Ivocerin® – a milestone in composite technology.
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 Special Feature 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® N-Ceram 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 N-Ceram 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 N-Ceram placed in 2-mm increments. Ultimately, Tetric N-Ceram Bulk Fill was produced on the basis of Tetric N-Ceram, 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 N-Ceram 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 N-Ceram Bulk Fill however, the combination of Ivocerin plus champhorquinone-amine has proven to be most successful at ensuring excellent cure in increments of 4 mm.

In this Special Feature, 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 N-Ceram Bulk Fill based on Tetric N-Ceram 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 depth of cure investigations with Tetric N-Ceram Bulk Fill. Dr Heintze and Dr Dieter discuss the clinical significance of simulation tests and the clinical performance of Tetric N-Ceram Bulk Fill respectively.
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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· 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 (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 (λ_max = 385 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, λ_max = 468 nm). It absorbs light in the visible spectrum and is used in combination with amine as the coinitiator (Fig. 3).

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).

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 ∝ [M]^{1/2}.

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].

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](image)

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](image)

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) State of the art: Photopolymerization in dentistry
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(CH₃)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].

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].

CQ-amine photoinitiator systems have also been combined with the above-mentioned Lucirin TPO (Fig. 2, λmax = 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).

CQ-amine photoinitiator systems have several drawbacks. They may cause discoloration 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 methacylate resins [26, 27]. In contrast to Lucirin TPO (λ_{max} = 385 nm) or Irgacure 819 (λ_{max} = 379 nm), Ge-1 (λ_{max} = 411 nm) and Ge-2 (λ_{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.

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 diacrylgermanes 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).

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) diethylgermane Ge-3 was selected as the optimum photo-
initiator 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°C. The synthesis of Ge-3 is started by metalling 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).

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 (XTT50- 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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J. W. Stansbury. Curing dental resins and composites by photopolymerization.
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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 complimentary 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.
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.

<table>
<thead>
<tr>
<th>Initiator in monomer</th>
<th>Flexural strength (MPa)</th>
<th>Modulus of elasticity (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 % Ivocerin</td>
<td>124 ± 8</td>
<td>7200 ± 300</td>
</tr>
<tr>
<td>0.15 % Ivocerin</td>
<td>124 ± 14</td>
<td>8500 ± 200</td>
</tr>
<tr>
<td>0.20 % Ivocerin</td>
<td>135 ± 9</td>
<td>9400 ± 600</td>
</tr>
<tr>
<td>0.40 % Ivocerin</td>
<td>140 ± 15</td>
<td>10300 ± 300</td>
</tr>
<tr>
<td>0.30 % CQ / 0.6 % amine</td>
<td>138 ± 10</td>
<td>9200 ± 600</td>
</tr>
</tbody>
</table>

**Table 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**

<table>
<thead>
<tr>
<th>Initiator in monomer</th>
<th>Depth of cure (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 % Ivocerin</td>
<td>4.7</td>
</tr>
<tr>
<td>0.4 % Ivocerin</td>
<td>5.1</td>
</tr>
<tr>
<td>0.3 % CQ / 0.6 % amine</td>
<td>4.7</td>
</tr>
</tbody>
</table>

**Table 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.

<table>
<thead>
<tr>
<th>Initiator concentration in monomer</th>
<th>Light sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 % Ivocerin</td>
<td>150 s</td>
</tr>
<tr>
<td>0.4 % Ivocerin</td>
<td>80 s</td>
</tr>
<tr>
<td>0.3 % CQ / 0.6 % amine</td>
<td>140 s</td>
</tr>
</tbody>
</table>

**Table 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.

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.

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

<table>
<thead>
<tr>
<th>Initiator concentration in monomer</th>
<th>Double bond conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite A with 0.4 % Ivocerin</td>
<td>65.3 ± 0.5 %</td>
</tr>
<tr>
<td>Composite B with 0.3 % Ivocerin</td>
<td>67.8 ± 1.0 %</td>
</tr>
<tr>
<td>Composite C with 0.2 % Ivocerin</td>
<td>62.3 ± 1.0 %</td>
</tr>
<tr>
<td>Composite D with CQ-amine</td>
<td>49.1 ± 1.7 %</td>
</tr>
</tbody>
</table>

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](image)

**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](image)

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.

<table>
<thead>
<tr>
<th>Initiator concentration in monomer</th>
<th>DHT (mm)</th>
<th>Vickers hardness at surface (N/mm²)</th>
<th>Vickers hardness at bottom, 4 mm Value (N/mm²)</th>
<th>% of the surface hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 % Ivocerin</td>
<td>4.7</td>
<td>489</td>
<td>333</td>
<td>68</td>
</tr>
<tr>
<td>0.2 % / 0.1 % CQ</td>
<td>4.9</td>
<td>511</td>
<td>378</td>
<td>74</td>
</tr>
<tr>
<td>0.2 % Ivocerin / 0.2 % CQ</td>
<td>5.1</td>
<td>524</td>
<td>414</td>
<td>79</td>
</tr>
<tr>
<td>0.4 % Ivocerin</td>
<td>5.1</td>
<td>536</td>
<td>437</td>
<td>82</td>
</tr>
<tr>
<td>0.4 % Ivocerin / 0.3 % CQ</td>
<td>5.6</td>
<td>538</td>
<td>462</td>
<td>86</td>
</tr>
<tr>
<td>0.6 % Ivocerin / 0.3 % CQ</td>
<td>5.6</td>
<td>546</td>
<td>465</td>
<td>85</td>
</tr>
</tbody>
</table>

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.

The fundamental research on Ivocerin has been incorporated into the development of Tetric® N-Ceram 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 N-Ceram Bulk Fill, can be placed in 4-mm thick increments, which are polymerized in 10 seconds with the Bluephase N® curing light (1,200 mW/cm²).

**Literature**

Since its introduction almost 8 years ago, Tetric® N-Ceram 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 N-Ceram. 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® N-Ceram 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® N-Ceram Bulk Fill

In addition to the new Ivocerin initiator described in detail in the previous chapters, Tetric N-Ceram Bulk Fill also contains camphorquinone and 2,4,6 trimethyl benzoyl diphenyl phosphine oxide (acyl phosphine oxide – comparable to Lucrin® 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 N-Ceram 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.

Tetric® N-Ceram Bulk Fill shades: IVA, IVB and IVW

Fig. 1: Tetric N-Ceram Bulk Fill shades: “A”, “B” and “W

Fig. 2: Experimental bulk-fill composite: Percentage bottom/top Vickers hardness in relation to the distance from the surface for different initiator blends.
Tetric N-Ceram 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.

The filler technology incorporated in Tetric N-Ceram Bulk Fill is based on that of the clinically proven Tetric N-Ceram. In order to fulfil the desired composite resin requirements, Tetric N-Ceram 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 N-Ceram 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: Scanning electron micrographs (magnification: 1000x) of the filler composition and surface structure of Tetric N-Ceram Bulk Fill (R&D Ivoclar Vivadent AG, 2012)

Fig. 5a: SonicFill/Kerr (1000x) (R&D Ivoclar Vivadent AG, 2013)

Fig. 5b: Venus Bulk Fill/Heraeus Kulzer (1000x) (R&D Ivoclar Vivadent AG, 2013)

Fig. 5c: SDR/Dentsply (1000x) (R&D Ivoclar Vivadent AG, 2013)

Fig. 5d: QuiXfil/Dentsply (1000x) (R&D Ivoclar Vivadent AG, 2010)
Filler composition of other bulk-fill composites and comparison with Tetric N-Ceram Bulk Fill

Other manufacturers of bulk-fill composites mainly use coarse fillers (see Fig. 5a, c and d). 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 restoration’s surface texture, polishing properties, wear behaviour and plaque resistance.

Polishing properties

The polishing properties are determined by the composition of the different-sized fillers. Tetric N-Ceram Bulk Fill contains the same type of fillers as Tetric N-Ceram. As a result, its polishing properties are just as good as those of the conventional filling material. QuiXfil contains coarse inorganic fillers and exhibits very little shine, even after 30 s of polishing.

Wear behaviour

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

Shrinkage and shrinkage stress and their influencing factors

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

The volumetric shrinkage of Tetric N-Ceram Bulk Fill after 1 h is below 2% and therefore comparable to that of conventional low-shrinkage composites.
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.

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

Tetric N-Ceram Bulk Fill exhibited the lowest shrinkage stress at 1.4 MPa compared to SonicFill and x-tra fil applied in 4 mm layers and also compared to conventional composites applied in 2mm increments.

**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. Moreover, the material is comparable to conventional direct filling composites in terms of its surface quality, working time and shade blend with natural teeth.
Depth of Cure
Investigations underpinning Tetric® N-Ceram 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]. Tetric® N-Ceram Bulk Fill, features an enamel-like translucency of 15%, ensuring adequate polymerisation at depth. The inclusion of the photoinitiator Ivocerin® means that Tetric N-Ceram Bulk Fill can be applied in increments of up to 4 mm, without compromising either cure or esthetics.

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 depth of cure investigations were conducted using these methods and confirm the effectiveness of Tetric N-Ceram Bulk Fill’s photoinitiator-formulation with Ivocerin®.
R&D Ivoclar Vivadent, Schaan, Liechtenstein:

Vickers Hardness of Tetric® N-Ceram Bulk Fill

Method
Samples of each of the three Tetric® N-Ceram Bulk Fill shades (IVA, IVB and IWI) were prepared, cured and then cut. The Vickers hardness was measured at the top of each sample 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 were expressed as a percentage of this value (Vickers Bottom/Top (B/T) ratio). Various light intensities were employed and the curing times were adjusted accordingly to ensure a similar light output in each case.

Results

![Graph showing Vickers B/T ratio with different light intensities and curing times]

Fig. 1: Vickers hardness B/T ratio: Tetric N-Ceram Bulk Fill at 4 mm depth after polymerisation using different light intensities (R&D, Ivoclar Vivadent)

Conclusion
The recommended maximum increment thickness for Tetric N-Ceram Bulk Fill is 4 mm. All of the shades achieved an adequate level of cure (> 80% of the surface hardness) at a depth of 4 mm – under all curing settings.


The objective of this study was to compare the depth of cure values obtained with various bulk fill materials using the ISO 4049 method and Vickers hardness tests.

Method
Four bulk fill products: Tetric N-Ceram Bulk Fill, QuiXX/Dentsply, x-tra fil/Voco and SonicFill/Kerr and two conventional composites: Tetric N-Ceram and Filtek Z350 XT/3M ESPE were tested according to the depth of cure methods mentioned above. Five specimens per product were prepared by condensing resin composites in a rubber mould (6 x 6 x 10 mm). A Bluephase® Style curing light was used to cure each specimen according to the manufacturers’ instructions.

ISO 4049: The measurements were carried out according to the standard. Three measurements were made per specimen and the mean was considered the final value.

Vickers Hardness: Specimens were polished using 1200 grit SiC paper under water spray. Vickers hardness was measured at a distance of 0.5, 2, 4 and 5 mm from the top surface 1 hour after curing. Specimens were stored in an incubator at 37°C under distilled water for 24 hours and hardness measurements were repeated to evaluate post-irradiation polymerization. Ratios of bottom/top (B/T) hardness values were calculated (2/0.5 mm, 4/0.5 mm, 5/0.5 mm). Adequate depth of cure was assumed if the bottom hardness corresponded to at least 80% of the top surface hardness.

Results

![Fig. 2: ISO 4049: Depth of cure in mm of various bulk fill and conventional composites (University of Buffalo, 2013)](image)

* not registered trademarks of Ivoclar Vivadent

All of the bulk fill composites achieved the manufacturers’ claimed depth of cure i.e. 4mm; except for SonicFill in which 3.96 mm fell short of the 5 mm claimed. As would be expected the conventional composites exhibited lower depth of cure compared to the bulk fill composites.
Vickers Hardness Ratio – 1 hour: Percentage Bottom/Top Vickers hardness ratios for various bulk fill and conventional composites 1 hour following polymerisation. (University of Buffalo, 2013)

Vickers Hardness Ratio – 24 hours: Percentage Bottom/Top Vickers hardness ratios for various bulk fill and conventional composites 24 hours following polymerisation. (University of Buffalo, 2013)

All bulk fill composites achieved more than adequate Vickers hardness ratios (> 80%) at the manufacturer’s claimed curing depth – after 24 hours and all except SonicFill (5 mm) achieved this after 1 hour. Tetric N-Ceram Bulk Fill showed the highest B/T hardness ratio at 4 mm after 1 hour, whereas x-tra fil showed the highest ratio after 24 hours, with Tetric N-Ceram the second highest. After 24 hours, bulk fill products exhibited a significant increase in B/T hardness ratio at 5 mm and conventional composites showed significantly lower depth of cure (4 mm) compared to bulk fill composites at both 4 mm and 5 mm height.

Conclusion
Both tests achieved manufacturers’ claimed depth of cure values. All of the bulk fill products had achieved the cure-levels claimed after 24 hours. The authors note that the ISO 4049 method exhibited lower depth of cure compared to hardness tested after 24 hours.

Summary
Tetric N-Ceram Bulk Fill achieved in excess of the necessary 80% bottom/top hardness ratio in 4-mm increments.
Literature


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 compensate 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. Such a material is indeed available and on the following pages we will show 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. Fillings placed in large three-surface cavities of extracted teeth, also 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].

Laboratory simulation tests with Tetric® N-Ceram Bulk Fill and their clinical significance
Tetric® N-Ceram 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.

The tooth was bonded to an aluminium base and then mounted onto a tooth model with adjacent plastic teeth. Before the composite resin was applied, a steel matrix was placed and secured with a wooden wedge. On one side of the tooth, Tetric® N-Ceram Bulk Fill was applied in a single increment; on the other side, Tetric® N-Ceram was applied in three increments: a horizontal gingival, an oblique buccal and an oblique lingual increment. Each layer was light-cured for 10 seconds with a Bluephase® Style curing light (1,100 mW/cm²).

Two adhesive systems were employed: the single-component etch & rinse system Tetric® N-Bond and the self-etching one-component system Tetric® N-Bond Self-Etch. Six fillings were placed for each test group and all restoration margins were confined to the enamel. After the fillings had been placed, the excess removed and the restoration surfaces polished, the teeth were first immersed in water for 24 hours and subsequently subjected to thermocycling (10,000 cycles between 5°C and 55°C) for 10 days. After that, the marginal quality of the entire margin (occlusal, axio-proximal and cervical) was evaluated by the author with a stereo microscope (Leica M125) at 8~20 magnification using a semi-quantitative evaluation approach (SQUACE) (Fig. 1) [8].

With this approach, a form with sketches of two-surface fillings was used and the length of irregular margins and those with gaps were drawn on the sketches with different coloured pens. Afterwards, the approximate percentage of irregular margins and gaps was calculated for the entire margin. It was also investigated whether the shrinkage or shrinkage stress of the filling procedure generates cracks in the enamel. For this purpose, the teeth were evaluated with a light microscope and light transmission probes before cavity preparation, after cavity preparation, one day after filling and during and after thermocycling. At each interval, digital pictures of the lingual and buccal tooth surface were taken which were later placed together and compared.

The light transmission of the teeth revealed no additional cracks that could be attributed to the filling procedure at any given interval.

As far as marginal quality is concerned there was no significant difference between fillings with one layer of Tetric N-Ceram Bulk Fill and 3 layers of Tetric N-Ceram – as the boxplot diagrams in Figure 2 clearly show. However, the quality of the enamel margin was better with the etch & rinse system Tetric N-Bond compared to the self-etch system Tetric N-Bond Self-Etch. Therefore, it can be concluded that the adhesive system is the determining factor for marginal quality, not the type of layering technique.

If one pools the results of both filling materials and filling techniques – irrespective of the adhesive system – there was no statistically significant difference with regard to all restoration sites and evaluation criteria between the fillings with Tetric N-Ceram (3 layers) and those with Tetric N-Ceram Bulk Fill (1 layer).

![Fig. 1: Occlusal view of two 2-surface fillings in two lower molars (magnification X 12.5): the filling on the left side of both teeth was placed with Tetric N-Ceram in 3 layers and the filling on the right side of each tooth with Tetric N-Ceram Bulk Fill in 1 layer only. The tooth substance of the tooth on the left side was conditioned with Tetric N-Bond Self-Etch and that of the right side with the etch & rinse system Tetric N-Bond.](image)

![Fig. 2: Boxplot of the percentage of regular margin evaluated via light microscope, in relation to the filling material and filling technique (1 layer versus 3 layers) and the adhesive system (self-etch versus etch & rinse).](image)

Explanation of Boxplot: 50% of the data lay within the box, the black line within the box represents the median value (50% of the values lay above and 50% below that value). The vertical lines show extreme values and the circles are outliers.
A similar result was found in another study in conjunction with the flowable bulk composite system SDR (Dentsply) and a variety of adhesive systems [9]: 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.

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 [10]. This study was followed by the publication of four more studies, including, in addition to SureFil [11], Prodigy Condensable/Kerr [12], QuiXfil/Dentsply [13] and Alert/Pentron Clinical [14]. The observation periods of these trials varied between 1 and 4 years. The study on QuiXfil/Xeno III included Tetric Ceram®Syntac® 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. 3).

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 [15]. 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. 4).

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 [16]. 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 defect margins are removed and then refilled with composite.
Summary

Tetric N-Ceram Bulk Fill, incorporating the innovative photo-initiator 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. Compared with the three-increment technique, 4-mm cavities filled with a single increment of Tetric N-Ceram 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 N-Ceram Bulk Fill allows for effective posterior restorations without compromises in quality.

Literature


Acknowledgement

Warm thanks are due to the staff of the Preclinical Department, Dominik Monreal, Monika Felder and Gaby Zellweger who conducted the practical experiments in the laboratory.
Introduction

In direct restorative dentistry, there is a strong trend towards faster, more efficient placement techniques for resin composite restorations. Dentists are demanding composite materials that can be applied simply and predictably in the daily practice without the need for sophisticated and time-consuming composite stratification techniques [1]. The potential benefits of layering composites in small increments has long been advocated due to issues of adequate polymerization, reduced shrinkage stress build-up and improved esthetics [2, 3]. The limited increment thickness of approximately 2 mm became an accepted paradigm in restorative dentistry – but this is now being put into perspective [4], as a significant reduction in polymerization shrinkage stress has been reported with some recently developed bulk-fill composites – whilst maintaining comparable curing efficiency at an increment thickness of 4 mm [5].

One of the remaining challenges for the clinician is to achieve good esthetics and natural anatomical contours with bulk fill materials [6]. The handling characteristics of the materials are particularly important with the bulk fill technique because the manipulation of a large volume of composite within a limited time frame can be quite challenging for the practitioner.

Time benefit (efficiency)

With Tetric® N-Ceram Bulk Fill, the clinician has a mouldable composite material at hand that offers an ideal combination of efficiency, quality and esthetics. Increments of up to 4 mm that require a short curing time of only 10 seconds (at a light intensity of > 1,000 mW/cm²) can be placed thanks to the innovative, patented light initiator Ivocerin.

When comparing polymerization times of various commercially available bulk fill composite materials, significant differences can be found (Fig. 1).

If desired by the clinician, the entire restoration can be completed with the same material, resulting in a uniform restoration with homogenous strength. The separate sculpting and modelling of a top surface layer – mandatory with flowable bulk fill
materials – is not necessary with Tetric N-Ceram Bulk Fill. In turn, this results in a significantly shorter chairside application time.

Potential time benefits were evaluated in a controlled application test in class II MO-cavities with 32 general practitioners comparing the layering technique (Tetric N-Ceram) and the bulk fill technique (Tetric N-Ceram Bulk Fill) on contralateral molar teeth with identical configuration and volume. The results revealed an average time benefit of 63% with the bulk fill technique (Fig. 2).

**Optimal handling characteristics required for bulk application**

Satisfactory function and esthetics of any posterior restoration largely depend on anatomically correct tooth contours and occlusal surfaces. This implies, however, that the bulk fill material in use is suitable for this purpose in terms of its consistency, mouldability and stability prior to polymerization.

Given its smooth and non-sticky consistency, Tetric N-Ceram Bulk Fill can easily be adapted to cavity walls (Fig. 3). When extended posterior defects have to be restored, the stability of Tetric N-Ceram Bulk Fill facilitates the exact build-up of anatomical contours. The material shows exceptional handling properties due to the incorporation of a specific ingredient – the Rheological Modifier – that allows the clinician to sculpt it quickly into an anatomical shape with just one single layer. After moulding anatomical tooth characteristics, such as marginal ridges, cusp slopes, triangular ridges and the fissure system these structures stay in shape as the material does not slump – even delicate details like para-fissures can be ideally reproduced (Fig. 4). Particularly when building up cusps and vertical walls Tetric N-Ceram Bulk Fill proves very stable during and after application. In addition, the material hardly sticks at all to any modelling instrument.

**Esthetics**

In comparison to the bulk-fill materials of other manufacturers, the translucency of Tetric N-Ceram Bulk Fill is ideally adjusted to natural enamel. The translucency level of 15% exhibits a life-like appearance and enables optimum esthetic integration. Materials with a higher translucency level do not demonstrate
such good shade adaptation and may result in greyish restorations – a notable problem in situations with deep cavities (4 mm) and particularly when discolored dentin is present.

A comparison of bulk-fill materials in class II molar cavities with simulated dentin discoloration displayed significant differences in terms of esthetic integration (Fig. 5).

Greater translucency means reduced esthetics: The darker, discolored dentin shines through the restoration more prominently with competitive materials that are more translucent. In contrast, restorations made of Tetric N-Ceram Bulk Fill blend well with the surrounding tooth tissue without any greyish effect – due to the enamel-like translucency level.

Clinical case 1

A pre-existing composite restoration in a second lower premolar of a 28-year old male patient needed to be replaced because of marginal staining and an open cervical margin with caries (Fig. 6). Prior to the removal of the defective restoration, Tetric N-Ceram Bulk Fill in shade 4A was selected using the dedicated shade guide. Upon removal of the old composite restoration and the decay, all enamel margins were finished with an oscillating ultrasonic-driven preparation tip (Fig. 7). The occlusal floor was approximately 3 mm deep (Fig. 8) and, the proximal box of the cavity was approximately 6 mm deep (Fig. 9). To optimize the bond quality, all enamel margins were covered with a phosphoric acid gel and left to react for 20 s (Fig. 10). Then the etching gel was spread over the entire dentin surface and left to react for another 10 s (Fig. 11). The etchant was rinsed off with water spray for 10 s and briefly air-dried leaving the dentin surface with a glossy wet appearance. Tetric® N-Bond was applied via the VivaPen®. A click of the VivaPen conveniently dispenses an exact amount of bonding agent. The adhesive was applied directly to all etched tooth surfaces and agitated for 10 s with the brush cannula (Fig. 12). A circular stainless steel matrix was applied over the tooth and Tetric N-Ceram Bulk Fill (4A) was injected into the proximal box from the Cavifil (Fig. 13). The material was easily adapted on the cavity floor (Fig. 14) using OptraSculpt® (cylinder shape) and polymerized with an LED-high power curing light (Bluephase N®, Fig. 15). A depth measurement of the cavity with a periodontal probe then revealed a remaining depth of 3 mm (Fig. 16). Thus, the entire remaining cavity could be filled with just one layer of Tetric N-Ceram Bulk Fill (Fig. 17). This final layer was quickly adapted and sculpted with OptraSculpt (chisel shape) to create anatomical tooth contours that do not slump (Fig. 18). These handling characteristics are important for the clinician in order to create true-to-nature contours within a short time. A final 10 second polymerization was conducted using Bluephase N. The 10-mm wide light guide facilitates just one curing cycle as
It covers the entire cavity. The anatomical tooth contours were refined and finished with a football-shaped fine diamond bur (Fig. 19). To adjust the colour of the occlusal fissure system to the adjacent tooth (optional) a small amount of a light-curing ochre staining material (Tetric® Color) was applied and polymerized (Fig. 20). The entire restoration was polished in one step to a glossy lustre using OptraPol® (Fig. 21). The final restoration displayed good optical integration with the surrounding enamel and a glossy appearance (Fig. 22).
**Fig. 12:** Tetric N-Bond is agitated for 10 s with the VivaPen

**Fig. 13:** Tetric N-Ceram Bulk Fill (IVA) is applied in bulk (3 mm)

**Fig. 14:** Adaptation on the cavity floor with OptraSculpt

**Fig. 15:** Polymerization with Bluephase N for 10 s

**Fig. 16:** Remaining cavity depth (3 mm) is verified with a periodontal probe

**Fig. 17:** Final layer of Tetric N-Ceram Bulk Fill (IVA) is applied
Fig. 18: Shaping of occlusal anatomy

Fig. 19: Refining the occlusal anatomy with a fine diamond bur

Fig. 20: Subtle characterization of the fissure system with Tetric Color.

Fig. 21: Polishing with OptraPol

Fig. 22: Final result
Clinical case 2

This lower second molar displayed enamel hypoplasia of the buccal cusps and a defective occlusal composite restoration (Fig. 23). After the removal of the existing restoration, an extended defect involving the entire occlusal surface and the buccal cusps had to be restored (Fig. 24). The bonding procedure was initiated by applying phosphoric acid gel first to the enamel margins for 25 s (Fig. 25) followed by the entire dentin surface (Fig. 26) for a short reaction time of 10 s. After rinsing off the phosphoric acid gel with copious amounts of water, the cavity was briefly air-dried. Tetric N-Bond Universal was applied and agitated on all etched tooth surfaces directly from the VivaPen (Fig. 27) with the dedicated brush cannula for 20 s. The solvent (ethanol) of the applied bonding agent was evaporated with air and light-cured for 10 s (Bluephase N). Dark discolorations of the dentin in the area of the buccal cusps were covered with IPS Empress Opaque to avoid them shining through the final composite restoration (Fig. 28). A thin layer of Tetric N-Flow (Dentin A3.5) was applied to add chroma to the deeper parts of the defect (Fig. 29). The buccal cusps were then built up first with Tetric N-Ceram Bulk Fill (shade IVW, Fig. 30), shaped with the OptraSculpt Pad instrument (Fig. 31) and light-cured for 10 s. Next, the entire remaining occlusal surface was reconstructed with just one single layer of Tetric N-Ceram Bulk Fill (IVW) and polymerized for 10 s. Re-contouring the composite build-up with fine diamonds and subsequent polishing with OptraPol accomplished the final restoration.

The final result (Fig. 32) shows functional anatomical contours and a seamless esthetic integration of the material with the surrounding tooth tissues. In addition, the restored composite surfaces show a glossy appearance with natural light reflections highlighting the very favourable surface characteristics of the material.
Fig. 26: Etching dentin with phosphoric acid gel

Fig. 27: Application of Tetric N-Bond Universal

Fig. 28: Application of IPS Empress Opaque

Fig. 29: Application of Tetric N-Flow (A3.5 Dentin)

Fig. 30: Application of Tetric N-Ceram Bulk Fill (IVW)

Fig. 31: Reconstruction of buccal cusps with OptraSculpt Pad
Conclusion

With Tetric N-Ceram Bulk Fill it is now possible to restore even extended posterior defects in a much more efficient, yet esthetically pleasing way. Thanks to the innovative photo-initiator Ivocerin, a 4-mm bulk application with 10-s light polymerization has now become a clinical reality - and this in turn, significantly reduces the total treatment time without compromising the overall quality of the final restoration. The favourable handling characteristics of Tetric N-Ceram Bulk Fill enable clinicians to create anatomically correct tooth contours and details that result in bulk-fill restorations with good esthetics and function.

Literature

Tetric® N-Ceram Bulk Fill and Bluephase N® form a part of the “Direct Restoratives” product category. The products of this category cover the procedure involved in the direct restoration of teeth – from preparation to restoration care. The products are optimally coordinated with each other and enable successful processing and application.

Would you like to know more about the products of the “Direct Restoratives” category? Simply get in touch with your contact person at Ivoclar Vivadent or visit www.ivoclarvivadent.com for more information.