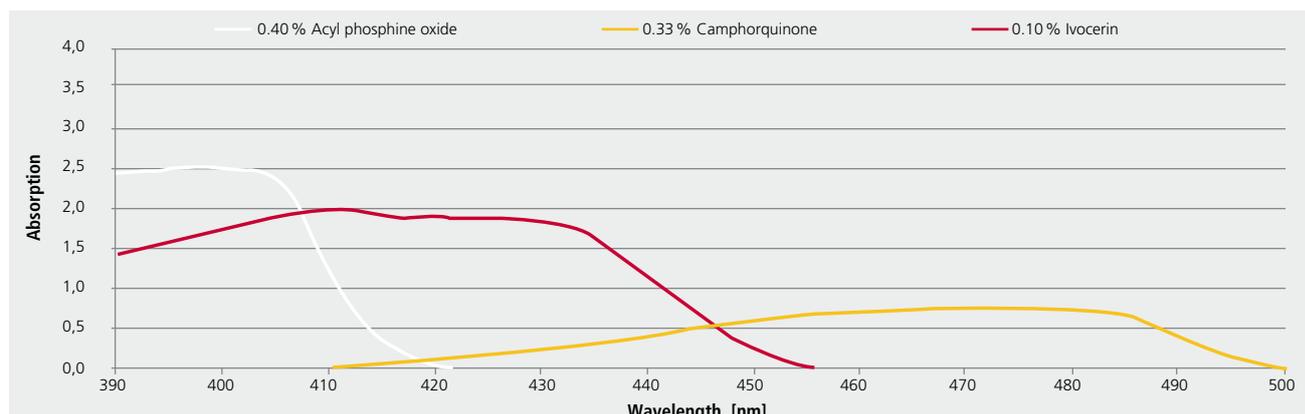


Fig. 2: Absorption spectra of acyl phosphine oxide (e.g. Lucirin TPO), camphorquinone and Ivocerin (R&D Ivoclar Vivadent, 2012)

## Investigations with Ivocerin®

Extensive studies were undertaken to examine the suitability of Ivocerin in dental composite resins:

### Determination of a suitable concentration of Ivocerin to obtain the same curing results as with camphorquinone

Camphorquinone is usually added to the monomer in a concentration of 0.3 wt%. At lower concentrations, reactivity declines, but at higher concentrations, depth of cure decreases, because more blue light is absorbed by the inherent colour of this initiator. Camphorquinone cannot be used on its own. It always has to be used together with a co-initiator, usually in the form of a tertiary aromatic amine. The concentration of this co-initiator has to be at least equimolar to that of camphorquinone. Amounts in excess of approx. 50 to 100 % have been shown to produce heightened reactivity. Nevertheless, an even larger amount of amine reduces the UV stability of the composite. Therefore, monomers were tested with 0.1–0.4 wt% Ivocerin in a Tetric-like formulation in order to examine the reactivity of this composition compared with that of a standard monomer with 0.3 wt% camphorquinone in combination with 0.6 wt% amine.

Initiator in monomer	Flexural strength (MPa)	Modulus of elasticity (MPa)
0.10 % Ivocerin	124 ± 8	7200 ± 300
0.15 % Ivocerin	124 ± 14	8500 ± 200
0.20 % Ivocerin	135 ± 9	9400 ± 600
0.40 % Ivocerin	140 ± 15	10300 ± 300
0.30 % CQ and 0.60 % amine	138 ± 10	9200 ± 600

Tab. 1: Flexural strength and modulus of elasticity in relation to the Ivocerin concentration in comparison to a standard initiator system

Table 1 shows that 0.2% Ivocerin in the monomer achieves comparable results to the conventional amount of camphorquinone and amine. Higher concentrations of Ivocerin increase the strength of the composite.

### Influence of the Ivocerin concentration on the depth of cure

Initiator in monomer	Depth of cure (mm)
0.2 % Ivocerin	4.7
0.4 % Ivocerin	5.1
0.3 % CQ / 0.6 % amine	4.7

Tab. 2: Depth of cure in relation to the Ivocerin concentration compared to a standard initiator system.

Similar to the results with flexural strength, table 2 shows that a concentration of 0.2 % Ivocerin, also achieves good results in terms of depth of cure i.e. the same as the standard concentration of camphorquinone and amine. A concentration of 0.4 % Ivocerin, increases the depth of cure significantly.

### Influence of Ivocerin on light sensitivity

Ivocerin can only be used within certain concentration limits. Due to the high reactivity of Ivocerin, the light sensitivity of composites increases when higher concentrations of the initiator are used. As all light-cured composite resins are polymerized with blue light and blue light is a component of ambient light, these materials are sensitive to ambient light also. The "light sensitivity" aspect of dental polymer-based restoratives is addressed in ISO 4049. According to this standard, dental composites should be able to withstand irradiation with 8000 lux for a period of 60 seconds without showing any signs of premature polymerization. The operatory lights used in dental offices generally emit 20,000 lux. Composite resins therefore react more sensitively in this setting. The influence of the Ivocerin concentration on the light sensitivity of a standard composite was compared with that of camphorquinone.

Initiator concentration in monomer	Light sensitivity
0.2 % Ivocerin	150 s
0.4 % Ivocerin	80 s
0.3 % CQ / 0.6 % amine	140 s

Tab. 3: Light sensitivity in relation to the Ivocerin concentration compared to a standard initiator system

Table 3 clearly shows the negative influence of a high Ivocerin concentration on the light sensitivity of a composite resin. Even though stabilizers can be added to reduce this light sensitivity,

they reduce initiator reactivity, which in turn has a negative impact on the material's strength and depth of cure. The simultaneous increase of the initiator and the stabilizer concentration leads to a situation which is comparable to that of pressing the accelerator pedal and pulling the handbrake of a car at the same time. An appropriate balance of Ivocerin, camphorquinone, amine and stabilizers needed to be found in order to produce a composite resin featuring both acceptable light sensitivity and high reactivity.

#### Influence of Ivocerin on the colour of dental composites

As shown in Figure 1a, pure Ivocerin has a deep yellow colour, which is responsible for the yellowish appearance of the composite resin in its unpolymerized state. Nevertheless, Ivocerin has very good "bleaching" properties. In other words, its inherent yellow colour diminishes during polymerization. This change is clearly visible to the naked eye.

	Before polymerization	After polymerization
Composite containing 0.2 % Ivocerin in the monomer		
Composite containing camphorquinone-amine		

Fig. 3: Comparison of the colour of composites before and after polymerization

The picture clearly shows that both the composite containing 0.2 % Ivocerin in the monomer and the composite containing camphorquinone-amine exhibit a similar initial yellow colouring and a much lighter appearance after polymerization.

#### Influence of Ivocerin on the colour stability of composite resins under artificial sunlight

The standard for polymer-based restorative materials (ISO 4049) describes a test which examines the colour stability of a composite resin under artificial sunlight. In this test, most of the systems containing camphorquinone and amine show a slight change in colour, since the amine component is not colour stable. Ivocerin does not require the addition of amine to

polymerize and is therefore more resistant to colour change. Figure 4 shows a composite containing a camphorquinone-amine initiator and a material containing Ivocerin. The composite sample was fabricated and then its right half was covered with aluminium foil. Subsequently, the disc was exposed to 24 hours of artificial sunlight. After the test, the change in colour of the camphorquinone-amine sample was quite distinct (top left). The composite containing Ivocerin, however, proved very resistant to the artificial sunlight exposure (bottom left).

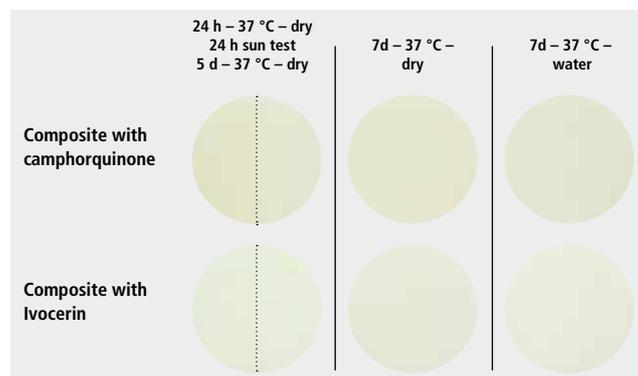


Fig. 4: Composite samples after various forms of aging

#### Influence on double bond conversion

As explained in the theoretical fundamentals, not all of the double bonds of the monomers react within a composite during polymerization. Double bond conversion describes the percentage of double bonds that are actually involved in the reaction process. Double bond conversion is dependent on the reactivity of the monomers themselves and on the initiator used. The following test results show that a significantly higher double bond conversion rate can be achieved with Ivocerin than with a camphorquinone-amine system. The composite resins listed contain the same monomer and filler composition, but different concentrations of the initiator in the monomer.

Initiator concentration in monomer	Double bond conversion
Composite A with 0.4 % Ivocerin	65,3 ± 0.5 %
Composite B with 0.3 % Ivocerin	67,8 ± 1.0 %
Composite C with 0.2 % Ivocerin	62,3 ± 1.0 %
Composite D with CQ-amine	49,1 ± 1.7 %

Tab. 4: Double bond conversion in relation to the concentration of Ivocerin and CQ-amine

The table clearly shows the influence of the initiator on the double bond conversion rate. It is considerably higher in the specimens containing Ivocerin, than in the sample containing the camphorquinone-amine initiator. The difference between 0.3 % and 0.4 % Ivocerin is not significant. A decrease in the double bond conversion rate is evident in the sample with 0.2 % Ivocerin.

### Influence on shrinkage stress

Naturally, the high reactivity of Ivocerin influences the shrinkage behaviour of the composite resin, however this depends on the amount of Ivocerin used in the monomer. The shrinkage stress of composites containing Ivocerin was measured with the Bioman Shrinkage-Stress Instrument developed by Prof. D. C. Watts at the University of Manchester, UK.

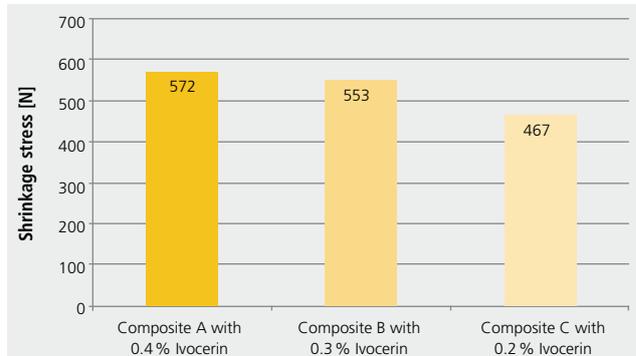


Fig. 5: Shrinkage stress in relation to the concentration of Ivocerin in the monomer

### Influence on polymerization shrinkage

The polymerization shrinkage was established using a mercury dilatometer.

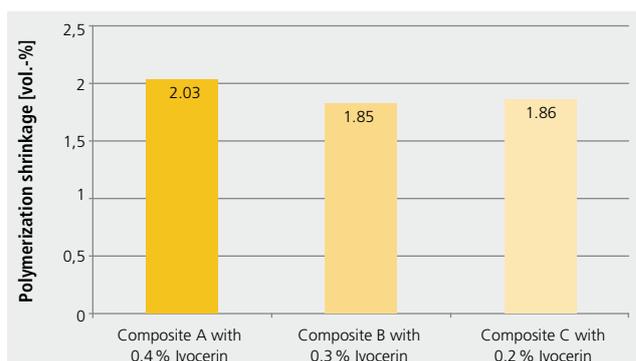


Fig. 6: Polymerization shrinkage in relation to the concentration of Ivocerin in the monomer

The influence of Ivocerin is evident only at the highest concentration. A direct correlation between the double bond conversion, the shrinkage stress and the polymerization shrinkage rates is not apparent in the present tables, since these parameters were measured at different times in accordance with the test method used.

### Combination of Ivocerin with other light-activated initiators

It was interesting to find out whether or not Ivocerin offers improved depth of cure in combination with other initiators. The ideal choice was to combine it with camphorquinone and amine. In this case, the amine concentration had to be twice as high as that of camphorquinone.

Determining the depth of cure is a quick method for examining the reactivity of a composite. Vickers hardness tests however provide more meaningful results. The composite material is polymerized in the recommended layer-thickness and Vickers hardness values are established at the top and bottom of the sample. According to a study by David Watts (University of Manchester), the material is adequately cured when the hardness established at the bottom of the sample corresponds to at least 80 % of that measured at the surface [1].

In the following investigation, the influence of the initiator system on the depth of cure (DOC, irradiation with Bluephase G1 in HIP mode for 10 s) and the Vickers hardness (same irradiation) were evaluated.

Initiator concentration in monomer	DHT (mm)	Vickers hardness at surface (N/mm <sup>2</sup> )	Vickers hardness at bottom, 4 mm	
			Value (N/mm <sup>2</sup> )	% of the surface hardness
0.2 % Ivocerin	4.7	489	333	68
0.2 % / 0.1 % CQ	4.9	511	378	74
0.2 % Ivocerin / 0.2 % CQ	5.1	524	414	79
0.4 % Ivocerin	5.1	536	437	82
0.4 % Ivocerin / 0.3 % CQ	5.6	538	462	86
0.6 % Ivocerin / 0.3 % CQ	5.6	546	465	85

Tab. 5: Depth of cure and Vickers hardness of composites containing different concentrations of initiator

The results show that the depth of cure and the hardness of 4-mm thick increments significantly improve in the cases where Ivocerin is used together with camphorquinone. However, it is also evident that higher concentrations of Ivocerin do not lead to further increases in curing-performance.

## Summary

The different evaluations of Ivocerin show that this initiator can be used successfully as an alternative to camphorquinone-amine. Excellent depth of cure is achieved in 4-mm increments, in particular when Ivocerin is used together with camphorquinone-amine. This initiator combination was used for the first time in the innovative Tetric EvoCeram Bulk Fill composite.

The fundamental research on Ivocerin has been incorporated into the development of Tetric EvoCeram Bulk Fill. Given all the different influences of Ivocerin on the physical properties of a composite resin, the concentration of this initiator was deliberately kept low in this product. As a consequence, the colour of the filling material before polymerization is only moderately influenced and the shrinkage stress is reduced to a minimum. The resulting composite resin is available in three basic shades to cover the esthetic demands of posterior teeth. Furthermore, Tetric EvoCeram Bulk Fill, can be placed in 4-mm thick increments, which are polymerized in 10 seconds with the Bluephase Style curing light (1,100 mW/cm<sup>2</sup>).

## Literature

- [1] D. Watts, O. Amer, E. Combe. Characteristics of visible light-activated composite systems. *Br Dent J* 156 (1984) 209-215



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## From Tetric EvoCeram® to Tetric EvoCeram® Bulk Fill

Since its introduction almost 10 years ago, Tetric EvoCeram® has been producing excellent clinical results. The composite filling material meets high standards with regard to its longevity and esthetics. Furthermore, it shows very good shrinkage behaviour and surface characteristics (polishing properties and wear resistance). Since the new bulk-fill material is intended for use without a capping layer, its surface properties have to meet the same requirements as those of Tetric EvoCeram. Alongside having to satisfy these typical composite requirements, the developers of the product were also faced with the challenge of engineering a tooth-coloured material that could be placed in 4-mm bulk increments.

### Tetric EvoCeram® Bulk Fill with Ivocerin®

The Ivocerin® light initiator has enabled the development of a composite resin that has an enamel-like appearance and the ability to be cured in bulk increments of 4-mm. Figure 2 shows that Ivocerin's (CQ + Ivocerin) heightened efficiency, compared with camphorquinone-amine (CQ), comes into play at a depth beyond 3 mm. The decrease in the bottom/top Vickers hardness ratios are far less obvious with CQ + Ivocerin than with camphorquinone/amine alone (CQ). Thus, Ivocerin helps generate the strength required for a composite resin suitable for the bulk-filling technique.

### Optimization of the monomer blend in Tetric EvoCeram® Bulk Fill

In addition to the new Ivocerin initiator described in detail in the previous chapters, Tetric EvoCeram Bulk Fill also contains camphorquinone and 2,4,6 trimethyl benzoyl diphenyl phosphine oxide (acyl phosphine oxide – comparable to Lucirin® TPO). These components are used in well-balanced proportions to ensure optimized reactivity, working time, depth of cure and strength.

### Light sensitivity (working time in ambient light)

Due to the incorporation of the light initiators, camphorquinone, acyl phosphine oxide and Ivocerin, Tetric EvoCeram Bulk Fill can be applied and cured in increments of 4 mm. However, it is of utmost importance to prevent premature polymerization as a result of the heightened conversion rate of the monomer. That is, an adequate working time, for placing and sculpting the restoration should be ensured. As light-cured composites generally contain photoinitiators that react to blue light, the blue light contained in ambient light or operatory light can also trigger premature polymerization in these materials.

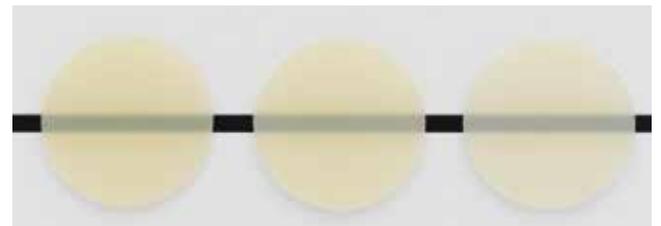


Fig. 1: Tetric EvoCeram Bulk Fill shades: IVA, IVB and IVW

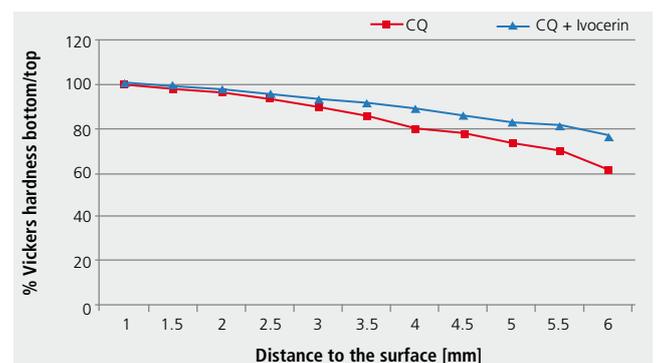


Fig. 2: Tetric EvoCeram Bulk Fill IVA: Percentage bottom/top Vickers hardness in relation to the distance from the surface for different initiator blends

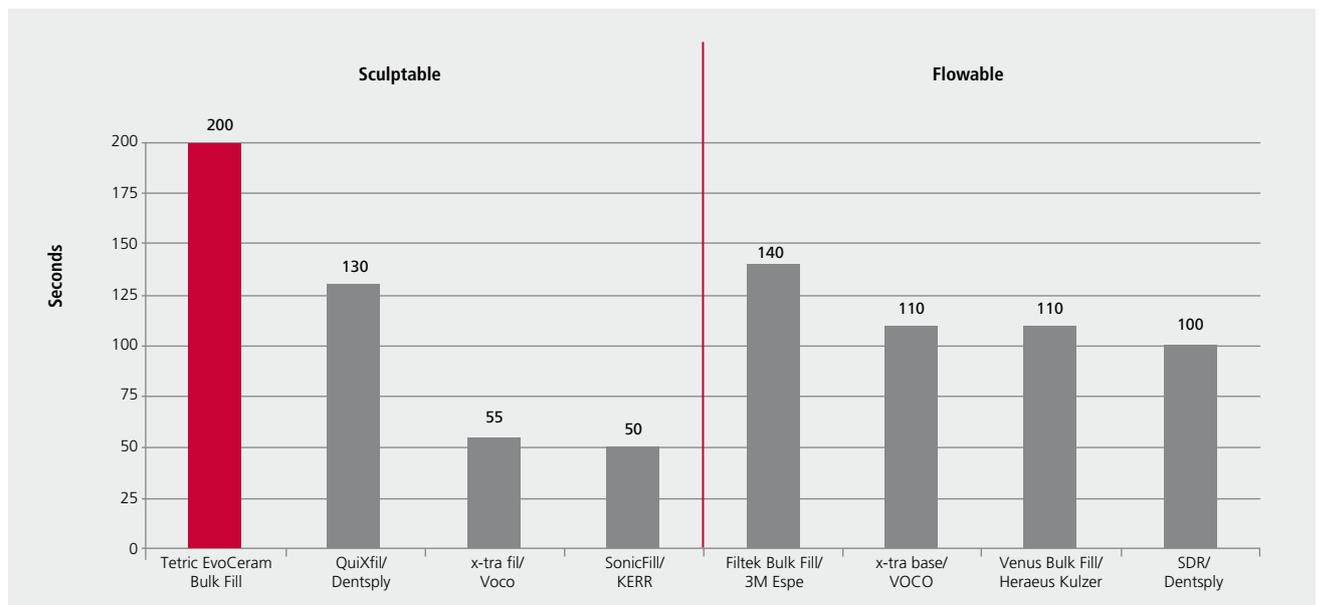


Fig. 3: Sensitivity to ambient light/working time of various bulk-fill composites established according to ISO 4049 (R&D Ivoclar Vivadent AG, June 2011)

Tetric EvoCeram Bulk Fill contains a patented light sensitivity inhibitor, which prevents premature polymerization and enables the filling material to be manipulated for three minutes (200 s) under defined light conditions (ISO 4049:2009) of 8000 lux. Conventional phenolic inhibitors (MeHQ, BHT) require a concentration of at least 1000 ppm relative to the monomer in order to delay a reaction to ambient light. Just 1/10 of this amount is necessary in the case of the light sensitivity inhibitor. This is advantageous, as the small amount of stabilizer/inhibitor delays the polymerization process at low-level blue light, without impairing the depth of cure or any of the other polymerization properties.

### Optimization of the filler composition in Tetric EvoCeram Bulk Fill

The filler technology incorporated in Tetric EvoCeram Bulk Fill is based on that of the clinically proven Tetric EvoCeram. In order to fulfil the desired composite resin requirements, Tetric EvoCeram Bulk Fill contains a number of different fillers. The fine primary particles of the fillers are responsible for the composite's wear resistance and its excellent polishing properties, which are manifested in a smooth surface texture and high lustre.

The largest particles of the inorganic fillers of Tetric EvoCeram Bulk Fill measure 3 µm. The composite fillers have a maximum size of 50 µm. In the polymerized state, they behave like the smaller inorganic primary particles. The large filler particles do not protrude from the surface. Consequently, the filling can be polished to a high-gloss finish.

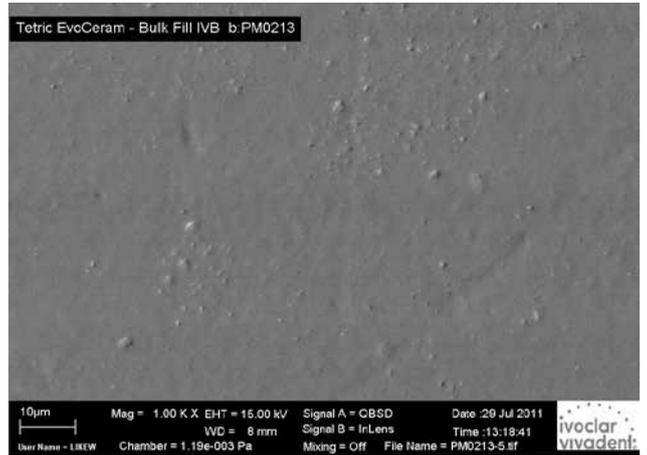
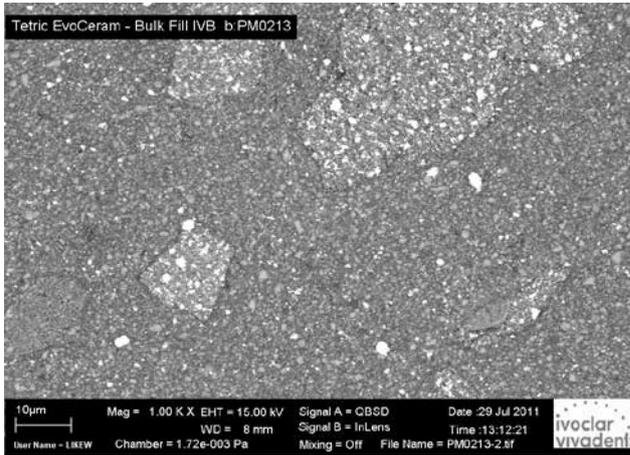


Fig. 4a and b: Scanning electron micrographs (magnification: 1000x) of the filler composition and surface structure of Tetric EvoCeram Bulk Fill (R&D Ivoclar Vivadent AG, 2011)

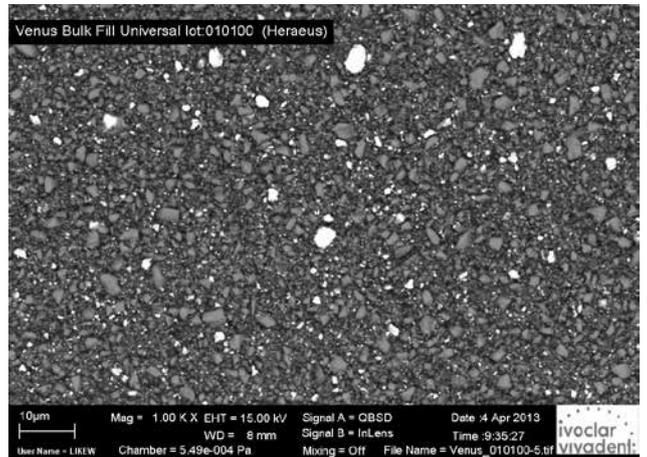
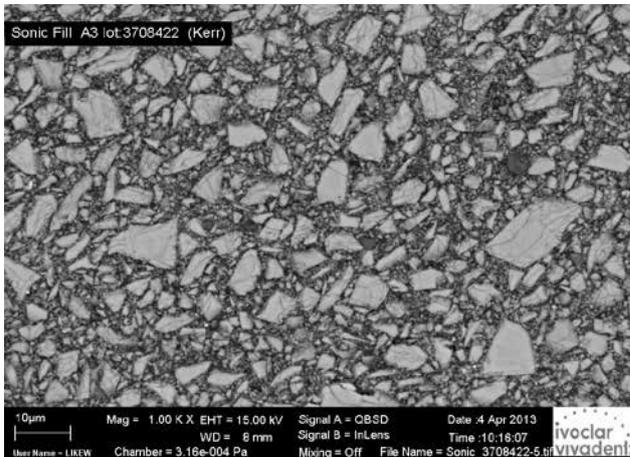


Fig. 5a: SonicFill/Kerr (1000x) (R&D Ivoclar Vivadent AG, 2011)

Fig. 5b: Venus Bulk Fill/Heraeus Kulzer (1000x) (R&D Ivoclar Vivadent AG, 2011)

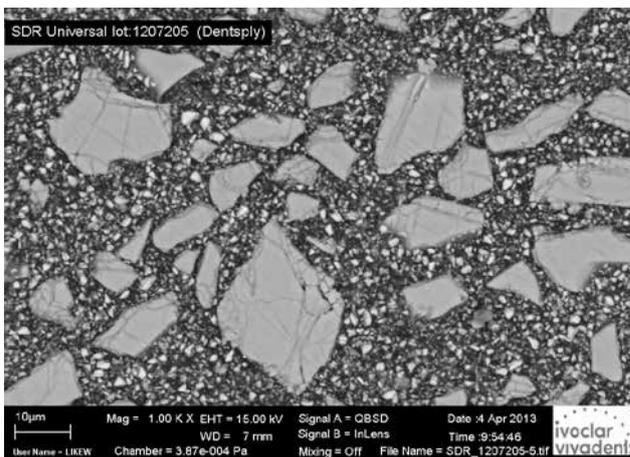


Fig. 5c: SDR Dentsply (1000x) (R&D Ivoclar Vivadent AG, 2011)

### Filler composition of other bulk-fill composites and comparison with Tetric EvoCeram Bulk Fill

Other manufacturers of bulk-fill composites mainly use coarse fillers (see Fig. 5a and c). This increases the filler content and reduces the polymerization shrinkage. However, when these materials are also used as the top-most layer, they have a distinct effect on the filling's surface texture, polishing properties, its wear behaviour and plaque resistance.

#### Polishing properties

The polishing properties are determined by the composition of the different-sized fillers. Tetric EvoCeram Bulk Fill contains the same type of fillers as Tetric EvoCeram. As a result, its polishing properties are just as good as those of the conventional filling material. The two composites (SonicFill from Kerr and SDR Flow from Dentsply) that contain the coarse inorganic fillers show very little shine, even after 30 s of polishing.

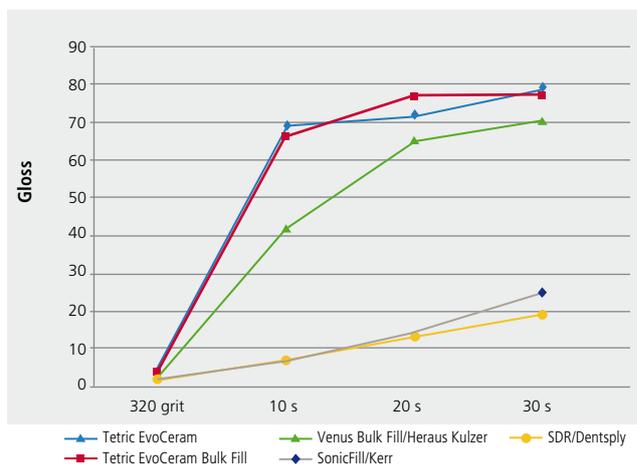


Fig. 6: Average surface gloss of five different composite filling materials compared with Tetric EvoCeram Bulk Fill after polishing with OptraPol Next Generation – in relation to the polishing time (R&D Ivoclar Vivadent AG, 2011)

#### Wear behaviour

Apart from affecting the polishing properties, the type of filler used also has a considerable influence on the wear behaviour of a composite resin. The materials containing the visibly coarser fillers are less resistant to wear than the composites featuring smaller filler particles.

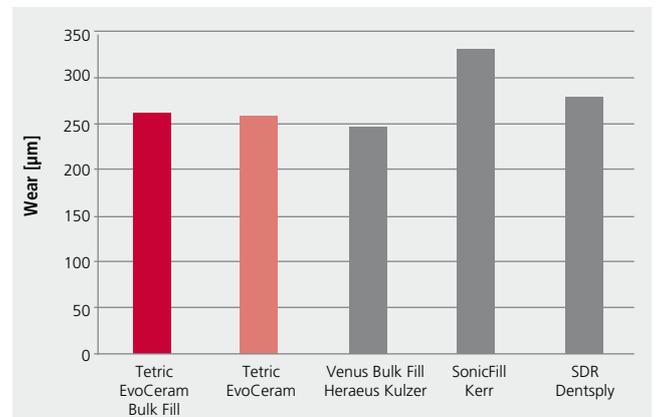


Fig. 7: Average vertical wear of Tetric EvoCeram Bulk Fill in comparison with Tetric EvoCeram and other bulk-fill materials (R&D Ivoclar Vivadent AG, 2011)

#### Shrinkage and shrinkage stress and their influencing factors

The composite filler is responsible for reducing polymerization shrinkage and lowering shrinkage stress. Tetric EvoCeram Bulk Fill contains a special composite filler that relieves shrinkage stress.

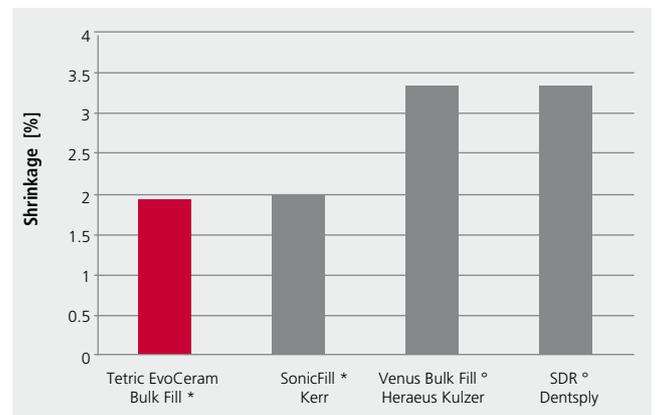


Fig. 8: Volumetric shrinkage of bulk-fill composites (\*) measured with a mercury dilatometer after 60 min (°) according to the Archimedes principle (K. Vogel, AADR 2012) [1]

The volumetric shrinkage of Tetric EvoCeram Bulk Fill and SonicFill after 1 h is below 2% and therefore comparable to that of conventional low-shrinkage composites. The shrinkage of flowable bulk-filling composites is significantly higher at 3.3%.

The composite filler acts as a shrinkage stress reliever. It is a “gentle giant”, which is capable of absorbing the shrinkage stress due to its low modulus of elasticity of 10,000 MPa compared with 70,000 MPa in conventional glass fillers. This is a particularly important factor in bulk-fill materials.

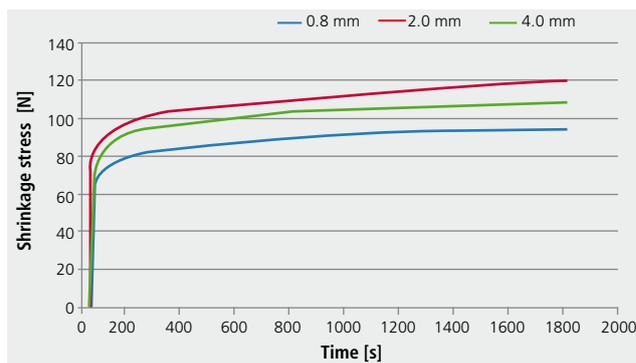


Fig. 9: Shrinkage stress of Tetric EvoCeram Bulk Fill in different layer thicknesses (R&D Ivoclar Vivadent AG, 2011)

The shrinkage stress of the composite rises, as the thickness of the increments increases from 0.8 mm to 2.0 mm. Nevertheless, the increase within the first few seconds of curing is lower in the thicker layers. This slow build-up reduces the risk of marginal gap formation. The shrinkage stress in 4-mm increments is lower than in 2-mm layers, and the slope of the curve is much shallower than that of increments of 0.8 and 2.0 mm.

### Shrinkage stress compared with that of other bulk-fill and conventional composites

The shrinkage stress rises in relation to the increasing thickness of the increment from 0.8 to 2.0 mm. At a layer thickness of 4 mm, the shrinkage stress ceases to increase. Furthermore, 4-mm increments of bulk-fill composites do not show higher shrinkage stress levels than conventional 2-mm layers. Tetric EvoCeram Bulk Fill shows the lowest shrinkage stress of all the sculptable bulk-filling materials in increments of 2 and 4 mm (Table 1).

### Summary

The new Ivocerin initiator has enabled the development of an esthetic bulk-fill material that can be applied in 4-mm increments and cured within 10 seconds. What's more, the material is comparable to conventional direct filling composites in terms of its surface quality, working time and shade blend with natural teeth.

### Literature

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### Shrinkage stress compared with that of other bulk-fill and conventional composites

Increment thickness	Sculptable bulk-fill composites			Flowable bulk-fill composites		Conventional composites		
	Tetric EvoCeram Bulk Fill	Sonic Fill / Kerr	x-tra fil / Voco	SDR / Dentsply	Venus Bulk Fill / Heraeus Kulzer	Filtek Supreme XTE / 3M Espe	Filtek Z250 / 3M Espe	Herculite XRV Ultra / Kerr
0.8 mm	1.21 MPa	1.38 MPa	1.16 MPa	1.11 MPa	1.34 MPa	1.51 MPa	1.22 MPa	1.64 MPa
2.0 mm	1.51 MPa	1.77 MPa	1.8 MPa	not measurable		1.93 MPa	1.63 MPa	1.60 MPa
4.0 mm	1.40 MPa	1.77 MPa	1.83 MPa			not indicated		

Table 1: Shrinkage stress of bulk-fill and conventional composites in different increment thicknesses (R&D Ivoclar Vivadent AG, February 2013)



Joanna-Claire Todd (BA, MPH)  
Research Associate: Scientific Service

## Materials Science Investigations underpinning Tetric EvoCeram® Bulk Fill and Ivocerin®

### Introduction

Before the introduction of bulk fill composites, standard dental teaching recommended a maximum layer thickness of 2 mm for composite fillings [1, 2]. This was in order to minimise shrinkage stress and to ensure adequate depth of cure. Assuming correct, adequate curing with a suitably functioning curing unit, translucency and shade have the most significant effect on the curing depth. The darker and more opaque a composite, the lower the depth of cure [3]. The characteristics of Tetric EvoCeram® Bulk Fill allow an enamel-like translucency of 15 %, which ensures adequate polymerisation at depth. The inclusion of Ivocerin® means that Tetric EvoCeram Bulk Fill can be applied in increments of up to 4 mm, without compromising cure or aesthetics.

### Depth of Cure

There are a number of ways to establish depth of cure in dental materials. The international standard ISO 4049 for polymer based restorative materials suggests measuring depth of cure via preparing cylindrical specimens 6 mm long and 4 mm wide, or if a depth of cure greater than 3 mm is claimed, the length should be at least 2 mm longer than twice the claimed depth of cure. After curing according to the manufacturer's instructions, the material is removed from its mould, the inhibition layer and other uncured material is scraped away and the height of the remaining material is measured. This value divided by 2 is considered to be the depth of cure. This method does not account for post-irradiation polymerisation. Alternatively, Vickers hardness (utilising a square-diamond pyramid indenter) and Knoop hardness profiles (utilising an elongated-diamond pyramid indenter) of the cured material are suitable and can be

conducted some time after curing, allowing for post-irradiation polymerisation. Cured specimens are usually prepared in cylindrical moulds and the hardness at the top and bottom of the cylinder is measured. For a hardness profile throughout the material, cured specimens are cut vertically into two pieces. The cut surfaces are polished and the hardness is determined at intervals from the top to the bottom. Hardness is often expressed as a percentage of the surface hardness which is considered 100 % [4]. Professor David Watts of the University of Manchester, UK, defined an acceptable curing depth as when the bottom hardness corresponds to at least 80 % of the surface hardness [5]. Experience has shown that the simple hardness measures (top and bottom) correspond well to the more thorough hardness profile measurements [6]. Measurements have shown that the degree of cure decreases continuously in areas deeper than approximately 0.5 mm. The degree of cure is highest at a depth of 0.55 mm, because of the uppermost inhibition layer. From this layer downwards, the light intensity entering the material decreases steadily as filler particles scatter light and colour pigments absorb it. A post light-curing reaction with remaining radicals tends to occur within 24 hours after initial polymerisation. Test samples are therefore usually stored for 24 hours before measurements are made.

The following internal and external laboratory tests, which were conducted using these methods, confirm the effectiveness of the photoinitiator formulation with Ivocerin, ensuring an adequate depth of cure (4 mm) in Tetric EvoCeram Bulk Fill restorations.

### R&D Ivoclar Vivadent, Schaan, Liechtenstein:

## Vickers Hardness of Tetric EvoCeram Bulk Fill

Samples of each of the three Tetric EvoCeram Bulk Fill shades were cut and the Vickers hardness measured at the top and at a depth of 4 mm after removal of the inhibition layer. The values measured at the top were set to 100 % and the values measured at 4 mm are expressed as a percentage of this value. Various light intensities were employed and the curing times were adjusted accordingly to ensure a similar light output in each case. For each of the shades, the 4 mm hardness value exceeded 80 % of the surface hardness under all curing settings.

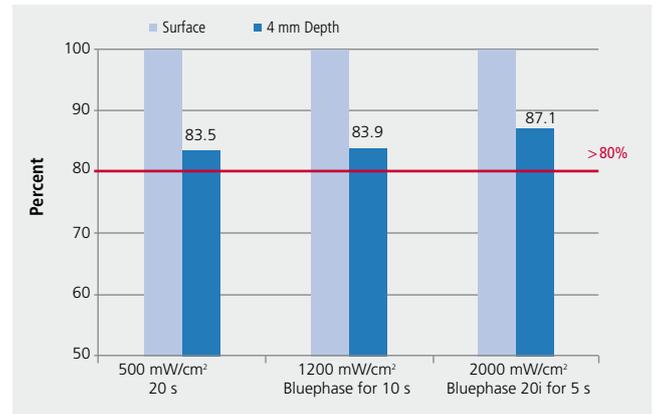


Fig. 1a: Tetric EvoCeram Bulk Fill **Shade IVA**: 4 mm depth hardness as percentage of surface hardness, measured with different light intensities (R&D, Ivoclar Vivadent)

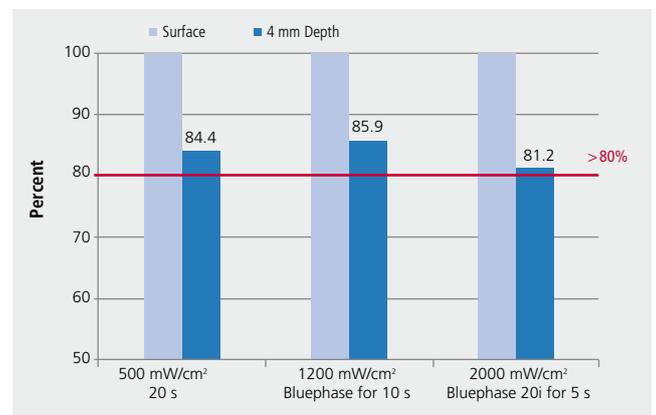


Fig. 1b: Tetric EvoCeram Bulk Fill **Shade IVB**: 4 mm depth hardness as percentage of surface hardness, measured with different light intensities (R&D, Ivoclar Vivadent)

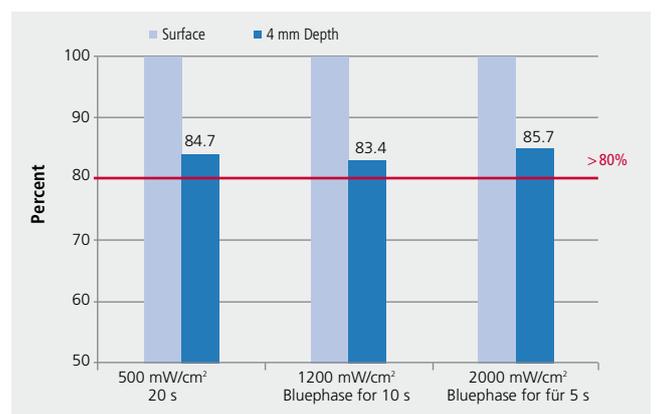


Fig. 1c: Tetric EvoCeram Bulk Fill **Shade IVW**: 4 mm depth hardness as percentage of surface hardness, measured with different light intensities (R&D, Ivoclar Vivadent)

**Dr. A. Rzanny, M Facht, Universitätsklinikum Jena, Deutschland (July 2012):**

### Depth of cure of Tetric EvoCeram® Bulk Fill cured with Bluephase® G2 and Bluephase® Style in comparison to other composites.

Rzanny et al. aimed to establish the performance and suitability of the Bluephase Style curing unit in comparison to Bluephase G2, on the basis of the depth of cure achieved in various composites. After curing for 10 seconds with Bluephase G2 (1200 mW/cm<sup>2</sup>) or Bluephase Style (1100 mW/cm<sup>2</sup>), the depth of cure of the composites: Tetric EvoCeram (A3), Tetric EvoCeram Bulk Fill (IVA) und Venus Bulk Fill (Universal) was calculated using a Penetrometer and Vickers hardness values were established.

#### Methods

**Depth of cure:** Specimens with a diameter of 6 mm and a height of 10 mm were fabricated and cured for 10 seconds with either lamp. The length of the cured section of the material was calculated immediately after polymerisation. A Penetrometer (AP4/3 Feinmess Dresden) was used to measure the depth of the uncured material on the underside. The difference in length was then divided by two (as stipulated in the standard DIN EN ISO 4049).

**Vickers hardness:** Each composite was applied in a 4 mm high and 8 mm wide Teflon mould and covered with a foil at the top and bottom. The light guide of the respective lamp was placed directly onto the foil and the composite was cured for 10 seconds. The Vickers hardness at the surface and bottom of the sample was calculated (load 5 kg/20 seconds at 23 °C) using a Zwick 3212 machine – immediately after polymerisation, after 24 hours and after 7 days.

#### Results

**Depth of cure (acc. ISO 4049):** There was no significant difference between curing lamps for any of the composites. Both bulk fill composites Tetric EvoCeram Bulk Fill and Venus Bulk Fill far exceeded the manufacturer indicated allowable increment thickness (4 mm) in terms of depth of cure (approx. 5 mm). Tetric EvoCeram is not a bulk fill composite and is intended to be applied in 2 mm increments.

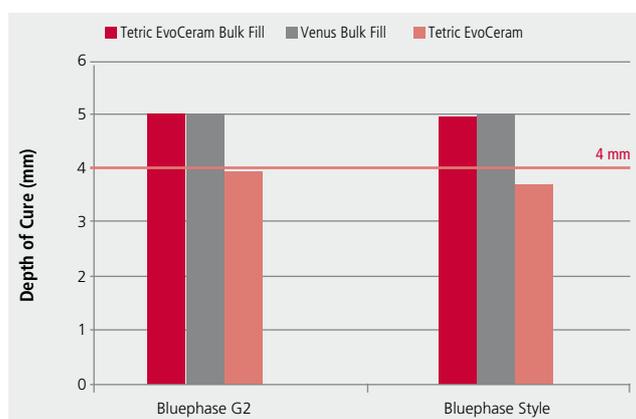


Fig. 2: Depth of cure for various composites when cured with Bluephase G2 and Bluephase Style for 10 seconds.

(Dr A. Rzanny, M Facht, Universitätsklinikum Jena, Germany)

**Vickers hardness:** The Vickers hardness results for Tetric EvoCeram Bulk Fill all exceeded the 80 % ratio necessary. When cured with Bluephase G2 the ratio was 87.6 % after 24 hours and 83.6 % after 7 days. When cured with Bluephase Style it was 80.3 % after 24 hours and 87.5 % after 7 days.

#### Conclusion

The authors conclude that both Bluephase G2 and Bluephase Style are equally suitable for polymerising the three composites investigated. After 1 day storage, both bulk fill products achieved the necessary 80 % hardness ratio.

**C. Sabatini, Dental Biomaterials Research Laboratory,  
State University of New York, Buffalo, USA,  
October 2012:**

### Evaluation of the depth of cure and surface micro hardness of a new bulk fill composite system

Sabatini evaluated the depth of cure and surface microhardness of Tetric EvoCeram Bulk Fill, two further bulk fill products: x-tra fil/Voco, SonicFill/Kerr and Tetric EvoCeram as a control.

#### Method

Two light curing units were employed: Bluephase G2 (1200 mW/cm<sup>2</sup>) and Bluephase 20i Turbo (2000mW/cm<sup>2</sup>) with exposure times of 10 and 5 seconds respectively. This yielded a total of 8 study groups for which 10 samples were fabricated (n=80).

	x-tra fil / Voco	SonicFill / Kerr	Tetric EvoCeram Bulk Fill	Tetric EvoCeram
<b>Bluephase G2</b>	XF-G2 n=10	SF-G2 n=10	TB-G2 n=10	TEC-G2 n=10
<b>Bluephase 20i</b>	XF-20i n=10	SF-20i n=10	TB-20i n=10	TEC-20i n=10

Tab. 1: Presentation of the 8 study groups according to material and light source – with respective abbreviations and sample sizes (n=80) (Sabatini October 2012)

All specimens were prepared in standardised moulds (6 x 6 mm) and polymerised according to manufacturer instructions. Specimens were removed from the moulds taking care not to disturb the inhibition layer at the top. Any unpolymerised material was scraped away from the bottom and specimens were stored undisturbed in a dark environment in 100% humidity at 37 °C for 24 hours, after which micro-hardness tests were recorded.

Knoop hardness tests were carried out on specimens on the top and bottom surfaces using a Leco M-400 hardness tester with a load of 300 g. After embedding the samples horizontally in

an acrylic resin block, the samples were then ground down to half their diameter and the internal surfaces polished. All procedures were performed under controlled lighting. Knoop hardness measures were then recorded at 0.5 mm intervals from the top to the bottom. Hardness measurements at a depth of 4 mm for x-tra fil and Tetric EvoCeram Bulk Fill, 5 mm for SonicFill and 2 mm for Tetric EvoCeram were used to calculate the bottom/top hardness ratios to determine whether the composite system met the generally accepted hardness ratio of 80 % for an adequate depth of cure.

#### Results

Two way analysis of variance (ANOVA) revealed no difference in the average bottom/top hardness values for the type of polymerisation unit used. However significant differences were found between certain restorative composites cured with the same light source ( $p < 0.001$ ).

	x-tra fil / Voco (4 mm)	SonicFill / Kerr (5 mm)	Tetric EvoCeram Bulk Fill (4 mm)	Tetric EvoCeram (2 mm)
<b>Bluephase G2</b>	70.6 %	47.1 %	85.7 %	85.1 %
<b>Bluephase 20i</b>	69.4 %	55.6 %	86.9 %	81.4 %

Tab. 2: Average bottom/top hardness ratios at the recommended increment thickness per material. (Sabatini October) 2012)

When polymerised with Bluephase G2 there were no significant differences between x-tra fil, Tetric EvoCeram Bulk Fill and Tetric EvoCeram but all were significantly different to SonicFill. When polymerised with Bluephase 20i, there were also no significant differences between x-tra fil, Tetric EvoCeram Bulk Fill and Tetric EvoCeram however Sonic Fill was significantly lower than Tetric EvoCeram Bulk Fill and Tetric EvoCeram but not significantly lower than x-tra fil. Notably both Tetric EvoCeram Bulk Fill at 4 mm and Tetric EvoCeram at 2 mm fulfilled the Watts criterion with all figures exceeding 80 %.

The diagram below shows the bottom/top hardness ratios at different depths for Tetric EvoCeram Bulk Fill when cured with both Bluephase lights.

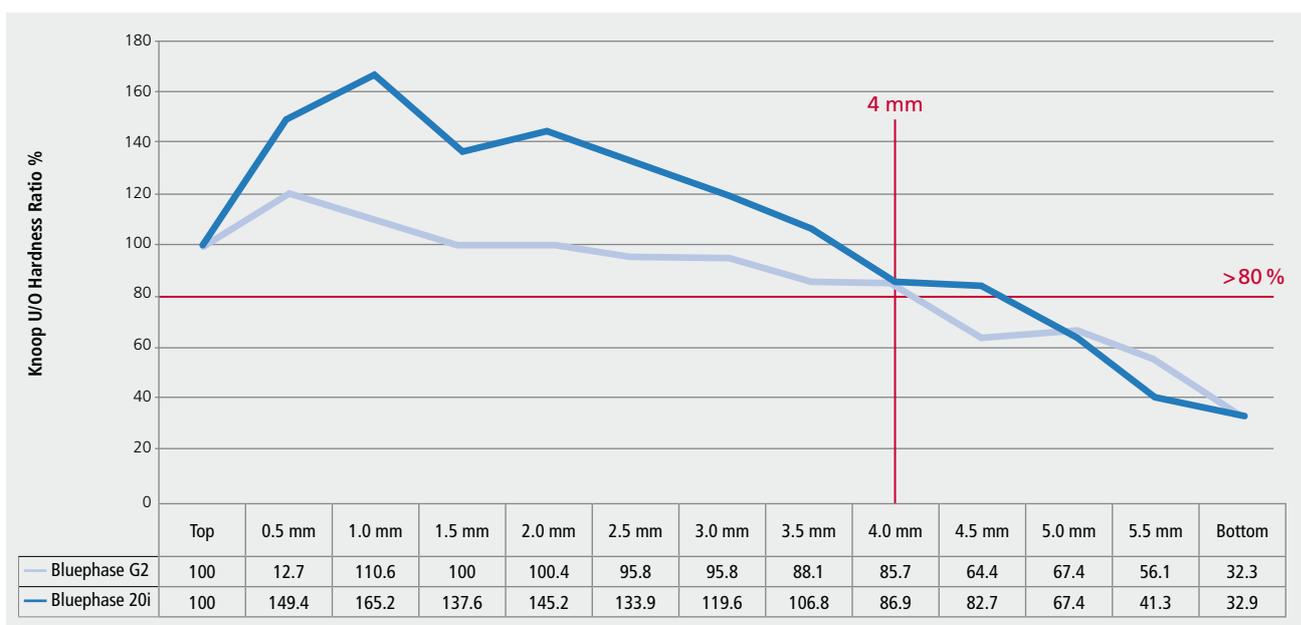


Fig. 3: Bottom/top Knoop hardness ratios at 0.5 mm increments for Tetric EvoCeram Bulk Fill. (Sabatini October 2012)

### Conclusion

Tetric EvoCeram Bulk Fill achieved in excess of the necessary 80 % bottom/top hardness ratio at a depth of 4 mm, independent of the light source. Tetric EvoCeram also achieved this at a depth of 2 mm. Tetric EvoCeram Bulk Fill achieved significantly higher hardness ratios than SonicFill/Kerr.

**S. Zawawi, N. Brulat und Prof. D. Nathanson,**  
**Restorative Sciences and Biomaterials, Boston**  
**University, Boston, MA, USA**

### Curing duration vs. depth of cure and modulus of bulk fill composites [7]

In vitro testing was carried out by Zawawi et al. to evaluate the effect of curing duration on the depth of cure and modulus of elasticity in bulk fill composites.

#### Method

Cylindrical resin specimens (4 mm x 8 mm) were prepared from three different composite materials: Tetric EvoCeram Bulk Fill, SDR/Dentsply and Venus Bulk Fill/Heraeus Kulzer. The Bluephase 16i (1600 mW/cm<sup>2</sup>) curing light was used to cure the composites for either 10 or 40 seconds. Specimens were then sectioned longitudinally and polished. Depth of cure was assessed using Vickers hardness measurements (100g, 20 seconds) at depths of 2 mm, 4 mm and 6 mm. Sixteen measurements for each test parameter were conducted. To assess the modulus of elasticity, specimens were formed into bars (4 mm x 25 mm x 2 mm) and tested in flexural mode using an Instron machine. Results were analysed with ANOVA.

#### Results

The Vickers hardness values for the composites at the surface and at a depth of 2 mm, 4 mm and 6 mm when cured for 10 seconds or 40 seconds are shown in Fig 4.

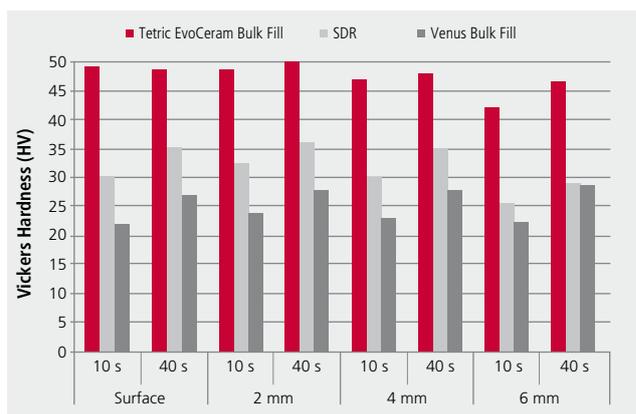


Fig. 4: Microhardness (HV) of various composites at various depths and curing times. (S. Zawawi, Boston University, USA)

Tetric EvoCeram Bulk Fill exhibited higher microhardness than SDR and Venus Bulk Fill at all depths and curing times.

The mean modulus of elasticity was also measured for each bulk fill composite with both 10 seconds and 40 seconds of curing (Fig. 5). There was no significant difference between Tetric EvoCeram Bulk Fill samples when cured for 10 seconds or 40 seconds. However there were significant differences in modulus between the different materials at both 10 and 40 seconds. Whereas curing duration had no discernible effect on the modulus of elasticity for Tetric EvoCeram Bulk Fill, this was not the case for SDR or Venus Bulk Fill – where there was a clear difference (increase) between 10 and 40 seconds polymerisation time.

#### Conclusion

Both the Vickers hardness and modulus of elasticity are related to depth of cure. Microhardness can be determined at various depths and the higher the modulus of elasticity, the greater the amount of cross-linkage i.e. polymerisation that has occurred. Tetric EvoCeram Bulk Fill achieves higher mechanical properties than the other products and is almost indifferent to the length of cure (10s vs. 40s).

Notably the bottom/top ratio of the Vickers hardness for Tetric EvoCeram Bulk Fill at 4 mm (10 seconds = 95.5 %, 40 seconds = 98.5 %) and even at 6 mm (10 seconds = 85.7 %, 40 seconds = 96.2 %) far exceeds the 80 % level stipulated by Watts.

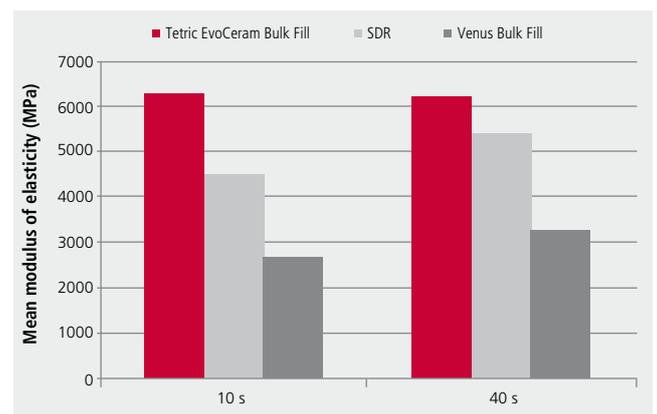


Fig. 5: Mean modulus of elasticity of various composites when cured for 10 vs. 40 seconds. (S. Zawawi, Boston University, USA)

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Dr Siegwald Heintze  
Head of Department: Preclinic

## Laboratory simulation tests with Tetric EvoCeram® Bulk Fill and their clinical significance

### Introduction

For decades, students of dentistry were taught that direct restorations made of composite resin should be applied into the cavity in increments. The main reason was the low depth of cure of conventional composites (1–2 mm). Additional reasons included the belief that the incremental technique could partially offset the shrinkage, or shrinkage stress, which takes place as the composite resin polymerizes. It was said that polymerization shrinkage may result in marginal gaps, debonding from the cavity floor and/or movement of the remaining tooth structure (cusp movement/deflection), with the latter being believed to entail the risk of enamel/dentin crack formation, infractions and cusp fractures.

Imagine a composite material that fully cures in thick increments of up to 4 mm when exposed to the light of a standard curing device and in addition is very tolerant of operator errors, e.g. oblique positioning of the light probe or polymerization from a substantial distance to the filling? Such a material is indeed available and on the following pages we will show which errors this material is able to tolerate and how it behaves in the cavities of extracted teeth. First, however, we should look to the past.

### In the past – the incremental technique

In the 1980s and early 1990s, it was thought that composite shrinkage could be controlled by the light source. The concept behind this was to use plastic strips and light-transmitting wedges and to guide the light of the polymerization device through the wedge towards the cervical part of the composite

filling to direct the shrinkage towards the wedge. Various studies disproved this concept [1, 2]. Composite always shrinks towards the centre of a mass and not towards the light source as it polymerizes. While a better marginal quality was observed in the cervical area of Class II fillings in vitro, this result is attributable to the lower degree of polymerization occurring in this region because the amount of light transmitted through the wedge is reduced, and as a result, the composite shrinks less. Finally, various incremental techniques were recommended and attempts were made to demonstrate the superiority of one or other of these techniques, by means of laboratory test methods. Notably dye penetration along the marginal interface, microscopic margin analysis, cusp movement and FEA calculations were used. The dye penetration test, for instance, does not correlate with the clinical performance of composite restorations at all [3,4]. This is also the reason why the differences observed between various incremental techniques in conjunction with this method were not confirmed clinically [5].

The studies on cusp movement found that the cusps moved inwards towards the cavity by just 10–20 µm. Furthermore, the largest part of this movement occurred within 10 minutes of the restoration being placed and no additional movement was observed after about 60 minutes. Recently, fillings placed in large three-surface cavities of extracted teeth showed that polymerization shrinkage was compensated for by hygroscopic expansion after 4 weeks [6]. This finding was borne out by the movement of the cusps, which was recorded at regular intervals using laser scanning technology. Another study carried out by the same group of researchers proved that cusp movement was independent of whether the composite was placed in the cavity in increments of 2 mm or 4 mm [7].

### Tetric EvoCeram® Bulk Fill and marginal gaps

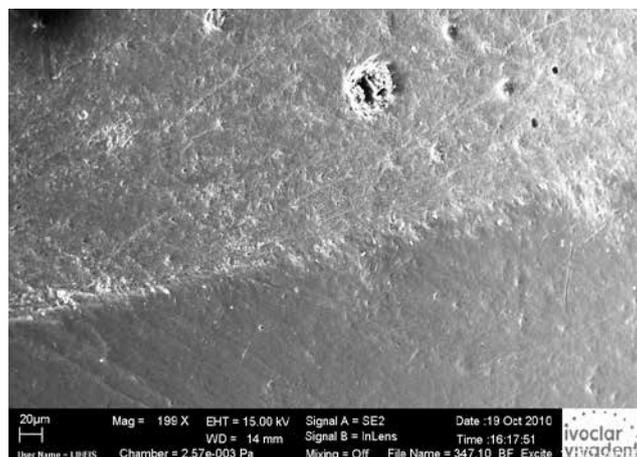
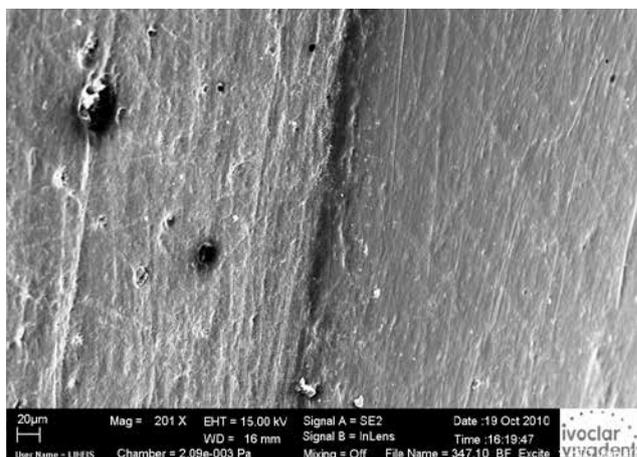
The aim was to confirm or refute the assumption that thick composite layers result in poorer marginal quality than composites applied using the conventional incremental technique. This question was investigated with an experimental setup that used an extracted mandibular molar in which proximal occlusal cavities were prepared on both the mesial and distal side. The cavity was designed with a proximal depth of 4 mm, an occlusal depth of 3 mm and a lingual-buccal width of 5 mm (Fig. 1).

The tooth was bonded to an aluminium base and then mounted onto a tooth model surrounded by plastic teeth. Before the composite resin was applied, a steel matrix was placed and secured with a wooden wedge (Fig. 1). On one side of the tooth,

Tetric EvoCeram Bulk Fill was applied in a single increment; on the other side, Tetric EvoCeram was applied in three increments: a horizontal gingival, an oblique buccal and an oblique lingual increment (Fig. 1). Each layer was light-cured for 10 seconds with a Bluephase® G2 curing light (1,200 mW/cm<sup>2</sup>). Two adhesive systems were employed: the single-component etch & rinse system Excite® F and the self-etching two-component system AdheSE®. Eight fillings were placed for each test group and all restoration margins were confined to the enamel. After the fillings had been placed, excess removed and the restoration surfaces polished, the teeth were first immersed in water for 24 hours and subsequently subjected to thermo-cycling (10,000 cycles between 5°C and 55°C) for 10 days. After that, replicas were produced and the marginal quality was evaluated using scanning electron microscopy (SEM) (Fig. 2).



Fig. 1: *Left*: Extracted lower molar with two-surface cavities. *Centre*: After placement of filling and removal of excess. *On the left*: Tetric EvoCeram Bulk Fill in one increment; *on the right*: Tetric EvoCeram in 3 increments. *Right*: Proximal view: above Tetric EvoCeram Bulk Fill, below Tetric EvoCeram



Figs 2a–b: SEM images (x200) of the margin of a filling placed with Tetric EvoCeram Bulk Fill and the etch & rinse system Excite F in an extracted molar after 10,000 temperature cycles, (left) axio-proximal enamel, (right) cervical enamel

Figure 3 shows the percentage of regular margin in the axio-proximal part. It is immediately evident that a) there is no difference between the bulk and incremental technique and b) that the adhesive system, rather than the incremental technique, is the determining factor for marginal quality. A similar result was found in another study in conjunction with the flowable bulk composite system SDR (Dentsply) and a variety of adhesive systems [8]: here too, no difference was found between the conventional incremental technique and the bulk technique and the individual adhesive systems constituted the major factor affecting the marginal quality in both the enamel and dentin. In both these studies, the etch & rinse system, which included enamel acid etching with 36 % phosphoric acid, resulted in significantly better margins (fewer gaps and irregularities) than the self-etching systems.

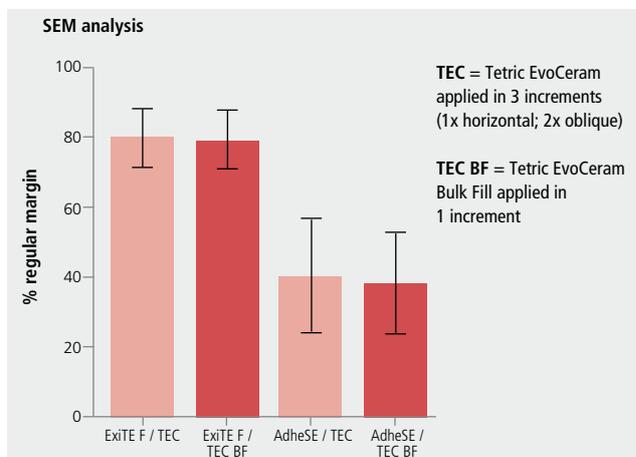


Fig. 3: Percentage of regular margin (and standard deviation) after SEM analysis (x200) in fillings on extracted lower molars after 10,000 temperature cycles in relation to filling material and filling technique

Furthermore, two of the teeth filled with Tetric EvoCeram Bulk Fill were X-rayed using high-resolution micro-CT (7  $\mu$ m resolution) while they were immersed in water. The scanning process took 9 hours and 800 slices were produced. Figure 4 shows the cross section of a dental filling. The filling shows a good adaptation to the cavity margin and hardly any major air bubbles.

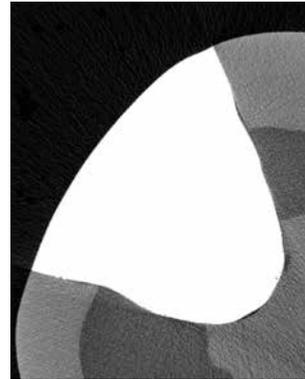


Fig. 4: Two-surface filling with Tetric EvoCeram Bulk Fill on a molar: horizontal section of a micro-CT image (7- $\mu$ m resolution; courtesy of Scanco Medical, Switzerland). Good adaptation to the margin with only few air bubbles.

What do the results on the marginal quality tell us in terms of long-term clinical effectiveness? Before we explore this question, we should find out if studies on large increments have already been carried out in the past - and indeed they have.

## Clinical studies on bulk increments

The first study on composite increments measuring between 3 and 5 mm was started as early as 1997 – the subject of the study was what was then called a “packable” material, SureFil/Dentsply [9]. This study was followed by the publication of four more studies, including, in addition to SureFil [10], Prodigy Condensable/Kerr [11], QuiXfil/Dentsply [12] and Alert/Pentron Clinical [13]. The observation periods of these trials varied between 1 and 4 years. The study on QuiXfil/Xeno III included Tetric Ceram/Syntax as control. Both materials were placed in the same patient’s oral cavity i.e. using split-mouth design. In sum, it can be said that the restorations placed in large, or bulk increments scored slightly lower than fillings placed in small increments in terms of clinical criteria such as marginal staining, marginal adaptation, secondary caries and need for replacement. However, the differences were neither dramatic nor statistically significant (Fig. 5).

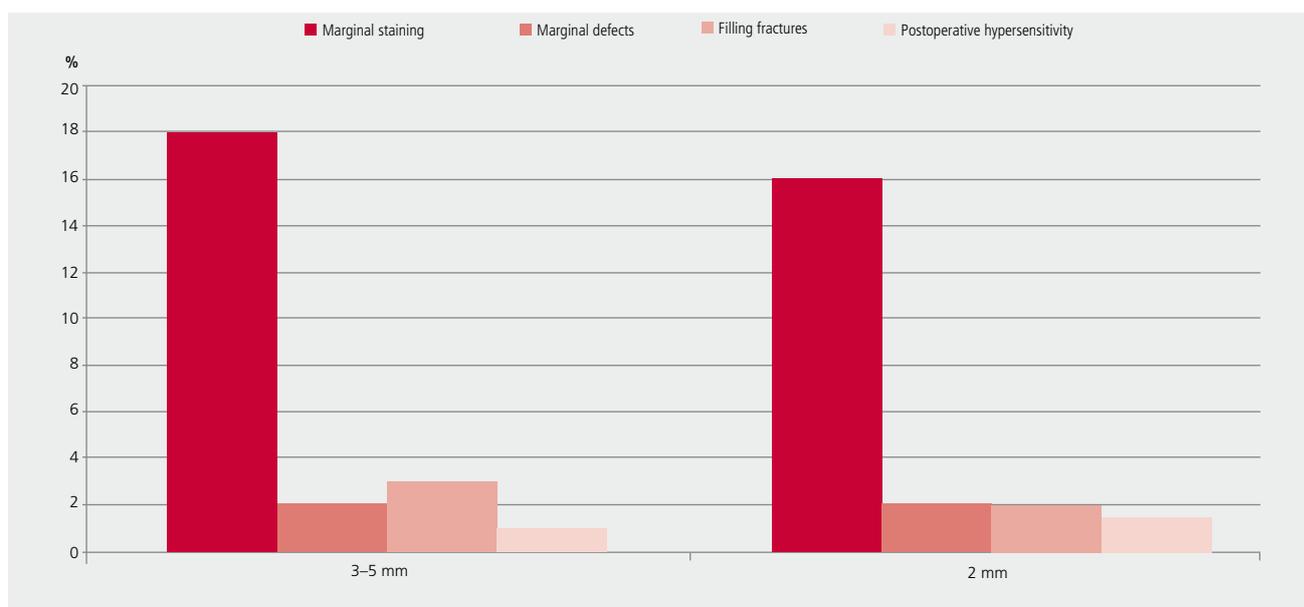


Fig. 5: Mean percentage frequency of clinical phenomena in relation to the thickness of the composite increments – data processed according to the database of [14]

### In vitro / in vivo correlation

Is there a relationship between in vitro findings and the phenomena that dental professionals observe in their patients' fillings? Enough evidence is now available to suggest that marginal gaps alone do not lead to marginal caries and even fillings with mainly open margins do not exhibit significantly more marginal caries. Strong evidence for this can be found in

studies from the 1970s – studies in which self-curing composites (already then applied in bulk) were placed into the cavity without enamel etching or a dentin/enamel adhesive system and followed up over an observation period of 5 years [14]. Although after 4 years these fillings were on average four times as likely to have marginal staining as fillings whose enamel margins were etched with phosphoric acid, marginal caries was only slightly more frequent (Fig. 6).

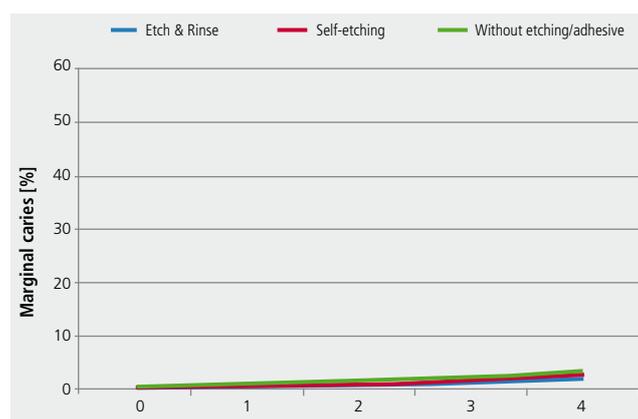
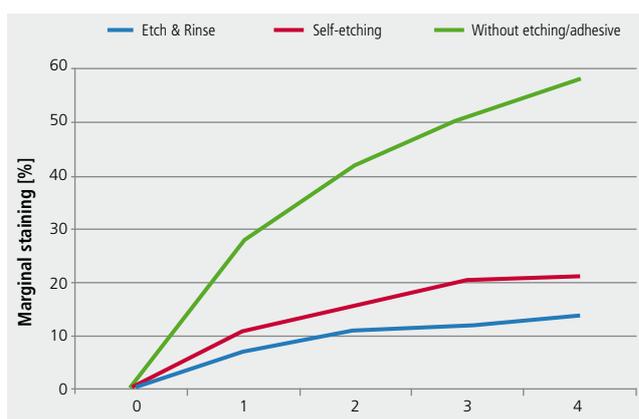


Fig. 6a–b: Mean percentage frequency of marginal staining (left) and marginal caries (right). Clinical study on composites in relation to the adhesive system (Etch & Rinse, self-etching, without etching and bonding) and observation period (0-4 years) – on the basis of a meta-analysis of 59 clinical studies [14]

This means that irregular margins, or marginal gaps, may lead to marginal staining but not necessarily to marginal caries. Marginal caries is primarily determined by the patient's caries activity [15]. Patients with a high level of caries activity (i.e. high caries incidence/many fillings in the past and/or high cariogenic bacteria counts and/or high sugar intake) are more prone to developing marginal caries than patients with low caries activity – even if marginal gaps are present. The worst however, is that a substantial number of dental professionals still mistake marginal staining for marginal caries and replace the filling – unnecessarily so. If esthetically unacceptable, marginal staining can be removed with e.g. rubber polishers or the margins may be ground and then refilled with composite.

Given that the laboratory tests did not reveal any difference between the fillings placed with Tetric EvoCeram Bulk Fill (1 increment) and Tetric EvoCeram (3 increments), would it not make sense to refer to the results of clinical studies on conventionally layered composite fillings placed together with Excite F (or any other etch & rinse system) and AdheSE? It could be expected that Tetric EvoCeram Bulk Fill would achieve similar results. Such studies do exist. Clinical results of up to 6 years are available for Tetric EvoCeram and Excite. In one study, almost 90 % of all the restorations were still intact after 6 years [16]; the main reasons for replacements were marginal caries and fractures, with marginal caries mainly occurring in patients with a high caries risk. In another study carried out by the same group of researchers, Excite and Tetric Ceram were used to place fillings in 59 patients and this study concluded with similar results [17]: after 7 years only about 10 % of the fillings showed marginal staining and only 2 fillings exhibited marginal caries. The same authors reported a similar outcome for two other composites (InTen-S, Point 4) and Excite [18]. In a further clinical study, a split-mouth design was used to select two quadrants in which Tetric Ceram HB fillings were to be placed – in one quadrant the self-etching two-component AdheSE was used as the bonding agent and in the other quadrant the etch & rinse single-component system Excite [19]. After 4 years, both types of filling - those with AdheSE and those with Excite showed no difference in terms of survival rate [20].

However, only 70 % of the fillings with AdheSE showed a good or very good marginal quality. By contrast, 93 % of the fillings with Excite achieved a good or very good rating in this category. These results tally with the above mentioned *in vitro* results. Other studies that used Excite and AdheSE confirmed the clinical superiority of Excite over AdheSE with regard to the marginal quality of posterior restorations [21–23].

If we take into account that a) clinical data on Class II restorations placed with Tetric EvoCeram and the adhesive systems Excite F and AdheSE are available from the Internal Clinic and that b) data from other published studies on other composite resins placed in combination with AdheSE and Excite confirm the reliable performance of the restorations, we may assume that the restorations placed in bulk will provide clinical results that are equivalent to the results achieved with Tetric EvoCeram and the incremental technique, bearing in mind, however, the limitations of laboratory tests and other physical characteristics such as flexural strength, expansion, shrinkage, etc. The results obtained with Tetric EvoCeram Bulk Fill in the laboratory suggest that possibly 10-15 % of the fillings placed with Excite F and 20–30 % of the fillings with AdheSE may show marginal staining after 4 years. Marginal caries is expected to occur only rarely, and if so, it will mainly affect patients with high caries activity.

How come the difference in marginal staining observed between the self-etch two-component system and the etch & rinse system was clinically smaller than the laboratory data would have led us to expect? The answer to this question is simple: In the laboratory, the margins of the fillings are evaluated far too minutely under a microscope; minor irregularities and gaps that are irrelevant for clinical performance, are discovered and recorded. If the fillings are evaluated *in vitro* in the same way as the dentist does in the patient – i.e. using magnifying glasses and a sharp explorer – the difference is less pronounced (Fig. 7).



Fig. 7a: Evaluation of fillings in extracted teeth, using magnifying glasses and an angled sharp explorer

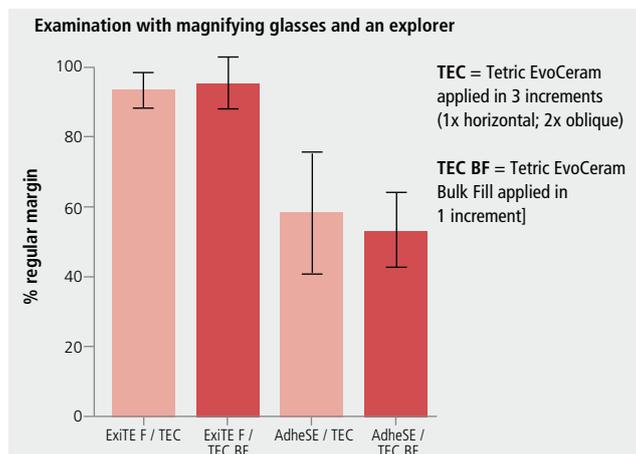


Fig. 7b: Percentage of regular margins (and standard deviation), examined with magnifying glasses and an explorer, in extracted lower molars after 10,000 temperature cycles in relation to the filling material and filling technique

## Tetric EvoCeram Bulk Fill – a forgiving material

Lecturers and opinion leaders often refer to practitioner-errors with the suggestion that such mistakes lead to the insufficient polymerization of composite materials. They demonstrate that a shadow is created if the light guide is held at an angle to the composite material to cure a proximal filling (Fig. 8). Untoward effects are also to be expected if the distance between the light probe and filling is too large or if the light probe is not positioned precisely over the filling. Interestingly, these statements are not backed up by study results – and hardly any studies on the above-mentioned various deviations from the standard position of the light probe can be found. Only the increase in distance to the composite has been investigated in a few studies and it was found that the depth of cure decreased with an increase in distance. However, these results were to some extent affected by the curing devices used [24]. How does Tetric EvoCeram Bulk Fill behave in the presence of polymerization-related errors? To investigate this issue, we drew up a test plan to examine a variety of scenarios:

- Test group 1:** Light probe in vertical position to the composite
- Test group 2:** Light probe at a 40° angle to the composite
- Test group 3:** Light probe in vertical position, at a distance of 5 mm to the composite
- Test group 4:** Light probe at a 40° angle, at a distance of 5 mm to the composite
- Test group 5:** Light probe in vertical position over the centre of the molar, so that both proximal sides are only partially illuminated
- Test group 6:** Same as group 5 but with a distance of 5 mm
- Test group 7:** Light probe in vertical position to the composite. The entire light emission window is covered with a layer of composite material (thickness: 0.8 mm).



Fig. 8: Oblique position of the light probe and 5-mm distance to the tooth

The same experimental setup was used as for the tests on marginal adaptation (see Fig. 1). Prior to the application of the composite, a steel matrix was placed and secured with a wooden wedge. The cavity was lightly isolated with glycerine gel to ensure that the composite could be removed in a single piece. Tetric EvoCeram Bulk Fill was applied in a single increment and polymerized for 10 seconds with Bluephase G2 (1,200 mW/cm<sup>2</sup>) – in the manner specified for the test groups above. Four fillings were placed for each group. After 24 hours of dry storage at 37 °C (incubator), the composite specimens were invested in epoxy resin in a darkroom, reduced to the centre by grinding and then polished. Subsequently, the hardness profile of the entire proximal length was determined, by making indentations every 0.5 mm using a Vickers Hardness tester (Fig. 9).

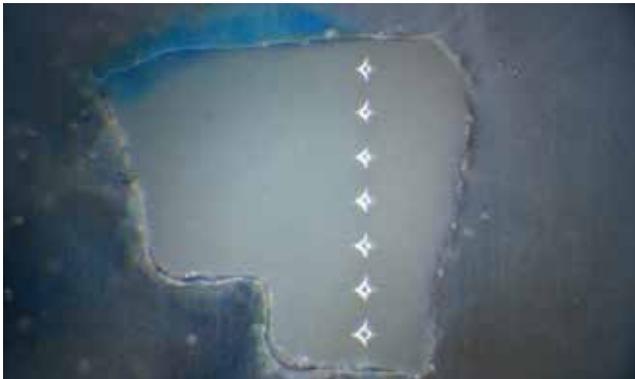


Fig. 9: Vickers hardness indentations in the 4-mm composite filling

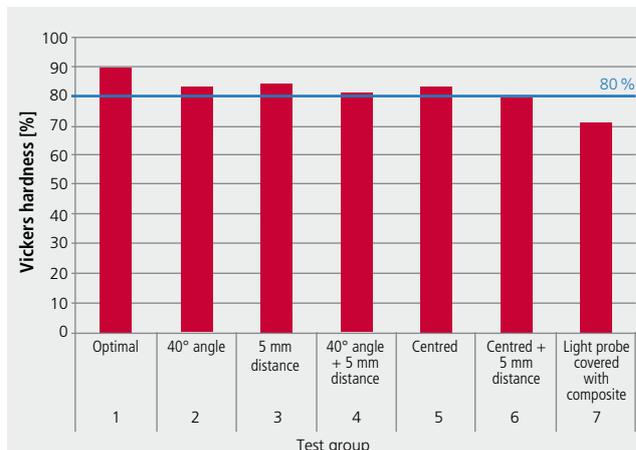


Fig. 10: Vickers hardness (%) of the cervical portion of the Tetric EvoCeram Bulk Fill filling relative to the Vickers hardness of the coronal part – depending on the position of the light probe

The data were averaged and processed graphically. The results came as a surprise (Fig. 10). None of the test groups 1–6 showed cervical hardness values below 80 % of the surface hardness. The exception was the group with the composite-covered light emission window. This group achieved merely 71 % of the coronal hardness value.

It can therefore be said that Tetric EvoCeram Bulk Fill undergoes complete curing even if the light probe is positioned incorrectly. Obviously, operators should use a curing light capable of generating the required light output. Additionally, the light performance should be checked regularly with a measuring device. A field test in general dental practices in Germany revealed that half of the curing lights tested failed to provide the expected performance [25]. It is equally important to ensure that the light emission window is not contaminated or covered with composite material. The same field study found that 37 % of the light probes were contaminated with composite or adhesive.

## Summary

Tetric EvoCeram Bulk Fill, incorporating the innovative photoinitiator system Ivocerin, is ideally suited for the direct restorative technique because it allows cavities to be filled in large increments of up to 4 mm. It is tolerant of errors related to light-curing; even careless positioning of the light probe still results in the sufficient curing of 4 mm layers. Compared with the three-increment technique, 4-mm cavities filled with a single increment of Tetric EvoCeram Bulk Fill did not lead to more marginal gaps or enamel cracks. Several studies have shown that the adhesive system, rather than the composite, is the determining factor for marginal quality. Tetric EvoCeram Bulk Fill allows for effective posterior restorations without compromises in quality.

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Director: R&D Clinic

## Tetric EvoCeram® Bulk Fill in clinical use

### Introduction

There is no question, that dentists would like to be able to place posterior restorations in thicker layers and thus in fewer working steps. The layering technique [1–3], in which thin layers of composite are placed in defined orientation – in order to compensate for shrinkage stress, is complicated and its advantages in terms of clinical quality are debatable [4, 5]. Furthermore, the low curing depth of composites has so far limited the possibility for dentists to efficiently adapt their application technique to their patients' individual anatomic situation. Bulk-fill composites should overcome these limitations.

### Cavity size

It is generally acknowledged that the average size of posterior cavities really does justify the need for a bulk-fill composite, but this issue has not been systematically investigated. Two in-house studies examining bulk-fill composites (an experimental bulk composite and Tetric EvoCeram® Bulk Fill) have now delivered relevant data on the cavity size of composite fillings. In these studies, the width and lowest point of the occlusal cavity, plus the lowest points of the proximal boxes were measured with a periodontal probe. The results are displayed in Table 1.

In more than half of these investigated cases, the cavity dimensions allowed these defects to be filled with one single increment of 4 mm (maximum). Approximately 40% of the restorations required two layers. Three layers were only necessary in exceptional cases, in which additional oral or buccal cavity extensions had to be filled.

In such cavities, bulk-fill composites enable a more efficient and ergonomic working technique due to the fact that they can be placed in thicker increments (usually 4 mm). However, bulk-fill composites with a conventional initiator system generally comprise larger filler particles in order to counteract shrinkage and polymerization stress and they demonstrate a high level of translucency in order to allow increased layer thickness. Both material properties have a significant influence on the clinical characteristics such as surface quality and esthetics (Fig. 1). Furthermore, such materials often require longer polymerization times to ensure sufficient curing (Fig. 2), or they react very sensitively to ambient light – limiting their processing time under operatory light (see Fig. 3 regarding light sensitivity, in article by Karin Vogel).

	Cavity width (absolute) (mm)	Cavity width in relation to inter- cuspidal distance (%)	Depth of occlusal cavity (mm)	Depth of mesial box (mm)	Depth of distal box (mm)
<b>Max.</b>	10	100	6	7	8
<b>Mean</b>	4.4	72.1	2.9	4.9	4.5
<b>SD (±)</b>	2	20	1.7	1.2	1.4

Table 1: Cavity dimensions defined in two studies performed by the Ivoclar Vivadent R&D Practice (n=85).

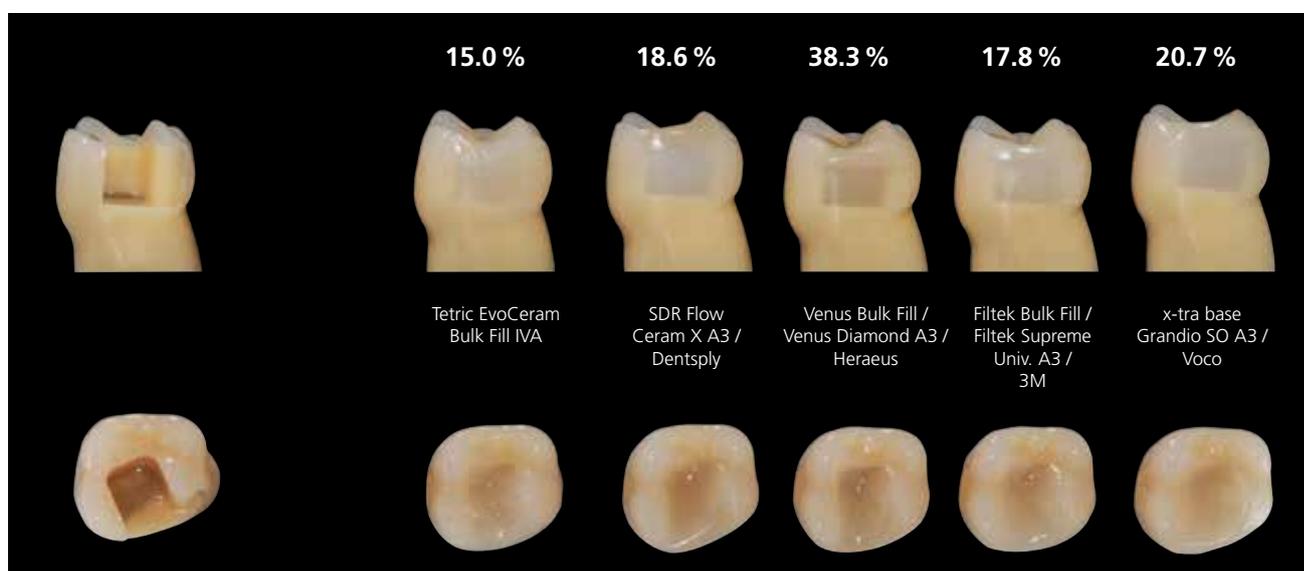


Fig. 1: Standardized Class II cavities in resin teeth with cavity floor characterized with IPS Empress Direct Color Grey and filled with various bulk-fill composites. Translucency is shown in percent. (ICDE Schaan, December 2012).

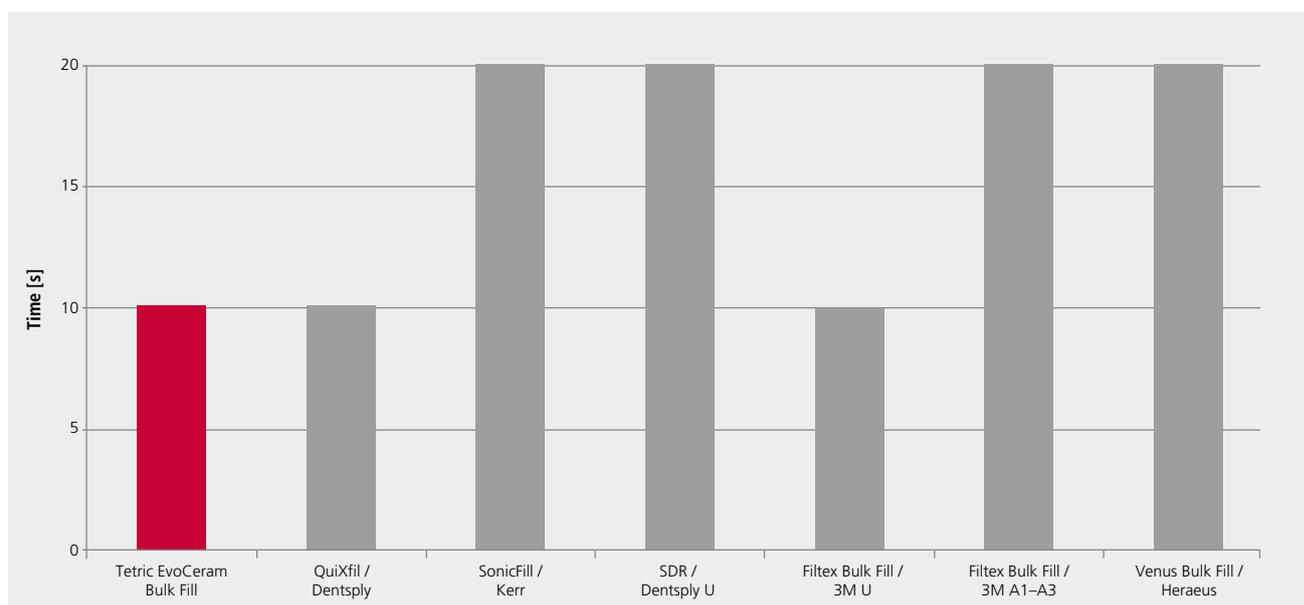


Fig. 2: Polymerization times of different bulk-fill materials according to the manufacturer's instructions (status: March 2013).

In comparison to the bulk-fill materials of other manufacturers, Tetric EvoCeram Bulk Fill with a translucency of 15%, shows optimum esthetic integration (Fig. 1). Materials with a higher translucency level do not demonstrate such good shade adaptation – a notable problem in situations with discoloured dentin.

Due to the addition of the innovative photoinitiator Ivocerin®, Tetric EvoCeram Bulk Fill can be polymerized in 10 seconds (Fig. 2) at a light intensity of  $\geq 1,000 \text{ mW/cm}^2$ . Tetric EvoCeram Bulk Fill is an exceptional product, featuring well-balanced properties, optimized for the posterior region. These properties are demonstrated by the excellent results attained in laboratory and preclinical tests, however only clinical studies can provide truly reliable information as to final clinical performance.

### In-house study: Tetric EvoCeram Bulk Fill

In order to obtain the necessary clinical results, Ivoclar Vivadent AG initiated a clinical study at its internal dental practice. As it is possible to answer the questions most important/interesting for the user after a relatively short observation period, first conclusions can be drawn after just 8 months of clinical service. Factors such as postoperative discomfort, esthetic integration, polishability, occurrence of enamel cracks and initial margin quality can be evaluated at baseline.

In this prospective clinical investigation of Tetric EvoCeram Bulk Fill, 35 restorations (11 Class I and 24 Class II) were placed in combination with a one-bottle etch & rinse adhesive system. The restorations were assessed according to FDI criteria [6, 7], using a semi-quantitative clinical evaluation (SQUACE method), which enables the documentation of marginal deficiencies in relation to the overall filling margin [8]. The results of the above mentioned clinical aspects are briefly described below.

#### Postoperative sensitivity

In the majority of cases (33), defective fillings represented the preoperative situation. Only two cases involved primary caries. In 51% of the cases (18), a superficial to medium caries pro-

gression towards the pulp was observed. Deep lesions were discovered in 46% (16) of the patients. Only in one case (3%), was Caries Profunda treatment (application of a calcium hydroxide compound) necessary, due to proximity to the pulp.

Despite the fact that the lesions were partly very close to the pulp, no occurrence of postoperative discomfort, related to the applied adhesive or the filling material, was reported at baseline or in the meantime. Two restored teeth showed a minimally increased sensitivity to cold. However, one of the affected patients did not notice this increased sensitivity in day-to-day life. In the other patient, who had reported a slightly increased sensitivity, this sensation could not be reproduced in the practice. No post-treatment or follow-up was required as the sensitivity levels were evaluated as “clinically good” and explained by exposed cervical dentin – for this reason, they are not listed in Table 2.

#### Esthetic integration

Tetric EvoCeram Bulk Fill enables not only a simplified layering concept in terms of increment thickness but also in terms of esthetics. The optical properties have been optimized to meet the requirements of posterior restorations so that the shade system could be reduced to just three shades (IVA, IVB and IVW). The Ivocerin photoinitiator allows a slightly higher composite opacity compared to other bulk-fill materials due to its high quantum yield. Therefore, the translucency of the material could be adjusted in such a way that its optical properties, combined with the composite’s favourable refraction index, blend in optimally with the tooth structure (particularly enamel). Thus, virtually invisible restorations can be achieved with average-sized fillings and in cases where the dentin is not discoloured. In the in-house study with Tetric EvoCeram Bulk Fill, the esthetic results of 35 restorations were assessed according to FDI criteria [7,9] at baseline. The examiner rated 71% of the restorations as “perfect” and 29% as “good” (minor shade deviations). None of the restorations were rated “satisfactory” or worse. Patients rated their restorations even more positively, with 97% of patients stating that the restorations integrated “perfectly” (Figs 3 to 6), and 3% rating the filling as “good” (slight shade deviations). These results document the material’s highly developed “chameleon effect”, especially given the fact that shade IVA was used in 80% of the restorations.

Those cases in which the examiner identified slight shade deviations mostly involved either deep cavities or discoloured dentin. In such situations it is advisable to apply a thin layer of opaque material, e.g. Tetric EvoFlow Dentin, onto the dentin to obtain optimum esthetic integration (Figs 7 to 11).

### Polishability

The clinical test also confirmed the material's excellent polishing properties. In 77% of the restorations placed in this clinical in-house study (n=35), the surface gloss was rated to be "clinically perfect" according to FDI criteria after polishing with the composite polishing instrument OptraPol Next Generation. The surface quality received a slightly lower rating in some cases where silky-mat regions in the occlusal contact area and

small pores could be observed. As a result, the surface quality of two restorations was rated "good" and six were rated "satisfactory".

### Occurrence of enamel cracks

Thick increments can cause cracks in the enamel due to their higher volume shrinkage and especially when good adhesion to the enamel is established [10,11]. Therefore, the clinical evaluation focused on this aspect in particular.

The majority of the treated teeth (71%) already showed enamel cracks before the placement of the restoration. The position of these cracks was noted to enable them to be distinguished from subsequently occurring cracks. Cold-light optical fibres



Fig. 3: Cavity preparation on tooth 16.



Fig. 4: Tooth 16 after one layer of Tetric EvoCeram Bulk Fill has been used. The esthetic integration is optimal.



Fig. 5: Adjacent cavities in teeth 14 and 15.



Fig. 6: Teeth 14 and 15 restored with one layer of Tetric EvoCeram Bulk Fill IVA.



Fig. 7: Preoperative situation showing a large amalgam filling and mesial proximal caries.



Fig. 8: Large, undercutting defect after removal of the filling and caries excavation.



Fig. 9: Placement of a 1.5-mm increment of Tetric EvoFlow Dentin A2 to reconstruct opaque tooth structure and to cover discolorations.



Fig. 10: The defect is filled with a second and final layer of Tetric EvoCeram Bulk Fill IVA.



Fig. 11: The final restoration is very well integrated into the surrounding tooth structure despite the deep undercutting defect.

(light probe from Lercher) were used for crack detection. However, no additional cracks were identified at baseline. This confirms that the tensions caused by Tetric EvoCeram Bulk Fill are not higher than those of other posterior composites which are applied in 2-mm layers. The results of this clinical study correspond with the preclinical data presented earlier. As it can be assumed that the water absorption of the composite compensates for the polymerization stress in a relatively short time [12], this baseline result can be considered reliable.

### Initial marginal quality

Tetric EvoCeram Bulk Fill restorations demonstrated excellent marginal quality at baseline. With regard to marginal discoloration, submargination and marginal irregularities, 99% of the examined marginal sections were rated as “clinically perfect”. None of the marginal sections were given a rating below “good”. Only one case showed slight submargination. A summary of the clinical results is displayed in the following table:

FDI criteria /evaluation	Excellent	Good (excellent after correction)	Acceptable	Inadequate (repairable)	Unacceptable (new restoration necessary)
	<b>Number (% of all restorations)</b>				
Postoperative sensitivity	35 (100 %)	0 (0 %)	0 (0 %)	0 (0 %)	0 (0 %)
Anatomic shape	34 (97 %)	1 (3 %)	0 (0 %)	0 (0 %)	0 (0 %)
Surface/gloss/pores	27 (77 %)	2 (6 %)	6 (17 %)	0 (0 %)	0 (0 %)
Esthetics	25 (71 %)	10 (29 %)	0 (0 %)	0 (0 %)	0 (0 %)
Surface discoloration	35 (100 %)	0 (0 %)	0 (0 %)	0 (0 %)	0 (0 %)
Patient satisfaction	34 (97 %)	1 (3 %)	0 (0 %)	0 (0 %)	0 (0 %)
Material fracture	35 (100 %)	0 (0 %)	0 (0 %)	0 (0 %)	0 (0 %)
Tooth integrity	34 (97 %)	1 (3 %)	0 (0 %)	0 (0 %)	0 (0 %)
Proximal contacts	33 (94 %)	1 (3 %)	1 (3 %)	0 (0 %)	0 (0 %)
	<b>% of the entire restoration margin</b>				
Marginal discoloration	99.9 %	0.1 %	0 %	0 %	0 %
Marginal deficits	99.1 %	0.9 %	0 %	0 %	0 %
Submargination	99.9 %	0 %	0.1 %	0 %	0 %

Table 2: Results of the baseline assessment according to FDI criteria (n=35)

## Summary

The preliminary clinical data of Tetric EvoCeram Bulk Fill confirm the good results of the preclinical tests. Due to the photoinitiator Ivocerin, the material can be applied in 4-mm layers, with esthetic properties that meet the requirements of posterior restorations. The increased curing depth of Tetric EvoCeram Bulk Fill gives the user more freedom without loss of quality: dentists can restore cavities quickly with horizontal 4-mm increments or – perhaps even more importantly – they can adapt their layering technique to individual anatomic situations, their ergonomic preferences (e.g. the centripetal build-up technique for restorations) [13] or to esthetic aspects.

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